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Small-Angle Neutron Scattering of Poly(γ-benzyl L-glutamate) in Deuterated Benzyl Alcohol

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ABSTRACT: Small-angle neutron scattering has been used to study poly(γ-benzyl L-glutamate) (PBLG) in deuterated benzyl alcohol (DBA) as the solution is brought from the isotropic phase into the gel phase. The results show that an aggregation of PBLG molecules exists up to 80 °C even in the isotropic phase and the size of the aggregate does not change with temperature within the isotropic phase for a given concentration. However, the size of the aggregate increases with concentration or as the gelation threshold is crossed. The measurement of fractal dimension at intermediate length scales of the aggregates in the isotropic phase shows that the aggregates are less dense at higher polymer concentrations. But at lower length scales of ~50 Å, the mesh size of the aggregates in the isotropic phase decreases with increasing polymer concentration. Studies of the fractal dimension of the resultant gels show that the thermal history of the sample in the isotropic phase influences the gel microstructure. The fractal dimension of the PBLG–DBA gel obtained by a step quench procedure is higher than that of a gel obtained by a sudden quench. We have also observed that the local concentration gradients become sharper as the polymer concentration increases in the gel phase.

Introduction

The gelation of anisotropic molecules is a perplexing phenomenon. This phenomenon is commonly utilized in the processing of rodlike polymers, yet it is neither well understood nor theoretically predicted. In 1956, using a statistical mechanical theory that is similar to his lattice theory for random coil polymers, Flory[1] predicted the temperature–concentration phase diagram of a solution of rodlike polymers. The key predictions are the following. At higher temperatures there is a phase transition from an isotropic phase to a liquid crystalline phase as the concentration is increased provided the molecules have a length to diameter ratio of at least 6.7. These two phases are separated by a narrow biphasic region. At lower temperatures, the biphasic region becomes wider.

Using nuclear magnetic resonance and polarized light microscopy, Miller and co-workers[2] found that poly(γ-benzyl L-glutamate) (PBLG) in dimethylformamide (DMF) has a phase diagram that is very similar to that predicted by Flory over a limited temperature–concentration region. This includes isotropic and liquid crystalline phases and a narrow biphasic region between the two at high temperature. This partial phase diagram was extended[3] to the complete temperature–concentration range using isopiestic and hydrodynamic measurements. The agreement between the experimental and theoretical phase diagrams was excellent. However, upon further investigation,[4] it was found that at low temperatures the system forms a gel which is a three-dimensional self-supporting polymer-rich network. In an attempt to explain this unpredictable result, Miller et al.[4] suggested that the gel is a result of kinetic phenomena. Spinodal decomposition and polymer immobility were claimed to be the mechanisms responsible for the formation of the gel at lower temperatures. The search for the appropriate mechanism still continues to be an active subject. Further studies[5,6] of PBLG showed that the gelation also occurs in other solvents, including benzyl alcohol (BA).

Many investigations have been completed in an attempt to understand the gelation phenomenon as well as to describe the gel itself. As already mentioned, nuclear magnetic resonance (NMR), isopiestic measurements, polarized light microscopy, and hydrodynamic measurements have been used[2–6] to determine the phase diagram of the PBLG–DMF system. Light scattering,[7a] dynamic light scattering,[7b] X-ray scattering,[6,8] differential scanning calorimetry,[6,9,10] rheology,[6,10,11] NMR,[12] and polarized optical microscopy[13] have all been used to study the PBLG–BA system and the resultant gel in hopes of obtaining a better understanding of the gelation phenomenon.

Although the identification and description of the gel phase and its molecular origins is a fundamental problem of current interest, the primary objective of the experiments reported in this paper is to determine the nature of interactions between PBLG molecules in dilute solutions at temperatures above and below the gelation temperature. For the complex system studied here, we have not yet determined either the precise phase diagram or the precise value of the gelation temperature.

Experimental Section

Poly(γ-benzyl L-glutamate) was purchased from Sigma Chemical Co. and used as received. The molecular weight, M_w, is 238 000 as reported from the manufacturer. Deuterated benzyl alcohol was purchased from the Medgenix Group and was also used as received.

The small-angle neutron scattering (SANS) experiments were completed on the instruments KWS I and II at the Kernforschungsanlage (KFA), Jülich, Germany.[14] The collected scattering intensity was corrected for electronic noise, incoherent and background scattering, solvent scattering, detector efficiency, and sample transmittance. To obtain the dependence of the scattering intensity on the wave vector q ($q = 4\pi/\lambda \sin(\theta/2)$; λ is the incident wavelength, and θ is the scattering angle), the corrected intensity was radially aver-

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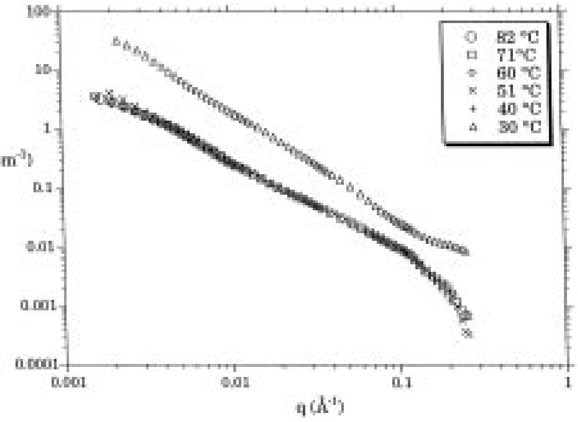

Figure 1. Plot of $I(q)/\phi$ vs q for the 1% solution at the temperatures studied.

aged. Each scattering pattern was reduced to an absolute intensity, I (q), (in cm^{-1}) with lupolen (polyethylene) as a secondary standard.

PBLG solutions (1, 3, 5, and 7 wt %) of the polymer were examined in this study. The solutions were prepared by adding the PBLG and deuterated benzyl alcohol to the cell and annealing at a temperature well into the isotropic range (~80 °C) for 3−5 days. No special precaution was taken to exclude moisture in this preparation, but once sealed, the samples were air-tight and all samples underwent parallel preparation conditions. Therefore, any effect of the presence of water on the behavior of the samples should be similar for all samples. The trends that are observed in the following study should not be influenced by any presence of moisture in the samples.

Results and Discussion

As a starting point, a qualitative description of the phase behavior of PBLG in DBA is necessary. For a M_w of 238 000, the PBLG−DBA system is in the isotropic phase above ~40 °C and below ~10 wt %. There exists a narrow biphasic region between the isotropic and cholesteric phases in the vicinity of 10 wt %, and the system is cholesteric above 40 °C at 14 wt %. Below ~40 °C and above ~1 wt %, the system is a gel. These observations are qualitative results based on observations during the completion of these and previous[11] experiments. They are meant to inform the reader so that the following experimental results may be better appreciated and are not meant to define the phase diagram of PBLG in DBA.

The scattering profiles for the 1, 3, 5, and 7% solutions at temperatures ranging from 80 to ~30 °C in ~10 °C temperature steps were collected. These results are summarized in Figures 1−4, which are plots of $I(q)/\phi$ vs q for the temperatures studied and the polymer concentrations (ϕ) of 1, 3, 5, and 7%, respectively. It can be seen from these figures that the scattering pattern does not change with temperature in the high-temperature regime for a given concentration, but increases at all values of q as the temperature is lowered. It should be noted that the temperature where a deviation in the scattering pattern is seen (~30−40 °C) is the same temperature for a given sample where a transition to a gel was seen using differential scanning calorimetry[9] and where the physical properties of the system changed dramatically. More specifically, this is the temperature where the sample became more rigid and seemed to "have gelled". From these observations we denote the isotropic phase as the high-temperature phase, where no deviation in the scattering pattern is seen with temperature. We denote the gel phase as the phase where the scattering pattern is temperature dependent and is different from that of the isotropic phase. The temperature at which the gel phase is observed from the scattering curves (i.e., $I(q)$ vs q plots) occurs at higher temperatures for the 5 and 7% solutions (~40 °C) than for the 1 and 3% solutions (~30 °C). Thus, there is a trend of an increase in the transition temperature between the isotropic and gel phases as the polymer concentration increases, although the precise value of the gelation temperature is not established using the present SANS studies (due to inherent limitations of the SANS facility).

For all four samples and for different temperatures, the SANS data of Figures 1−4 show that we may identify three regimes in terms of the q dependence of the various scattering curves, viz., $q < 0.01$, $0.01 < q <$

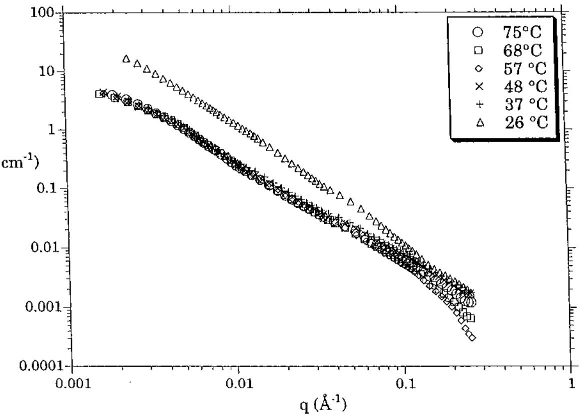

Figure 2. Plot of $I(q)/\phi$ vs q for the 3% solution at the temperatures studied.

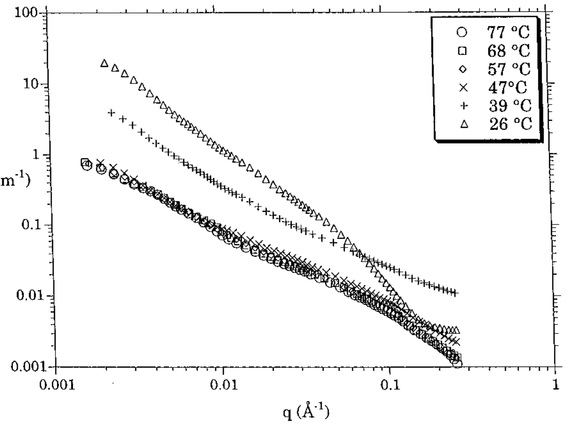

Figure 3. Plot of $I(q)/\phi$ vs q for the 5% solution at the temperatures studied.

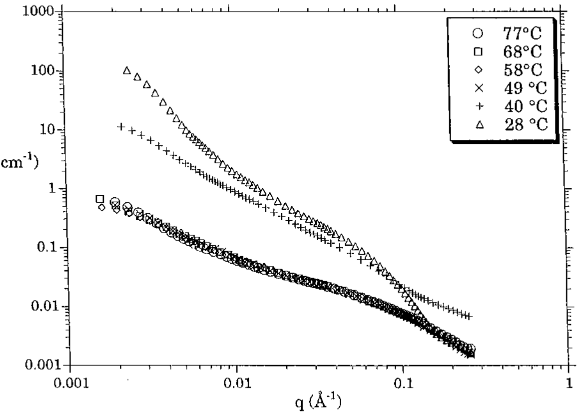

Figure 4. Plot of $I(q)/\phi$ vs q for the 7% solution at the tempeatures studied.

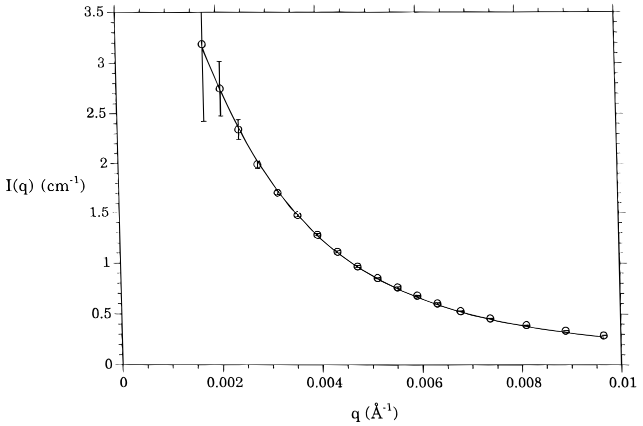

Figure 5. Fit to eq 1 for a 1% solution of PBLG in DBA at 82 °C.

Table 1. Zimm Analysis of SANS Data in the Isotropic Phase at $q < 0.01$

concn (wt %)	R_g (Å)	$I(q{=}o)$
1	697 ± 20	4.65 ± 0.25
3	795 ± 18	7.11 ± 0.32

0.1, and $q > 0.1$. The first regime, where $q < 0.01$, corresponds to the overall global structure of the polymer and the mean radius of gyration R_g of a polymer chain or a cluster of aggregated polymer chains in dilute solution can be determined if $qR_g < 1$. The data in the second regime, $0.01 < q < 0.1$, contain information about the interior structure of the polymer. Assuming that the interior structure of the present system is a statistical fractal, we determine the fractal dimension of the system using data in the second regime. The third regime, $q > 0.1$, contains data pertinent to local structure of the chain and the formation of local concentration gradients.

We have analyzed the SANS data of Figures 1 and 2 for the polymer concentrations of 1 and 3% in the first regime using the standard Zimm analysis,

$$I(q) = \frac{I(0)}{1 + (^1/_3)q^2 {R_g}^2} \tag{1}$$

The data for $q < 0.01$ have been fit using eq 1 to obtain the mean radius of gyration. In the present analysis, the scattering intensity, $I(q)$, has been normalized by $\phi V_\omega \Delta p^2$, where V_ω is the volume of a PBLG molecule and Δp is the contrast factor,

$$\Delta p = \left(\frac{b_{\mathrm{PBLG}}}{\Omega_{\mathrm{PBLG}}} - \frac{b_{\mathrm{DBA}}}{\Omega_{\mathrm{DBA}}}\right) \tag{2}$$

with b_i and Ω_i being respectively the scattering cross section and the molar volume of the ith component. We have taken V_ω to be 1.136×10^{-19} cm^3/molecule and $\Delta p^2 = 2.8 \times 10^{10}$ cm^{-2}. This normalization is carried out so that the extrapolated zero angle scattering $I(0)$ gives the number of PBLG molecules in the scattering particles.

An example plot of the analysis of SANS data in the isotropic phase for $q < 0.01$ is shown in Figure 5, where the solution is at 82 °C and at 1% polymer concentration. The results of this analysis are shown in Table 1 for the 1 and 3% solutions in the high-temperature isotropic phase. This analysis fails at lower temperatures for these concentrations and also at all temperatures for higher concentrations due to the inability to satisfy the criterion $qR_g < 1$. The key result emerging from Table 1 is that the PBLG molecules aggregate even in the isotropic phase and that the average number of chains in the aggregates increases with polymer concentration. Also, the observed radius of gyration is much larger than the largest value allowed for a single chain. Assuming that the PBLG chain is a perfect α-helix with a repeat distance of 1.5 Å along the chain backbone per monomer, the contour length L of the chain of molecular weight 238 000 (degree of polymerization being 1092) is 1637 Å, so that R_g is $(L^2/12)^{1/2} = 472$ Å. However, the measured R_g is approximately 700−800 Å. Thus, it is clear that the scattering particle in the isotropic phase of PBLG in DBA at 1 and 3% polymer concentrations is much bigger than the size expected for an α-helix and consequently is not a single molecule. This conclusion is consistent with the observation from Table 1 that the scattering particle is an aggregate of four to five molecules for the 1% solution and about seven molecules for the 3% solution in the isotropic phase.

Table 2. Dependence of Fractal Dimension of the Gel on Thermal History

concn (wt %)	temp (°C)	fractal dimension: step quench	fractal dimension: sudden quench
1	30	1.88	1.68
3	26	2.03	1.78
5	37	1.15	
5	27	1.89	1.74
7	38	1.57	
7	28	1.86	1.76

Next, we present the results of SANS data in the second regime, $0.01 < q < 0.1$. For temperatures corresponding to the isotropic state. we observe, from Figures 1−4, a power law decay of $I(q)$ with q. This behavior of $I(q)$, $I(q) \sim q^{-D}$, is expected for statistically self-similar structures with D being the fractal dimension.[15] The value of D is 1.5 ± 0.1 for the 1 and 3% solutions of PBLG in DBA in the isotropic state. However, at higher polymer concentrations of 5 and 7%, D changes to 1.0 ± 0.1 and 0.9 ± 0.1, respectively, in the isotropic phase. As an increase in the fractal dimension is equivalent to an increase in the compactness of the structure, we conclude that the aggregates in the isotropic state of PBLG in DBA are less dense, indicating the presence of increased spatial inhomogeneities within the aggregates, at higher polymer concentrations.

The fractal dimension of the PBLG−DBA system in the gel phase depends on the thermal history of preparation of the gel. We have used two protocols to prepare the system at lower temperatures: (i) a step quench with a series of temperature lowering in 10 °C steps from 80 to 30 °C with an equilibration time at each temperature of 7−8 h; (ii) a sudden quench where the sample is brought from 80 °C to the room temperature of ~27 °C in one step. The results of D of the gel phase, from SANS data of Figures 1−4 in the second q regimes, are presented in Table 2 for both step quench and sudden quench. For a given concentration, the fractal dimension increases as the temperature is lowered in consecutive steps, indicating the densification of the aggregates at lower temperatures. Also, the fractal dimension of the gel obtained by step quench is higher than that obtained by sudden quench, suggesting that equilibration times at different steps in the step quench allow the system to rearrange or relax into more

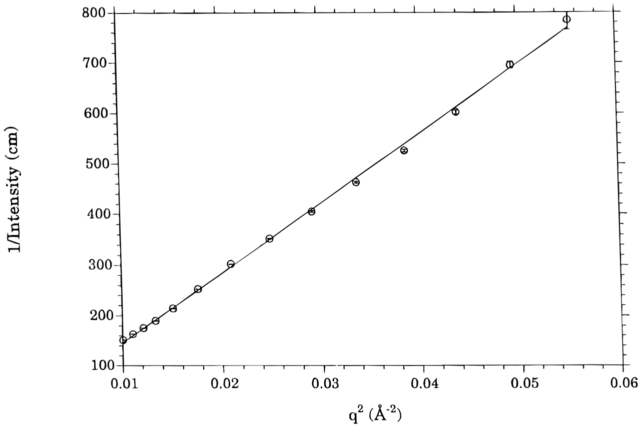

Figure 6. Fit to eq 3 for a 3% solution of PBLG in DBA at 75 °C.

Table 3. Mesh Size of the Aggregates in the Isotropic Phase

concn (wt %)	ξ (Å)	concn (wt %)	ξ (Å)
1	47 ± 5	5	28 ± 1.1
3	35 ± 4	7	23 ± 5

Table 4. Values of *n* in the Range 0.06 ≃ *q* < 0.2 for Low-Temperature Gels

concn (wt %)	temp (°C)	n
5	27	2.78 ± .04
7	28	3.44 ± .07

compact structures. Therefore, the thermal history of the sample in the isotropic phases is an important parameter in determining the self-similar structure of the resultant gel at intermediate length scales.

The SANS data of Figures 1–4 in the third regime if $q > 0.1$ were fit to the Ornstein–Zernicke[16] form,

$$I^{-1}(q) = I^{-1}(0)(1 + q^2\xi^2) \tag{3}$$

where ξ is some correlation length. For the present problem, ξ corresponds to the characteristic wavelength of the fluctuations of the polymer concentration or, in other words, the mesh size within the aggregate. An example of the fit of the data to eq 3 is shown in Figure 6 for the 3% solution at 75 °C. The values of ξ obtained by such fits are presented in Table 3 for all polymer concentrations in the isotropic phase. We see from Table 3 that as the polymer concentration increases in the isotropic phase, the mesh size decreases, indicating that the system becomes more dense at length scales shorter than the size of the molecule.

It is to be noted from Figures 3 and 4 that, at the lowest temperatures studied, the 5 and 7% samples show a steeper power law decay of $I(q)$ with q, $I(q) \sim q^{-n}$, is the range $0.06 \le q \le 0.2$. By fitting the data in this range of this power law, the values of n for the 5% solution at 27 °C and the 7% solution at 28 °C are obtained and are presented in Table 4. The value of n indicates the sharpness of interfaces present in the system. For a sharp interface, the Porod law[17] holds where $n = 4$, and values of n lower than 4 indicate the extent of diffuseness of the interfaces. We observe from Table 4 that the interfaces in the 7% solution at 28 °C are sharper than those in the 5% solution at 27 °C.

We now discuss the relevance of our results to the most recent discussions in the literature. There is much controversy over the mechanism that causes the gelation of solutions of PBLG. There are basically two schools of thought on how a solution of PBLG forms a gel. Miller et al.[4] proposed that the gel is a manifestation of spinodal decomposition which occurs in the solvent–solute system. Stabilization of the gel occurs due to the polymer immobility caused by the anisotropy of the slow polymer diffusion. Others[6,8] believe that the junction points of the polymer network are crystalline in nature. Horton and Donald[18] recently studied the role of phase separation on the process of gelation in the PBLG–BA system. Using DSC, X-ray scattering, and polarized optical microscopy, they showed that phase separation can occur separately from gelation at high temperature for different concentrations and solvent quality conditions. From their observations, Horton and Donald[18] proposed that gelation occurs in the following manner: upon solvent quality reduction, PBLG solutions will begin to phase separate, by spinodal decomposition or nucleation and growth, but crystallization follows to arrest the phase separation. The result is a gel with the crystalline portion as the stabilizer although any significant crystallinity is not shown by X-ray scattering data.

Our results show that there is an aggregation even at high temperatures which has not been previously reported or incorporated into a gelation mechanism. Our study of the effect of thermal history on the structure of the ultimate gel demonstrates that the gel becomes more compact as the annealing time in the high-temperature phase increases. Nucleation and growth or late-stage spinodal decomposition as a method for phase separation is not consistent with this result, as for either process, the final phase formation would not be affected by the annealing time. Therefore, we believe that, if phase separation plays a role in the formation of the gel, this phase separation must only be in the early stage of spinodal decomposition when the separation is frustrated and frozen for the conditions studied in these experiments.

Conclusion

In the neutron scattering experiments reported here, it is observed that the size of the scattering particle is 3–7 times greater than even the extended size of a single molecule. We find that an aggregation of PBLG molecules exists in the isotropic phase in deuterated benzyl alcohol up to 80 °C. The size of the particle does not change with temperature in the isotropic phase for a given concentration. However, as the concentration is increased, the size of the scattering particle increases. It is also seen that an increase in concentration densifies the local structure of the aggregate, while the apparent fractal dimension becomes lower at intermediate length scales.

Our study of the fractal dimension of gels formed from different annealing procedures shows that, for a given concentration, a step quench procedure produces a more condensed structure than a sudden quench. This indicates a rearrangement or relaxation of the structure during the annealing process. It is also seen that the compactness of the gel structure increases with decreasing temperature and concentration. This result coincides with the interface studies which show that the local interfaces at low temperatures become more sharp as the concentration increases.

Though our results do not define a specific mechanism by which gelation of PBLG solutions occurs, our results suggest that if phase separation plays a role in the gel formation, this mechanism of phase separation is spinodal decomposition and the phase decomposition process is in the early stages and it subsequently becomes frustrated and frozen.

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