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Thermoreversible gelation of an isotropic solution of poly(γ -benzyl-L-glutamate) followed by small-angle X-ray scattering

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The gelation and melting processes in an isotropic solution of the helical polypeptide poly(γ -benzyl-L-glutamate) [PBLG] were followed by small-angle x-ray scattering measurements. These suggest that above the gelation temperature PBLG exists as isolated helices. A sharp gelation transition is marked by an increase in the intensity scattered at low angles. Hysteresis of 20°C is observed between gelation and melting temperatures. The melting transition is gradual, suggesting that thinner units melt before thicker ones.

Introduction

The phenomenon of thermoreversible gelation in solutions of some polymers is complex and may involve a combination of effects such as conformational changes, liquid-liquid phase separation and crystallization [1]. PBLG solutions have been used as a model system for studies of phase transitions in rigid polymer solutions, due to the stability of the rigid α -helical conformation. Thermoreversible gelation is observed even in dilute isotropic solutions, at concentrations below the onset of liquid crystallinity. The gel microstructure and its mechanism of formation have been a subject of extensive research, but are yet far from being well understood [2]. Structural inhomogeneities on a micron level were shown to develop during gelation, which obey characteristic scaling relations [3]. Studies by electron microscopy revealed networks of interconnected microfibrils having diameters in the range of 5-50nm [4,5].

The aim of this study is to follow the structural changes on the microfibrillar level during the gelation and gel-melting processes in an isotropic PBLG solution.

Experimental

PBLG was obtained from Sigma Chemical Co. Ltd., having nominal molecular weight of 86,000. Spectroscopic grade benzyl alcohol [BA] was obtained from Merck and distilled before use. SAXS measurements were performed using Ni filtered CuK α radiation with a compact Kratky camera having a temperature controlled sample chamber (A. Paar) and a linear position-sensitive detector system (Raytech). The scattering data at each temperature were normalized to that from pure BA at high angles ($h > 4.0 \text{ nm}^{-1}$, $h = 4\pi \sin\theta/\lambda$, 2θ being the scattering angle and λ the wavelength) and the scattering from the solvent was subtracted.

Results and Discussion

A central question in this study was to determine whether the gelation transition occurs at a well defined temperature. For this purpose a temperature cycle between 70° to 20°C, with steps of 2°C while holding the sample for about 2 hours at each temperature, was followed. Scattering patterns from a 1% (w/w) PBLG solution in BA during slow cooling are shown in figure 1a. It can be seen that cooling down to 34°C does not produce significant changes in the pattern, while a large increase in the intensity scattered at low angles is observed between 34°C and 32°C. The excess small angle scattering indicates the microheterogeneity of the gel structure, due to aggregation of the PBLG helices.

The scattering pattern from the isotropic solution was fit using the Guinier approximation for a system of long noninteracting cylinders having random orientations (model I in Table I). This model was compared with the measured data by applying first the smearing integral due to the length profile of the slit-collimated incident beam [6]. A good fit of the data was obtained with the radius of gyration of the cylinder cross-section (r_c) having a value of 0.47nm, in accord with the value reported by Luzzati et al. for PBLG in dimethyl formamide [7]. The diameter of the cylinder, estimated as 1.33nm, is comparable to that of an isolated PBLG helix. The value of 0.2nm for r_c estimated previously [8] for PBLG (MW=236,000) in BA using the infinite slit hypothesis (see Table I) is therefore incorrect. Recent small-angle neutron scattering (SANS) measurements yielded a value of 0.55nm for r_c [9]. These measurements therefore indicate that above the gelation temperature PBLG helices do not aggregate side by side. However, in another report of SANS measurements on PBLG/BA solutions [10], the radius of gyration of the complete molecule was estimated to be much larger than the calculated value based on its molecular weight. This suggests that if aggregation occurs it is in a head to tail fashion.

Heating the gels resulted in a melting transition. Scattering patterns from the 1% PBLG gel during the heating cycle are shown in Figure 1b. Two effects are prominent, as demonstrated in Figure 2, were the intensities at two scattering vectors ($h = 0.29$ and 0.55nm^{-1}) are shown as a function of temperature. First, there is hysteresis of about 20°C between the gelation and melting temperatures. Hysteresis is quite common in several polymer solutions, such as agarose [11,12], where it is associated with the complex kinetics of aggregation coupled to conformation changes. Its origin in PBLG solutions is not clear. The second effect is that the intensity at the higher scattering vector starts decreasing at a lower temperature than that at the lower scattering vector. This may be interpreted as resulting from thinner microfibrils melting at a lower temperature than thicker ones.

Table I: Models used for analysis of SAXS patterns

model	point collimation	slit collimation*
I. cylinders	$I(h) = \frac{A}{h} \exp\left(-\frac{r_c^2 h^2}{2}\right)$	$I(h) = A' K_0\left(\frac{r_c^2 h^2}{2}\right) \exp\left(-\frac{r_c^2 h^2}{2}\right)$
II. "fractal"	$I(h) = A h^{-D_f}$	$I(h) = A' h^{-D_f+1}$

A, A' - constants; r_c - radius of gyration of the cylinder cross section ($=\text{radius}/\sqrt{2}$)

K_0 - modified Bessel function; D_f - fractal dimension;

(*) - assuming infinite slit length

Fig. 1 Scattering Patterns from 1% PBLG in BA during (a) gelation and (b) melting

Fig. 2 The scattered intensity at two scattering vectors: o - $h=0.29$ and + - $h=0.55 \text{ nm}^{-1}$ as a function of temperature during gelation and melting, relative to the intensity at 20°C .

The structure of the gel formed in the slow gelation process was compared to a more rapidly formed gel, using a temperature step from 40° to 30°C ($13^\circ/\text{min}$), holding for 2 hours and another step to 20°C . The Scattering patterns from the gels formed by the rapid and slow processes are compared in Figure 3. Figure 3a shows the apparent power law at low angles (model II in Table I). It indicates that the apparent "fractal dimension" of the gel formed more rapidly is somewhat higher than the slowly formed gel. (2.77 and 2.45 respectively). This power law has been interpreted as a fractal dimension [8,10], however, we believe it to indicate just the wide polydispersity in the sizes of the microfibrils forming the gel network. At wider angles a broad scattering peak is observed about a spacing of 2nm, only in the rapidly gelled solution. This small peak, indicates the ordered packing of helices within the microfibril. It is difficult to observe due to the low PBLG concentration, and its dependence on the gelation rate is not understood.

Fig. 3 The scattering patterns from 1% PBLG gels at 20°C formed by slow and rapid gelation, (a) - fit of a power law at the lower angles. (b) - the higher angular range.

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