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Analysis

A New Look at the Molecular Structure of Isotactic Polystyrene Physical Gels as Revealed by Neutron Diffraction

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Summary

Neutron diffraction experiments have been performed on isotactic polystyrene (iPS) gels as-prepared (i.e. no drying and no stretching) containing deuterated iPS and deuterated cis-decaline (C_{pol}=40%). This paper reports that gels on one hand and cis-decaline in the liquid state on the other hand exhibit the same diffraction pattern with a peak at 0.53 nm These results are briefly discussed.

Introduction

Physical gels of iPS are prepared from concentrated solutions quenched below room temperature(1) (typically 0°C). Under these conditions, the usual 3_1 helix observed in chain-folded crystals is absent in the gel. X-ray diffraction patterns recorded on stretched samples reveal an intense reflection at 0.51 nm(2) which has been assigned to a new helical structure. After having discussed the possibility of stereoregular defects(2) and disregarded it(3), it has been suggested that this new helical structure could be a 12_1 helix which is close to an extended backbone. Some evidences exist for stretched and dried gels(4) showing layer lines particularly at 3.06 nm which are apparently in agreement with the aforementioned helical structure. Yet, the origin of the 0.51 nm reflection is still puzzling since it is not really consistent with a 12_1 helix. In addition, intensities calculated on the basis of an oriented 12_1 helix are far from matching the experimental one(3). Clearly, further experimental investigations are needed to throw some light on these points.

The purpose of this note is to report neutron diffraction studies on these systems. The results obtained are puzzling and may lead to pose more questions instead of bringing clear-cut conclusions. Yet, they also might provide a new issue to the problem raised by the 0.51 nm reflection.

Neutron diffraction

Neutron diffraction has two major advantages over X-ray diffraction:
i) Neutrons only interact with nuclei which makes it possible to regard atoms as point scatterers. Accordingly, the scattering factor f_N is a constant with diffraction angle(5). Conversely, the electronic scattering factor f_{XR} for X-rays presents a fall-off with diffraction angle. This can be a major drawback for X-rays when dealing with poorly crystalline or liquid materials resulting in a loss of resolution(5).

ii) For polymeric systems, the use of deuterium labeled molecules which does not significantly alter physical properties(6) enables one to "visualize" the order of one component only in a blend by an appropriate choice of protonated and deuterated species.

Experiments reported in this note solely take advantage of property i).

Experiments were performed on the high resolution spectrometer 3T2 located at "Orphee" (Laboratoire Léon Brillouin CEA-CNRS C.E.N. Saclay). Intensities are recorded by steps of 0.05 degree with a neutron wavelength λ = 0.1225 nm obtained by diffraction of the primary beam on the (335) crystallographic plane of Germanium. Counting times at constant flux are of about 24 hrs.

Samples

Deuterated isotactic polystyrene (iPSd) has been prepared in the laboratory by the Natta method(7). An iPSd fraction, $M_w = 2.5\ 10^5$ and $M_w/M_n = 1.15$ has been employed(8). Deuterated cis-decalin has been purchased from Spectrométrie spin et techniques (Paris). A gel at a concentration of 40% polymer (w/w) has been formed by heating at 180°C until complete homogeneization then quenching into iced-water. Amorphous silica tubes of 4 mm diameter have been used as required for neutron diffraction.

Results and discussion

Neutron diffraction results are drawn in figure 1 (gel) and figure 2 (liquid cis-decaline). As apparent from these figures, both diffraction patterns are virtually identical and exhibit a narrow peak at 0.53 nm. Before further discussing these results, two remarks have to be made:

i) The gel diffraction pattern does not arise from "islands" of decaline. DSC experiments(9) indicate that for a 40% concentration all the solvent is bound (there is no longer free molecules of solvent capable of forming solvent crystals). These experiments which consist of measuring ΔH_{sol} as function of polymer concentration in the gel reveal that $\Delta H_{sol} = 0$ for $C_{pol} \cong 30\%$ in cis-decaline. Therefore results of figure 1 do correspond to the gel diffraction pattern only.

ii) The 0.53 nm reflection certainly corresponds to the 0.51 nm one recorded by X-ray diffraction. The slight discrepancy (~4%) may simply arise from the use of deuterated material instead(6).

The outcomes of these diffraction experiments are manifold and far-reaching. Firstly, the wet and unstretched gel possesses mainly the features of a liquid. The analysis in terms of liquid order type leads to reconsider the statement according to which the 0.51 nm reflection is a diffraction peak due to a 12_1 helical structure made up with dimer elements. In the case of a liquid, the narrower first peak is related to the distance between first neighbor molecules yet not necessarily through a simple Bragg's law:

$$\lambda = 2d \sin {}^{\theta}{}_{m}/2$$

Deviations from this law(10) depend on many parameters such as the arrangements of molecules as well as their shape. The only way to exactly

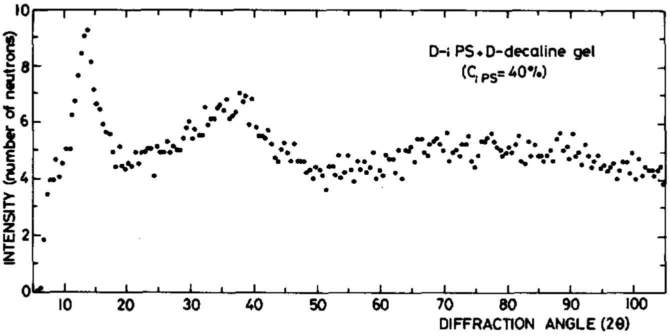

Fig. 1: iPSD-cis- D-decaline gel

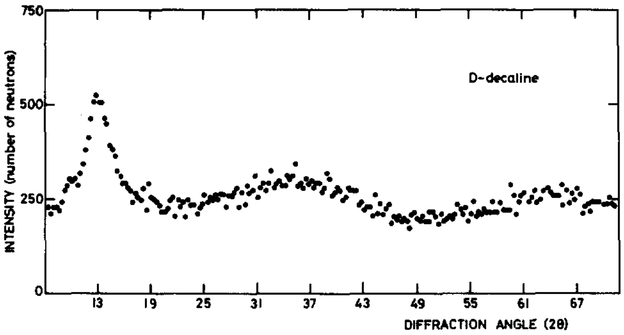

Fig. 2: cis-D decaline (note that the abscissae scale is more expanded than in Fig. 1).

know the structure is to calculate the Fourier transform of the experimental intensity over the entire range of diffraction and use a model. Yet, worth noticing is if the EHRENFEST law:

$$1.23\lambda = 2d \sin \theta_m/2$$

is used in an attempt to determine the distance d between first neighbours, one ends up with $d \leq 0.65$ nm which happens to be close to the pitch of a 3_1 helix. Is such a result merely fortuitous or not? This remains an open question.

Results reported here might suggest that decaline molecules are trapped by polymer chains in the same state they were in the liquid, hence the observation of the 0.53 nm reflection in the gel as well (and possibly its appearance as a meridional reflection in stretched gels?). Such an assumption entails solvation of the gel structures and has already been put forward by Sundararajan et al(11) for iPS gels and supported by recent findings(12). Other examples can be found in the literature such as the case of poly γ methyl-L-glutamate with dimethyl phthalate. For this system, Watanabe et al(13) have also observed a strong meridional reflection at 0.507 nm (incidentally note this value close to what is found with iPS physical gels) which comes from solvent incorporation into the α-helical form so as to give a crystalline complex.

However, if the 0.53 nm reflection is only due to trapped decaline molecules, there is no trace of order concerning the polymer itself. While it would be unwise to definitely dismiss at the moment the presence of crystalline structures of 12_1 type in a freshly prepared gel, these are certainly less than minute. Despite the observation of the features expected from a 12_1 helical form (3.06 nm layer line) on highly stretched and dried gels, there is no reason to state that this form has grown owing to gel formation. The appearance of the 12_1 form might well be the result of stretching as in natural rubber(14). According to the experiments reported here, basing an analysis on the only 0.53 nm (or 0.51 nm for X-rays) reflection is irrelevant since liquid decaline does exhibit the same peak (which might be the case also for solvents of comparable size).

Finally, if chain crystallization is virtually absent the question is now to discover what type of mechanism or process holds the chains together. The structures involved, although possessing a liquid order, must show a first order transition on melting (the gel melting is undoubtedly a first order transition). These conditions are reminiscent of nematic liquid crystals. Accordingly, a possible structure would consist of rod-like chain portions (but not necessarily under any well-defined helical form) that would align, the solvent molecules acting then as bridges between chains (Ladder-like model). If such a model might prove to be relevant, the nature of solvent-chain interaction remains nevertheless to be explicited.

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