Existence of a Poly(vinyl chloride) (PVC)−Solvent Compound in PVC Thermoreversible Gels As Revealed by Neutron Diffraction†

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Introduction

Thermoreversible gels usually form out of solutions of highly stereoregular polymers[1] although atactic PVC stands as a noticeable exception to this tendency.[2] PVC thermoreversible gels exhibit unexpectedly high values for the elastic moduli, a fact which has long puzzled scientists working in this field.[2−5] In an attempt to cast some light on this phenomenon, it has recently been suggested that a compound is liable to form between the less syndiotactic sequences and the solvent,[6,7] thus enhancing the rigidity of the fibers that constitute PVC gels and eventually increasing the elastic modulus. So far, the existence of this type of compound relies upon circumstantial evidence.[5−7] Herein, neutron diffraction experiments are reported that reveal directly the occurrence of such a compound.

Experimental Section

Deuterated PVC (PVCD) was synthesized by radical polymerization at 50 °C using AIBN as initiator with a deuterated monomer purchased from EURISOTOP. The polymer was dissolved in THF, precipitated with methanol, and dried at 40 °C under vacuum. NMR characterization was achieved at 90 °C in deuterated dioxane with a Varian XL 300 MHz spectrometer operating at 75.5 MHz. The following proportions for the heterotactic, isotactic, and syndiotactic triads were obtained: heterotactic = 50%, isotactic = 21%, syndiotactic = 29% These values are virtually identical to those determined for hydrogenous PVC within experimental uncertainties.

Hydrogenated diethyl oxalate (DEOH) was purchased from Aldrich and used without further purification. Deuterated diethyl oxalate (DEOD) was synthesized by reacting oxalate dichloride with deuterated ethyl alcohol, the latter also being purchased from EURISOTOP.

Two gel samples were studied: PVCD/DEOH and PVCD/DEOD. They were prepared by heating at 150 °C a mixture of PVCD and solvent in 3 mm diameter cylindrical quartz tubes sealed from the atmosphere. After quenching to room temperature for producing the gel, the system was aged for a minimum of 1 week prior to measurements. For both samples, the PVCD concentration was $C_{PVCD} = 0.135$ g/cm^3.

Diffraction experiments were carried out at Laboratoire Leon Brillouin (Saclay, France) on the two-axis diffractometer G-4-1. This spectrometer is equipped with a banana-type detector composed of 800 BF_3 cells each separated by 0.1°. A wavelength of $\lambda = 0.243$ nm was used (pyrolytic graphite monochromator).

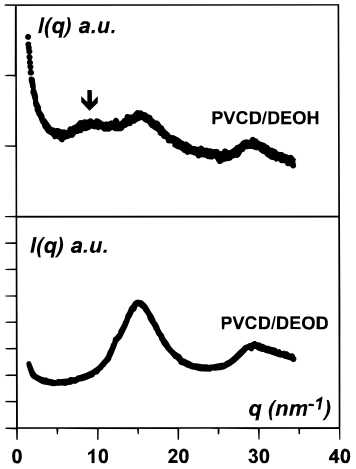

Figure 1. Diffracted intensity (in arbitrary units) as a function of the transfer momentum $q = 4\pi/\lambda \sin(\theta/2)$ (in nm^{-1}): upper curve = PVCD/DEOH gel; lower curve = PVCD/DEOD gel. The arrow highlights the reflection at 9 nm^{-1}.

Results and Discussion

The intensity diffracted by a two-component system can be written in the general form[8]

$$I(q) = \langle A_p(q)\rangle^2 S_p(q) + \langle A_s(q)\rangle^2 S_s(q) + 2\langle A_p(q)\rangle\langle A_s(q)\rangle S_{ps}(q) \quad (1)$$

in which A_P and A_S are the scattering amplitudes related to the polymer and to the solvent, respectively, $S_P(q)$ and $S_S(q)$ are the scattering factors of the polymer and of the solvent, and $S_{PS}(q)$ is a cross-term scattering factor.

The scattering amplitudes per unit volume are expressed as follows:

$$\langle A(q)\rangle = v_m^{-1}\langle \sum_1^N a_i \exp(iq\rho_i)\rangle \quad (2)$$

in which a_i is the scattering length of atom i located at a distance ρ_i from the center of gravity of the molecule or of the monomer unit. v_m is the molar volume of the species. Scattering amplitudes reach constant values at low q, independent of the scattering vector.

If the polymer forms a compound with the solvent, then the use of deuterated solvent instead of hydrogenated solvent must alter the diffraction pattern. This is so because the labeling will affect the cross-term in relation 1.[9,10]

Conversely, if the polymer crystallizes on its own without incorporating solvent, then the diffracted intensity reduces to

$$I(q) = \langle A_p(q)\rangle^2 S_p(q) + \langle A_s(q)\rangle^2 S_s(q) \quad (3)$$

Under these conditions, changing the labeling of the solvent will not alter the intensity diffracted by the polymer.

Experimentally, it can be seen in Figure 1 that whether DEOD or DEOH is used, two different diffraction patterns are obtained. In particular, a diffraction peak can be seen at $q = 9$ nm^{-1} in the case PVCD/DEOH which is absent in the case PVCD/DEOD. The appear-

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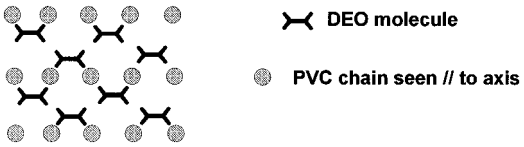

Figure 2. Possible sheet-like structure for the compound as proposed in ref 7.

ance of a new reflection by simply changing the labeling of the solvent while using in both cases PVCD gives decisive support to the existence of a PVC−DEO compound. It is worth noting that the reflection at $q = 15$ nm^{-1} corresponds to the liquid-like diffraction of the free solvent, which explains why it is seen to increase from DEOH to DEOD.

The distance associated with the diffraction maximum due to PVCD at $q = 9$ nm^{-1} corresponds to a distance of $d = 0.7$ nm as calculated from the Bragg law. This distance is not known for crystallites constituted of syndiotactic sequences[11] and is therefore due beyond doubt to the PVC−DEO complex. Recent results[7] obtained from small-angle neutron scattering have been interpreted by considering a sheet-like structure for the PVC−DEO compound (see Figure 2). In this structure, rows of PVC molecules alternate with rows of solvent molecules. This reflection is likely to correspond to the diffraction by the rows of PVC. The fact that this reflection vanishes when using deuterated diethyl oxalate is rather consistent with this model as the scattering amplitudes of PVCD and of DEOD are very close to one another in this q range (this is no longer the case at larger q values). The conclusions drawn from the SANS results suggested, however, that the distance between PVC rows should be about 1.5 nm, that is approximately twice the value found here. Does this mean that the reflection at 9 nm^{-1} is a second order of a reflection that would be at 4.5 nm^{-1}? Clearly, additional experiments are needed in this q range to elucidate the precise structure of the PVC−DEO complex.

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