Effect of pressure on hydrodynamic properties of poly(ethylene oxide) in deuterated and in non-deuterated solvents

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(Received 4 April 1990; accepted 14 May 1990)

Dynamic light scattering measurements of poly(ethylene oxide) (PEO) in deuterated methanol (CH_3OD and CD_3OD) and in non-deuterated methanol have been carried out in the pressure range 1–2500 bar. The pressure dependence of the hydrodynamic radius of PEO is observed to be quite different depending on the degree of isotope substitution of the solvent. The pressure dependence of the diffusion coefficient is also reported for these polymer–solvent pairs. At elevated pressure all polymer–solvent systems exhibit signs indicating formation of molecular clusters, which probably are associated with the preliminary stage of a pressure induced solution crystallization process.

(Keywords: dynamic light scattering; pressure; poly(ethylene oxide); solutions; crystallization; methanol and deuterated methanol)

INTRODUCTION

Hydrostatic pressure is known [1–12] to have a significant influence on the physical properties of macromolecular solutions. In the last few years the dynamic light scattering (d.l.s.) technique has been employed[11,13–18] in the study of both the diffusion behaviour as well as monitoring the average size of macromolecules in solution as a function of pressure. Several proteins have been observed[2,3,7,11,15,19] to display interesting denaturation and aggregation phenomena in aqueous solutions at elevated pressure. It is generally believed[7] that these effects are closely correlated to pressure induced alteration of intra- and intermolecular interactions controlling protein stability and macromolecular association. The stability of proteins as well as their dynamical behaviour in solution are both, to a large extent, governed[7,8] by specific interactions (hydrogen bonds and electrostatic interactions) and a class of less understood interactions between non-polar groups of the solute grouped together as hydrophobic interactions.

In the present study the synthetic polymer poly(ethylene oxide) (PEO) has been employed. This is a linear flexible polymer[20] which is not only soluble in water but also in many organic solvents, for example, in benzene, chloroform, dioxane, and methanol. PEO displays some basic features which are reminiscent of proteins. For example, the monomer contains one hydrophobic region ($-CH_2-CH_2-$) and one hydrogen bonding site ($-O-$) and may, from a chemical point of view, be considered as a simple model compound. Aqueous solutions of PEO should, in some aspects, mimic some fundamental characteristics of protein molecules in solution. Judging from a number of investigations[21–26] on aqueous solutions of PEO it may be argued that PEO exhibits a complex solution behaviour, e.g., that PEO molecules associate to form unstable aggregates or microgels by inter- and/or intramolecular interactions, and that crystallites may be formed.

On the other hand, a few years ago it was reported from a d.l.s. study[26] of PEO dissolved in methanol (a solvent which also has the potential to form hydrogen bonds) that the polymer is molecularly dispersed and that the solution is stable over a long period of time. In this context we may also note the work of Devanand and Selser[27], who carried out d.l.s. studies on dilute solutions of PEO in water and in methanol. They observed no evidence of aggregation of PEO in either of the solvents. Furthermore, from intensity light scattering measurements[28] on PEO in methanol the theta temperature was determined to be close to 16.7°C. In light of these findings and the possibility of studying solvent isotope effects, methanol seems to be an interesting solvent for PEO.

In the present study d.l.s. measurements on a narrow PEO fraction dissolved in non-deuterated methanol and in deuterated methanol (CH_3OD and CD_3OD), respectively, were carried out over a wide range of pressure for both dilute and semidilute solutions. The pressure dependence of both the hydrodynamic radius and the diffusion coefficient is reported. The results reveal some peculiar features which seem to be related to a pressure triggered crystallization process in solution.

Crystallization is a well documented[20,25,30–32] phenomenon in aqueous solutions of PEO upon a rapid temperature change. In contrast, the effect of pressure alterations on PEO solutions is practically unknown. However, there are a few studies[33,34] dealing with pressure dependence of thermodynamics and conformation of PEO in aqueous solutions. In the cited works the issue of pressure induced crystallization was never debated.

The principal aim of this paper is to examine how the pressure dependence of hydrodynamic properties of PEO molecules in solution is affected by solvent isotope

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0032-3861/91/050904-05

substitutions. Changes in hydrogen bond strength may be anticipated when deuterium is substituted for hydrogen[29]. The results may also shed some light on the complex interplay between hydrogen bonds and hydrophobic interactions operating in this type of system.

In the past it has frequently been assumed in the interpretation of data, e.g., data from n.m.r. experiments, that it is harmless to neglect the solvent isotope effects. However, the present results reveal that such assumptions may be false.

EXPERIMENTAL

Materials and preparations of solutions

A sharp fraction of PEO with a molar mass of $M_W = 8.6 \times 10^4\,\mathrm{g\,mol^{-1}}$ and $M_W/M_n \leqslant 1.02$ (manufacturer's data for type SE-8, lot. no. RE-10) was purchased from Toyo Soda Co. Ltd., Japan. The solvents used were methanol p.a. from Merck AG, methanol-d_4 (CD_3OD) purum > 99.5 atom% D from Fluka AG and methanol OD (CH_3OD) from Service des Molécules Marquées C.E.N.-Saclay. Both the polymer and the solvents were used without further purification.

The solutions were prepared by weighing. After addition of solvent the polymer was allowed to swell (12 h) before the solution was homogenized by stirring for at least 12 h. Because methanol and deuterated methanol are fairly poor solvents for PEO at the temperature of measurement (25°C) a careful heating (up to about 35–40°C) was exercised in order to dissolve the polymer properly. The solutions were then slowly cooled to 25°C. All solutions were filtered in an atmosphere of filtered air through 0.22 μm Millipore filters directly into precleaned specially designed quartz cuvettes.

Equipment and data analysis

The design and operation of the high pressure vessel[35] as well as the experimental set-up[36] for photon correlation spectroscopy under high pressure have been described in detail previously and the main features only are summarized here.

A three-window portable optical high-pressure vessel is used, containing the sample solution within a cylindrical quartz cuvette (path length 16 mm), which has an optically flat bottom and two oppositely placed, optically flat windows. The cuvette is sealed with a movable piston, which transmits the pressure and isolates the sample solution from the pressure-transmitting fluid glycerol. Pressure is applied with a hydraulic press and the pressure in the cuvette is known within ± 1.5%. In all measurements, the pressure is slowly increased and the sample solution is allowed to equilibrate (1.5–2 h) before data are accumulated. The high pressure cell is enclosed in an insulating jacket, through which water is circulated from a thermostated bath. By this arrangement the temperature in the sample cuvette may be maintained constant within ± 0.1°C. The experiments were carried out at 25°C.

The beam from an argon ion laser (Model 165 from Spectra Physics) operating at a wavelength of 488 nm was focused in the centre of the scattering cuvette and the 90° scattered light was collected and imaged onto a photomultiplier tube. The discriminated output was fed into a 60-channel digital lin-log correlator K-7027 from Precision Devices, Malvern.

The correlator was interfaced to a PC, which was programmed to calculate the normalized correlation function, and to analyse and store data.

Intensity correlation data were routinely analysed using the method of cumulants[37] in order to provide the average decay rate $\bar{\Gamma}$ and the normalized variance Q. This latter quantity is a measure of the width of the distribution of the decay rates.

The diffusion coefficient D is determined from the average decay rate according to

$$\bar{\Gamma} = Dq^2 \tag{1}$$

where $q = (4\pi/\lambda)n\sin(\Theta/2)$ is the magnitude of the scattering vector, λ is the incident light wavelength, n is the index of refraction of solution, and Θ is the scattering angle. In this study n is determined from the measured refractive index of the solution at atmospheric pressure and the known[38] pressure dependence of the refractive index of methanol.

RESULTS AND DISCUSSION

D.l.s. constitutes a powerful tool to study diffusion as well as to determine the actual average size change of macromolecules exposed to pressure. The effective hydrodynamic radius R_H may be obtained from the Stokes–Einstein relation

$$R_H = RT/N_A 6\pi\eta D_0 \tag{2}$$

where R is the gas constant, N_A is Avogadro's constant, T is the absolute temperature, and η is the solvent viscosity. In this work, values of η at different pressures were estimated from the known viscosities of the solvents and the reported[39,40] pressure dependence of the viscosity of methanol and CH_3OD.

The pressure dependence of the effective hydrodynamic radius for PEO in non-deuterated and in fully deuterated methanol (CD_3OD), respectively, is depicted in *Figure 1*. R_H increases with pressure for the system PEO/CH_3OH, while for PEO in CD_3OD R_H is practically constant up to 1600 atm; above which R_H increases.

In light of the observation that the increase in size is accompanied by a significant increase in scattered light

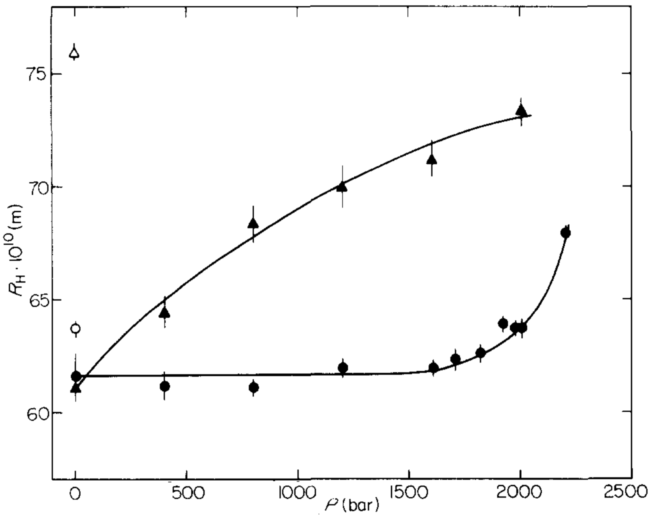

Figure 1 The pressure dependence of the hydrodynamic radius for dilute solutions of the systems indicated: (▲) PEO/CH_3OH (9.98 $\mathrm{kg\,m^{-3}}$); (●) PEO/CD_3OD (9.97 $\mathrm{kg\,m^{-3}}$). The open symbols represent the values after pressure release (see the main text)

intensity, as well as increasing values of Q, the results suggest formation of clusters and/or a preliminary stage in the process of forming pressure generated crystals. This process appears to be more pronounced at lower pressures when CH_3OH is used as a solvent. From a physical point of view an increase in pressure may, in certain respects, be reminiscent of cooling a system.

Upon releasing the pressure (from 2400 bar) the return of R_H is illustrated in *Figure 1* (open symbols). For the CH_3OH repeated measurements performed after 48 h at atmospheric pressure did not reveal any significant change of R_H. In the case of the PEO/CD_3OD system the return of R_H was more pronounced, but also here pressure induced changes seem to have taken place.

The differences in behaviour between the two systems revealed in *Figure 1* can probably be attributed to changes in hydrogen bond strength when deuterium is substituted for hydrogen, and from differences in the strength of the hydrophobic interactions between nonpolar groups when PEO is dissolved in CH_3OH and CD_3OD, respectively.

Figure 2 displays a normalized plot of the hydrodynamic radius as a function of pressure for the dilute solutions of the same systems as in *Figure 1*, together with a dilute solution of PEO in CH_3OD. In this context it may be noted that the experimental correlation functions for these systems at atmospheric pressure were all found to be well represented by single exponentials ($Q < 0.05$). In order to be able to reproduce the results, all the pressure experiments were carried out in the same manner, both when it comes to the procedure of applying pressure and the time between pressure increase and the total time for a series of measurements.

The most striking feature in *Figure 2* is that the reduced hydrodynamic radius for PEO in CH_3OD exhibits the strongest pressure dependence. Upon releasing the pressure, the return of R_H for this system also displays pronounced irreversibility effects, namely, after a pressure release the value of R_H is still about 40% higher than the original value at atmospheric pressure, even after a long time. Incidentally, we may mention that at sufficiently high pressure fast and strong fluctuations in the scattered intensity were observed for all systems. The trends observed in *Figure 2* seem to indicate that pressure induced molecular association effects are most prominent in solutions of PEO in CH_3OD. A rational explanation of the difference in pressure dependence of the quantities for the systems depicted in *Figures 1* and *2*, probably involves a variety of factors such as the strength and nature of the hydrogen bonds, structure, polarity and quality of the solvents, and the strength of the 'hydrophobic effect' operating in this type of systems. These factors probably interplay in a complex manner.

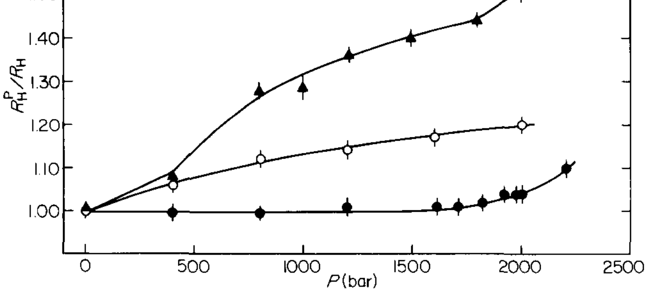

Figure 2 The pressure dependence of the reduced hydrodynamic radius for dilute solutions of the systems indicated: (▲) PEO/CH_3OD (9.85 kg m^{-3}); (○) PEO/CH_3OH (9.98 kg m^{-3}); (●) PEO/CD_3OD (9.97 kg m^{-3})

Before discussing the diffusion features for dilute and semidilute solutions at elevated pressure it may be instructive to recall some main ingredients of a theoretical model[41] which has the potential to analyse the interplay between hydrodynamics and thermodynamics in diffusion of flexible polymers over an extended concentration range. This model is constructed with the aid of renormalization-group methods incorporating perturbation calculations for the determination of both hydrodynamic and thermodynamic quantities. If hydrodynamic screening is neglected the approach yields a relationship of the following closed analytical form[41]:

$$D/D_0 = [1 + bx(1 + x)^B]/(1 + x)^A \tag{3}$$

or

$$D = (RT/N_A 6\pi\eta R_H) \times \frac{1 + bx(1 + x)^B}{(1 + x)^A} \tag{3a}$$

where $b = \exp[B(1 + \ln 2)]$. The exponents in equation (3a) may be expressed[42,43] as $A = -(\nu - 1)/(3\nu - 1)$ and $B \equiv (2 - 3\nu)/(3\nu - 1)$, where ν is an exponent characterizing the molar mass dependence of the radius of gyration. For Gaussian coils $\nu = 0.50$ and, as solvent quality increases, ν rises smoothly to the asymptotic value $\nu = 0.588$. The magnitude of the mutual diffusion coefficient D is determined by the competition between thermodynamic and hydrodynamic effects which are manifested in $1 + bx(1 + x)^B$ and $(1 + x)^A$, respectively. Equations (3) and (3a) constitute a simplified version (without hydrodynamic screening) of the original expression[41], which has been successful in analysing[43] the concentration dependence of the diffusion coefficient for solutions of flexible polymers over a large concentration regime at good and marginal solvent conditions. However, this simplification is not critical for the purpose intended in this study, namely to serve as a guide in the interpretation of the interplay between thermodynamic and hydrodynamic properties in diffusion.

The variable x denotes a universal overlap parameter which may be cast[41] in the form $x = 2A_2Mc/b$, where A_2 is the second virial coefficient, M is the solute molar mass, and c is the concentration (mass/volume) of the solution. This scaled variable was constructed for the purpose to be able to make a direct comparison, without any adjustable parameter, between the theoretical prediction (equation (3a)) and experimental results.

In order to analyse polymer diffusion at elevated pressure we need an analogous relation to equation (3a). This seems to be a straightforward procedure; a reasonable supposition should be of the following form

$$\begin{aligned} D^p = {} & (RT/N_A 6\pi\eta^p R_H^p) \\ & \times (1 + b^p x^p (1 + x^p)^{B^p}/(1 + x^p)^{A^p}) \end{aligned} \tag{3b}$$

Here $x^p \equiv 2A_2^p Mc/b^p$ and the superscript p denotes the pressure dependent variables. The small pressure dependence of c is omitted in this consideration. Combining equations (3a) and (3b) we may obtain

$$D^p/D \simeq \frac{\eta R_H}{\eta^p R_H^p} \times \frac{(1 + x)^A}{(1 + x^p)^{A^p}} \times \frac{1 + b^p x^p (1 + x^p)^{B^p}}{1 + bx(1 + x)^B} \tag{4}$$

Let us now, with aid of equation (4), consider three different cases. For a polymer/solvent system where both the thermodynamic and the hydrodynamic factors are independent of pressure we expect $R_{\mathrm{H}} = R_{\mathrm{H}}^{p}$, $x = x^{p}$, $A = A^{p}$, $B = B^{p}$, and $b = b^{p}$. This situation has previously[14] been studied experimentally. In that work it was shown by means of d.l.s. on the system polystyrene/toluene that the pressure dependence of D, for solutions covering an extended concentration range, is entirely correlated to the change in solvent viscosity and may be cast into the predicted form $D^{p}/D = \eta/\eta^{p}$. In the case when pressure improves the thermodynamic conditions of the system we expect $R_{\mathrm{H}} < R_{\mathrm{H}}^{p}$, $x < x^{p}$, $A < A^{p}$, $B < B^{p}$, $b < b^{p}$, and $D^{p}/D > \eta/\eta^{p}$. When the solvent power diminishes with pressure it is postulated that $R_{\mathrm{H}} > R_{\mathrm{H}}^{p}$, $x > x^{p}$, $A > A^{p}$, $b > b^{p}$, and $D^{p}/D < \eta/\eta^{p}$.

In light of the above considerations we may now analyse the pressure dependence of the reduced diffusion coefficient D^{p}/D displayed in *Figures 3* and *4* for a dilute and a semidilute solution of the systems PEO/CH_3OH and PEO/CD_3OD, respectively. In both figures the dashed curve represents the expected behaviour of the reduced diffusion coefficient only if the pressure dependence of the solvent viscosity is taken into account. The observed pressure dependence of D^{p}/D for the low concentration of PEO in CH_3OH (the lowest curve in *Figure 3*) is consistent with the conjecture of diminishing solvent power and/or enhanced cluster formation with increasing pressure.

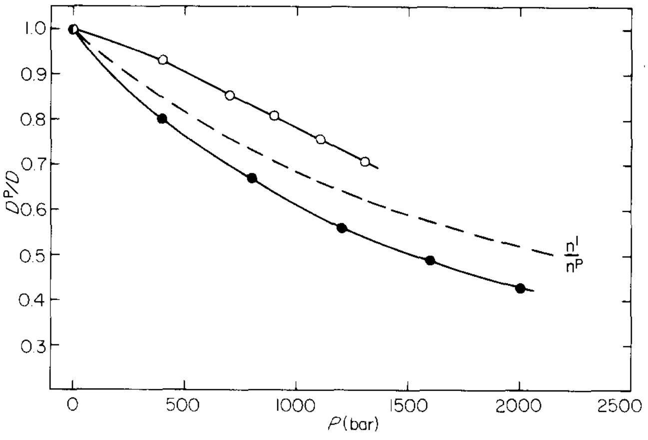

Figure 3 The pressure dependence of the reduced diffusion coefficient for the system PEO/CH_3OH at the concentrations (kg m^{-3}): (●) 9.98 (dilute); (○) 48.7 (semidilute). The dashed curve represents the behaviour if only the change in solvent viscosity with pressure is taken into account (see the main text)

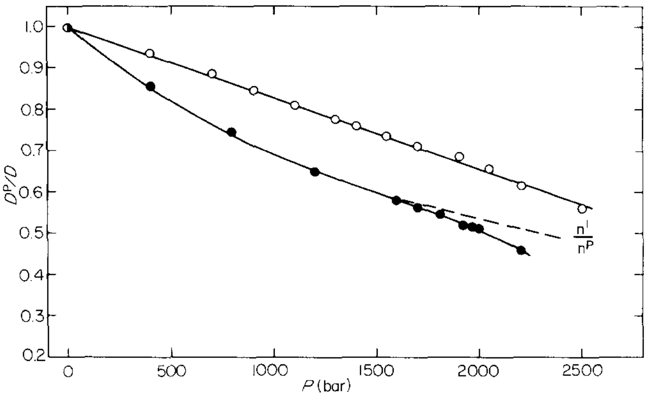

Figure 4 The pressure dependence of the reduced diffusion coefficient for the system PEO/CD_3OD at the concentrations (kg m^{-3}): (●) 9.97 (dilute); (○) 50.1 (semidilute). The dashed curve represents the behaviour if only the change in solvent viscosity with pressure is taken into account (see the main text)

The curve representing the pressure dependence of D^{p}/D for the semidilute solution (topmost curve in *Figure 3*) seems to be in contrast to that found for the low concentration. The observed difference in diffusion behaviour between the low and the high concentration may, at a cursory glance, be suspected to arise from trivial concentration effects. This conjecture was tested with the aid of equation (4). However, the result indicates strongly that the data for the two concentrations should coincide or only exhibit a very minor deviation from each other. In addition, different hydrodynamic and thermodynamic situations were simulated within the framework of equation (4).

From these considerations three interesting conditions seem to appear. When the thermodynamic and hydrodynamic properties are independent of pressure the diffusion data should fall on the viscosity corrected curve. In the case of improved thermodynamic conditions with pressure the data are expected to condense above the viscosity corrected curve, whereas when the solvent quality diminishes with pressure the data for both concentrations are predicted to fall below the viscosity corrected curve.

In light of these considerations the observed departures in diffusion behaviour between the low and the high concentration displayed in *Figures 3* and *4* seem to be difficult to unambiguously rationalize within the framework of the model (equation (4)). A tentative explanation for the apparent anomaly may be that pressure generated ordered domains are formed in semidilute PEO solutions. This effect is probably a result of a pressure induced preliminary stage of crystallization. The mechanism for this may be related to a previously advanced theoretical model[44], in which polymer crystallization is suggested to be controlled by an equilibrium distribution of intramolecular clusters. Furthermore, it is known[31,32] that PEO has the ability to form crystals in solution. If this type of phenomenon takes place it may be important for the evaluation of diffusion coefficients to know the q-dependence of the static structure factor at various pressures. Unfortunately, our present experimental set up does not allow us to change the scattering angle. Hence this type of information cannot be extracted.

In *Figure 5* the pressure dependence of the reduced diffusion coefficient for semidilute solutions, of the same concentration, of PEO in CH_3OH and in CD_3OD, respectively, is compared. The divergent behaviour between these two systems probably, to a large extent, reflects differences in the interaction situation with pressure.

Upon releasing the pressure from sufficiently high pressure, signs of irreversibility were also detected for the semidilute solutions. For the PEO/CH_3OH system molecular association effects were observed already at 1300 bar, while for the PEO/CD_3OD system symptoms of this type were registered first at 2500 bar. It is worth mentioning that semidilute solutions from both systems became turbid when exposed to high pressure for some time (less than 1 day) and gradually the polymer precipitated.

The central question of pressure triggered crystallization and its repercussions on the diffusion features should be analysed in detail. However, this phenomenon is too complex to be mapped out only on the basis of the present measurements.

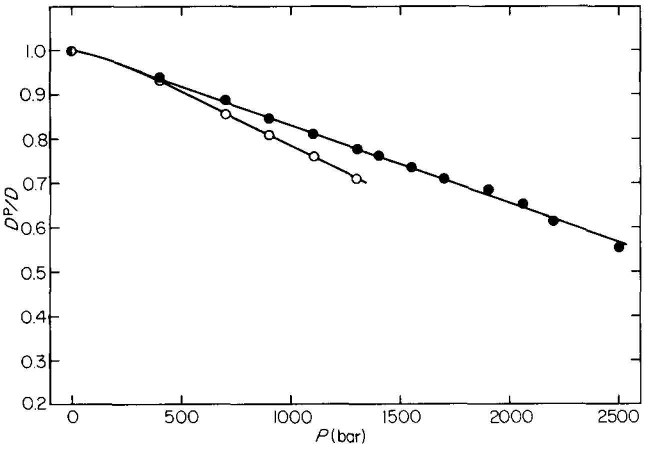

Figure 5 The pressure dependence of the reduced diffusion coefficient for the semidilute solutions of the systems indicated: (●) PEO/CD_3OD; (○) PEO/CH_3OH

CONCLUSIONS

In this paper we have utilized d.l.s. to measure the size of the molecules as well as to probe mutual diffusion coefficients of PEO in deuterated and non-deuterated methanol as a function of applied hydrostatic pressure. It has been established that the degree of isotopic substitution of the solvent has a substantial effect on the pressure dependence of the hydrodynamic radius of PEO in solution.

The departure in behaviour between the systems is probably associated with changes of the interaction situation due to solvent isotope effects. The observed difference in pressure dependence of the reduced diffusion coefficient for a dilute solution of PEO and a semidilute solution of the same polymer–solvent pair may perhaps be attributed to the formation of pressure generated ordering in semidilute solutions. However, we should stress that this is only speculation at present. The postulated working hypothesis of pressure induced formation of clusters and/or a preliminary stage of crystallization seems to constitute a rational basis for an interpretation of the experimental results.

ACKNOWLEDGEMENT

Financial support from the Norwegian Research Council for Science and the Humanities (NAVF) is gratefully acknowledged.

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