

Neutron-Scattering Evidence of Polymer Persistence-Length Enhancement Caused by Physical Gelation

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The chain trajectory in physical gels prepared from isotactic polystyrene has been investigated by neutron scattering. It is found that the chain possesses a wormlike conformation with a persistence length of about 80 Å, a value most unusual for this polymer ($b \approx 20$ Å in the vitreous state). Accordingly, the gel state may be the third state for this type of polymer.

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Physical gels prepared from solutions of natural macromolecules in water have been known for a long time. More recently solutions of synthetic polymers in organic solvents have also been found to have the propensity of forming thermoreversible networks.^{1,2} They are now being investigated with special emphasis on networks prepared from isotactic polystyrene (iPS),³⁻⁵ a crystallizable polymer. Previous x-ray diffraction studies^{3,6,7} had concluded on the basis of a 5.1-Å reflection, otherwise absent in iPS crystals, that physical gelation proceeds from crystallization with another type of helical form. To account for the 5.1-Å reflection, a 12_1 helix⁷ possessing a sixfold symmetry had to be invented (either "anhydrous"⁷ or solvated⁸) in lieu of the usual 3_1 helical form. However, recent neutron diffraction experiments⁹ question the very existence of the 12_1 form and correspondingly the crystalline nature of the gels. Rather, it is now suspected that the gel structure is to some extent reminiscent of nematic liquid crystals. A model, designated as a "ladderlike" model, where solvent molecules (the rungs) bridge rodlike chain portions, is hoped to describe as correctly as possible the actual structure.⁹

Clearly, the knowledge of the chain conformation is needed to further test the ladderlike model. To achieve such an investigation, neutron scattering is the appropriate tool. The possibility of deuterium labeling allows the single-chain behavior to be studied. As neutron-scattering investigations of iPS either in the amorphous state¹⁰ or in the crystalline state^{11,12} are available, a comparison can be made.

Protonated and deuterated isotactic polystyrene samples were prepared following the method described by Natta.¹³ Techniques of characterization are available in Guenet *et al.*¹⁴ Characteristics of the samples used in this study are listed in Table I.

Deuterated and hydrogenated polymer fractions were weighed together in a test tube and the volume of solvent (*cis*-decalin) needed to obtain 15% solutions was added. Concentrations of deuterated material in the gel were then ranging from 1% to 3%.

To match the scattering cross section of protonated

isotactic polystyrene, a mixture of 20% perdeuterated *cis*-decalin and 80% protonated *cis*-decalin was used as a solvent. As a result, only the coherent scattering due to the deuterated chains emerged from the incoherent background.

Homogeneous solutions, prepared by heating the above mixture at 170 °C for a few minutes, were poured out into a special mold held at 0 °C to form the gel. This mold allows disk-shaped gels of 1 mm thickness and 1.5 cm diameter to be made.

The experiments were performed at the high-flux reactor of the Institut Max von Laue-Paul Langevin (Grenoble, France) on the D17 small-angle camera. The transfer momentum q available was in the range

$$1 \times 10^{-2} \leq q \leq 1.3 \times 10^{-1} \text{ \AA}^{-1} \quad (\lambda = 12 \text{ \AA}).$$

A mechanical wavelength selector was used ($\Delta\lambda/\lambda = 90\%$).

The samples were held in containers made up with two quartz plates (2 cm diameter, 1 mm thick) spaced 1 mm apart by a ring-shaped piece of glass (1.5-cm internal diameter). The system was tightly closed so as to prevent solvent evaporation while the data were collected.

As usual, the data were collected for background intensity, sample-cell scattering, and sample transmission and eventually normalized by an incoherent spectrum scattered by protonated water.

A typical Kratky plot of the data collected in the intermediate range is given in Fig. 1. As can be seen, two regimes can be identified: (i) for $q < q^*$, although very narrow, a domain wherein $I(q)$ behaves as q^{-2} and (ii) for $q > q^*$ a domain where $I(q)$ varies as q^{-1} .

TABLE I. Sample characteristics. M_w is the weight average molecular weight and M_n is the number average molecular weight.

	M_w	M_w/M_n
iPSH	3.2×10^5	2.8
iPSD	2.5×10^5	1.15

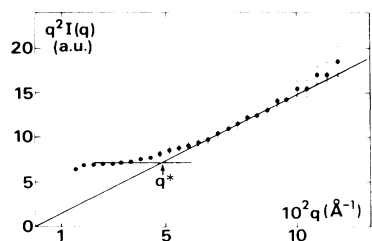


FIG. 1. Kratky plot, $q^2 I(q)$ vs q , $C_{\text{IPSD}} = 1\%$.

Such a plot is characteristic of a wormlike chain, that is a chain which globally obeys Gaussian statistics but possesses a statistical segment far larger than its monomeric unit. Theoretical calculations of the structure factor $S(q)$ for such a conformation were carried out by Heine *et al.*¹⁵ and more recently by Des Cloizeaux.¹⁶ It can be schematically shown in the limit of very long chains that two regimes are expected for $S(q)$ in the intermediate range: regime 1

$$S_1(q) \sim 12/q^2 b^2, \quad q < q^*, \quad (1)$$

regime 2

$$S_2(q) \sim \pi/qb, \quad q > q^*, \quad (2)$$

where b is the persistence length (or in other words the statistical element of the wormlike chain).

If q^* is defined as the intersect between the asymptotes of $q^2 I_1(q)$ and $q^2 I_2(q)$ [note that $I(q) \sim S(q)$ and subscripts refer to the regime], then it can be straightforwardly demonstrated that q^* reads

$$q^* = 12/\pi b. \quad (3)$$

The persistence length b of the chains in the gel state calculated from relation (3) is therefore

$$b \approx 80 \text{ \AA}.$$

Such a magnitude for the persistence length was not known to exist for this polymer (usual size $b \approx 20 \text{ \AA}$).^{10,17} Rodlike chain portions of about the same size can only be found in the crystalline state. However, in this state the chain does not remain globally Gaussian. Chain folding, which propagates along an $(h, k, 0)$ crystallographic plane in the course of crystallization, gives birth to a thin-sheet structure¹² [amusingly enough, this structure possesses a form factor $S(q)$ which behaves just as the reverse of the wormlike chain form factor, that is, q^{-1} at the smallest q and q^{-2} at the largest ones].

Further, the observation of the q^{-1} behavior with polystyrene in the vitreous state is usually unattainable on account of its rather large chain cross section.¹⁸ As a

matter of fact, for threadlike systems with finite radial dimensions $S(q)$ reads, for $q > q^*$,

$$S(q) \sim (\pi/qb) \times \exp(-q^2 \langle R_c^2 \rangle / 2), \quad (4)$$

where $\langle R_c^2 \rangle$ is the mean square radial radius of gyration. Should b be far larger than the thread diameter, then the exponential term reduces to unity in the range $1/b > q > 1/\langle R_c^2 \rangle^{1/2}$ and Eq. (2) is retrieved. Concerning polystyrene, $b \approx 20 \text{ \AA}$ in the vitreous state while the thread diameter is of about 8 \AA ¹⁸ which entails that $S(q)$ usually behaves only as q^{-2} in the intermediate range. Only the use of partial chain labeling (backbone labeling) allows the q^{-1} behavior to be observed as recently reported by Rawiso *et al.*¹⁸ for atactic polystyrene. Because of the large value of b , no special labeling need be brought about in iPS physical gels.

As apparent from this short discussion, the wormlike chain behavior with a persistence length of nearly 80 \AA is observed neither in vitreous iPS nor in crystals. Following up recent results obtained by neutron diffraction, those reported herein also suggest that the physical gel state may well be the "third state" for this type of polymer. In addition, the recently proposed ladderlike model is partly backed up by the observation and the magnitude of the persistence length.

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