Molecular Structures in Poly(vinyl chloride) Thermoreversible Gels: Effect of Tacticity and of Solvent Type[†]

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ABSTRACT: Neutron scattering and neutron diffraction studies have been carried out as a function of the solvent type and of poly(vinyl chloride) (PVC) tacticity. In diesters, while the large scale structure of the gel does not depend significantly upon the nature of the alcohol group, the short-range structure differs markedly. In both cases a PVC−solvent complex is nevertheless formed. Neutron diffraction allows confirmation of the existence of such a complex in PVC/diethyl oxalate gels. By using bromobenzene, it has been observed that gels prepared from a PVC of higher syndiotacticity do not possess the same large scale structure as those produced from usual atactic PVC. Conversely, they are similar to those obtained in diethyl oxalate with the usual atactic PVC. These results highlight again the equivalence between tacticity and solvent type. This equivalence originates, however, in differing short-range molecular arrangements: complex formation in usual PVC/diethyl oxalate gels, "syndiotactic" crystals formation in highly syndiotactic/bromobenzene gels.

Introduction

Reports on the thermoreversible gelation of atactic poly(vinyl chloride) (PVC), a poorly crystalline polymer, date back the late Forties.[1−3] Yet the existence of high elastic moduli did not receive any satisfactory nor consistent explanation for several years. While the degree of crystallinity could be accounted for by considering incorporation of isotactic defects into the crystalline domains made up with syndiotactic sequences,[4] it remained nevertheless too low to be consistent with unusually high moduli. This was especially conspicuous when comparison was made with systems thought to be similar, such as those gels prepared from multiblock copolymers containing an equivalent amount of crystallizable sequences. These gels are known to possess elastic moduli about 2 orders of magnitude lower than those of PVC gels.[5] Clearly, a reappraisal of both the conventional structure and of the gelation mechanism was needed.

The notion of a PVC−solvent complex,[6,7] together with the mesoscopic fibrillar structure,[8] was then contemplated. The complex was said to form within the less stereoregular domains of the fibrils, the latter owing their stability to the "syndiotactic" microcrystallites.[6]

The concept of PVC-complex formation associated with the fibrillar morphology accounts for both the existence of a first-order transition at 50 °C (melting of the complex)[9,10] and the stiffening of the gel fibrils. In the latter case, elasticity is no longer regarded as entropic but as enthalpic instead. This implies that the gel elastic modulus is not only dependent upon the number of junctions per unit volume but also upon the fiber stiffness.[11]

This paper reports on neutron scattering and neutron diffraction experiments intended to test further the notion of the PVC−solvent complex, in particular with solvents of differing qualities.

Experimental Section

1. Materials. Three different hydrogenous PVC samples were used in this investigation, of which two were kindly provided by Rhône-Poulenc. They consisted of PVC synthesized at 50 °C (HTPVC1) and PVC synthesized at −40 °C (LTPVC) (the acronyms are those already used in previous papers[6,7,9]). A third sample, HTPVC2, was obtained by molecular weight fractionation of HTPVC1 by using THF/ethanol as solvent/precipitant. Size-exclusion chromatography (SEC) in THF gave the following weight-averaged and number-averaged molecular weights: HTPVC1, $M_w = 1.23 \times 10^5$, $M_w/M_n = 2.3$; HTPVC2, $M_w = 1.1 \times 10^5$, $M_w/M_n = 1.4$; LTPVC, $M_w = 2.0 \times 10^5$, $M_w/Mn = 3.3$.

NMR characterization provided the following proportions for the triads: HTPVC samples, iso = 0.19, syndio = 0.32, hetero = 0.49; LTPVC sample, iso = 0.12, syndio = 0.39, hetero = 0.49.

A deuterated PVC sample (PVCD) was synthesized by radical polymerization at 50 °C using AIBN as initiator. The reaction was carried out for 5 h until a conversion of 25% was reached. 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 hetero, iso, and syndio triads were obtained for the PVCD sample: iso = 0.21, syndio = 0.29, hetero = 0.5.

As can be seen, these values are, within experimental uncertainties, virtually identical to those determined for hydrogenous HTPVC.

Hydrogenous diethyl oxalate (DEOH) and dibutyl oxalate (DBOH) were purchased from Aldrich and used without further purification. Deuterated diethyl oxalate (DEOD) and deuterated dibutyl oxalate (DBOD) were synthesized by reacting oxalate dichloride either with deuterated ethyl alcohol or with deuterated dibutyl alcohol. Deuterated bromobenzene

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(BrBzD) was purchased from EURISOTOP as well as all the deuterated materials used in this study.

2. Small-Angle Neutron Scattering. Small-angle neutron scattering experiments were performed on the PAXE camera located at Orphée (Laboratoire Léon Brillouin, Saclay, France) and on the D11 camera located at ILL (Grenoble, France). These cameras are both equipped with two-dimensional sensitive detectors made up with 128 × 128 cells. These detectors can be moved to different positions, thus allowing the sample−detector distance to be changed. In both systems a mechanical selector provides neutrons with a wavelength distribution characterized by a relative full width at half-maximum, $\Delta\lambda/\lambda_m$, of about 10%. By using different sample−detector distances and $\lambda_m = 0.6$ nm, a q range of $0.1 \leq q$ (nm^{-1}) ≤ 2.5 was made available, with $q = 4\pi/\lambda \sin(\theta/2)$ (θ = scattering angle).

Two series of gels were prepared.

(a) A series intended for studying the PVC chain conformation within the gel: The sample consisted of some hydrogenous chains imbedded in a deuterated matrix composed of deuterated polymer together with a mixture of deuterated and protonated diethyl oxalate. The solvent mixture had a volume fraction composition of 94.1% DEOD and 5.9% DEOH so as to match the coherent scattering amplitude per unit volume of the deuterated polymer. Under these conditions, a blank sample free of hydrogenous chains showed a virtually flat scattering in the whole scattering range. The use of hydrogenous chains as the labeled species allowed one to keep the background scattering substantially low, thus enhancing the signal/noise ratio. After the usual transmission corrections, the background subtracted from the sample intensity consisted of the superposition of the flat background scattered by the blank sample and of the incoherent scattering of the hydrogenous chains, the latter being calculated through a method devised by Fazel et al.[12]

(b) A series of gels with hydrogenous chains in deuterated solvent intended for studying the gel structure was prepared. The background subtracted from the sample intensity consisted of two terms: the flat coherent scattering of the deuterated solvent reduced to its proportion in the gel and the incoherent scattering of the hydrogenous chains calculated as above.

Gels were prepared in hermetically sealed quartz cells. A mixture of the necessary constituents was heated at 150 °C until a clear, homogeneous solution was obtained. The gels were produced by a rapid quench of these solutions to room temperature and were aged for a minimum of 1 week prior to any investigation.

As usual the position sensitive detectors were calibrated by using a solvent the scattering of which is virtually purely incoherent (in the present case *cis*-decalin). Under these conditions the absolute intensity, $I_A(q)$ is written as

$$I_A(q) = \frac{I_N(q)}{K} \tag{1}$$

in which $I_N(q)$ is the intensity obtained after background subtraction, transmission corrections, and detector calibration. K is a constant which includes the contrast factor and is written as

$$K = \frac{4\pi N_A \delta_{dec} T_{dec} (a_P - y a_M)^2}{g(\lambda) m_0^{\,2} (1 - T_{dec})} \tag{2}$$

in which N_A is Avogadro's number; m_0 is the monomer molecular weight; T_{dec} and δ_{dec} are the cis-decalin sample transmission and thickness, respectively; a_P and a_M are the scattering amplitudes of the polymer species and of the matrix, respectively; $y = V_P/V_M$ (V = molar volume); and $g(\lambda)$ is a corrective term which depends upon the neutron wavelength, the wavelength distribution, and the camera. This parameter was determined by means of a method devised by Cotton[13] for PAXE and using previous determination given in ref 14 for D11.

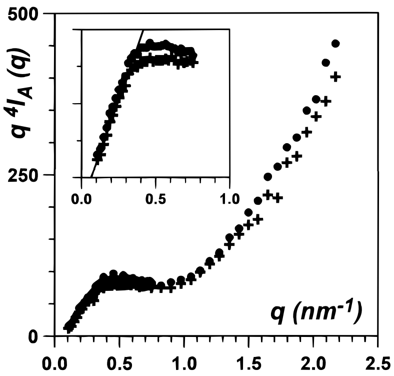

Figure 1. $q^4 I_A(q)$ vs q for PVC−DEO gels, $C_{PVC} = 0.093$ g/cm^3: (●) HTPVC2, (+) HTPVC1. Inset shows enlargement of the low-q range.

3. Neutron Diffraction. The diffraction measurements were performed at Laboratoire Leon Brillouin (Saclay, France) on the two-axis G-4-1 diffractometer. 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 (pyrolitic graphite monochromator). Cell efficiency was corrected by means of a vanadium sample. Intensities are given in arbitrary units.

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 achieving gelation by a rapid quench to room temperature, the gels were aged for a minimum of 1 week prior to measurements. For both samples the PVCD concentration was $C_{PVCD} = 0.135$ g/cm^3.

Results and Discussion

In this study, three solvents were selected on the basis of their different behavior toward PVC gelation. According to Najeh et al.[7] a polymer−solvent complex is formed in DEO and DBO. The main difference between these two solvents lies in their swelling properties. When a piece of gel is immersed in an excess of preparation solvent, no significant swelling occurs in DEO, unlike what takes place in DBO.[7] In the latter case, a swelling ratio of about 2.5 is reported ($V_{final}/V_{initial}$). It is worth mentioning that the magnitude of the gel elastic moduli remains practically the same in DEO and DBO when comparing at identical equilibrium concentration (concentration calculated after swelling). The situation differs with bromobenzene gels, for which elastic moduli are much lower. It is not known so far whether a complex is formed between PVC and bromobenzene, although the same type of electrostatic interaction as that considered for diesters is liable to be established.

This part will be divided into three sections. The first section will be devoted to the molecular structures in DEO, which will include the molecular structure of the gel as a function of the PVC fraction and of PVC concentration, the chain conformation, and the molecular structure of the PVC-DEO complex. The second section will discuss the molecular structure of gels produced in DBO. Finally, the third section will deal with the effect of tacticity on the molecular structure of gels produced in bromobenzene.

PVC/Diethyl Oxalate Gels (PVC-DEO). 1. Gel Structure. In Figure 1 are plotted by means of a $q^4 I(q)$ vs q representation the results obtained with 10% gels ($C_{pol} = 0.093$ g/cm^3) prepared from either HTPVC1 or HTPVC2. As can be seen, there is little difference between either curves. A small yet significant discrepancy can only be detected in the q range $0.4 < q$ (nm^{-1})

< 0.7, while above $q \approx 1.5$ nm^{-1} the slight mismatch between either curves arises from the error inevitably caused by subtracting the background. Both curves can be interpreted in the low-q range by using a theoretical approach recently proposed by Guenet,[15] in which the gel framework is regarded as an array of straight cylinders of cross-sectional dimensions described by a distribution function of the type $w(r) \sim r^{-1}$ bounded by two cutoff radii, $r_{\min}$ and $r_{\max}$. As has been already reported elsewhere,[15,16] a so-called transitional q range can be observed for $q < 0.3$ nm^{-1} in HTPVC−DEO gels. In this q range, the intensity is written[15] as

$$q^4 I(q) = \frac{C_{\mathrm{pol}} \times 2\pi\rho(\pi q - 2/r_{\max})}{\ln(r_{\max}/r_{\min})} \qquad (3)$$

in which ρ is the polymer density within the fibers.

The Porod range is reached for $qr_{\min} > 1$, which corresponds to $q > 0.4$ nm^{-1} in the present case. Here the intensity reads

$$q^4 I(q) = \frac{4\pi\rho C_{\mathrm{pol}}}{r_{\mathrm{n}}} + \frac{A}{q^2} \qquad (4)$$

in which r_{n} is the number-average mean cross section radius. According to Guenet,[15] and later supported by Lopez et al.,[16] the magnitude of A in relation 4 (q^{-6} terms) is related to the number of connections per unit volume between fibers, that is the number of physical links per unit volume. As the q^{-6} terms become negligible for large q values, a plateau regime is expected to be reached from above in a $q^4I(q)$ vs q representation. This eventually gives rise to the occurrence of a maximum whose importance is proportional to the number of junctions per unit volume.

The plateau regime is barely visible in the present case since the intensity eventually varies as q^{-2} at larger q, a behavior said to reflect the short-range structure of the fibers.[16]

The main discrepancy between HTPVC1 and HTPVC2 is therefore only found in the Porod range (see inset of Figure 1). The curve turns out to be flatter for HTPVC1 than for HTPVC2, which indicates that more physical links are created with HTPVC2 than with HTPVC1. Before elaborating further on this point, it should be stressed that physical links between fibers can be established through the PVC−solvent complex but also through the "syndiotactic" crystals. This is clear from the fact that the gel final melting temperature increases with increasing polymer concentration.[8,9] If only the complex allowed formation of junctions between fibers, then gel melting would always proceed near 50 °C. That HTPVC2 forms more junctions than HTPVC1 possibly arises from the fact that HTPVC2 contains a lower proportion of low-molecular weight chains than HTPVC1. Low molecular weight chains contain shorter syndiotactic sequences than high molecular weight chains, as has been highlighted by Mutin.[17] By assuming Bernouillian statistics for the placements of the dyads, Mutin derived the following expression for the fraction $[F_{\mathrm{s}}(N)]$ of syndiotactic sequences of length N larger than N_{o}:

$$F_{\mathrm{s}}(N) = \beta^{N_{\mathrm{o}}-1}[N_{\mathrm{o}}\alpha + \beta - (N_{\mathrm{o}}\alpha^2/P) + N_{\mathrm{o}}/P(\alpha - 2\beta) - 2\beta/\alpha P] \qquad (5)$$

in which α and β are the fraction of isotactic dyads and syndiotactic dyads, respectively, and P is the number of monomers. While the fraction of syndiotactic dyads is kept constant, relation 5 indicates that the fraction $F_{\mathrm{s}}(N)$ increases upon increasing the number of monomers. As a result, the proportion of "syndiotactic" crystallites as well as their size should increase with increasing molecular weight. Findings reported by Yang and Geil do show that the gel modulus and the gel final melting temperature increase with increasing PVC molecular weight.[8]

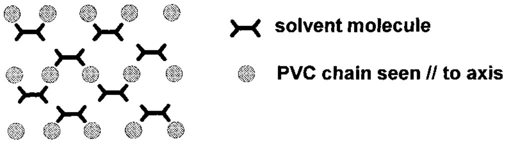

Figure 2. Schematic representation of the PVC−DEO complex structure as seen parallel to the chain axis.

These arguments may suggest that low-molecular weight chains cannot be incorporated into the fibers so that the q^{-2} scattering observed at larger q should arise from these free chains. This model is, however, ruled out, as no significant difference between either PVC samples is observed in this q range. Conversely, this gives further support to the view which states that the q^{-2} behavior essentially reflects the local molecular arrangement of the fibers (sheetlike structure; see Figure 2). The existence of free chains might have been worth taking into account if aggregation only arose from "crystallization" of the syndiotactic portions. Yet, aggregation is also due to complex formation, which is now known to occur in the less stereoregular domains[16] and is thereby little sensitive to the length of syndiotactic sequences.

To summarize, "syndiotactic" crystals and/or PVC−solvent complex domains promote the formation of fibers with a minimum of nonincorporated chains, although the former seem more efficient for establishing physical links between fibers than the latter.

As has been pointed out above, a linear variation can be seen in the so-called transitional q range in a $q^4I(q)$ vs q representation. The transfer momentum q_{o} obtained by extrapolation to $q^4I(q) = 0$ is related to $r_{\max}$ through

$$r_{\max} = \frac{2}{\pi q_{\mathrm{o}}} \qquad (6)$$

Similarly, the value of $r_{\min}$ can be obtained by determining the scattering vector q^* at which the straight line from the transitional q range and the plateau from the Porod q range intersect. q^* is simply written as

$$r_{\min} = \frac{2}{\pi q^*} \qquad (7)$$

In Figure 3 are plotted the values of $r_{\max}$ and $r_{\min}$ determined at different polymer concentrations. While $r_{\max}$ is a constant at low PVC concentrations, where only aggregates of finite size grow, it eventually decreases linearly with increasing concentration once the system gives an infinite network. The crossover occurs in the vicinity of the critical gelation concentration ($C_{\mathrm{gel}} \approx 2.2\%$).[18] Conversely, $r_{\min}$ remains a constant within the whole concentration range ($r_{\min} = 1.8 \pm 0.2$ nm). These outcomes are worth examining in the light of equilibrium conditions which are only reached when gels are aged in an excess of preparation solvent.[7] The invariance of $r_{\max}$ in the case of aggregates may correspond

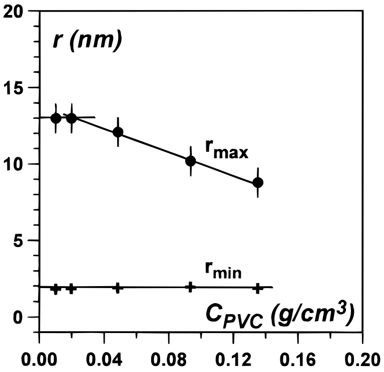

Figure 3. Variation of $r_{\max}$ (●) and $r_{\min}$ (+) as derived from relations 6 and 7.

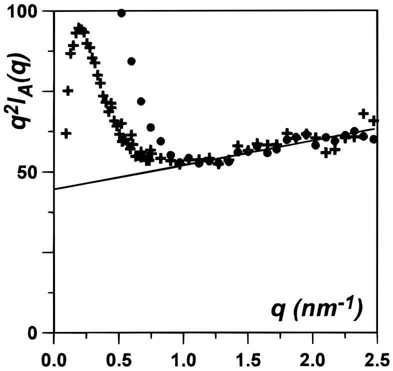

Figure 4. Intensity scattered by a few hydrogenated chains imbedded in a deuterated gel matrix of zero coherent scattering (Kratky plot, $q^2 I_A(q)$ vs q). Total polymer concentration $C_{PVC} = 0.15$ g/cm^3. Concentration in hydrogenous chains: (●) $C_H = 0.06$ g/cm^3 and (+) $C_H = 0.03$ g/cm^3 (the intensity has been multiplied by 2 for the latter case).

to an equilibrium or near-equilibrium value. All happens as if the growth of aggregates occurred in an excess of preparation solvent, i.e. the condition required for attaining equilibrium. Conversely, when increasing the polymer concentration, equilibrium is not achieved, which would account for the lower values for $r_{\max}$. The invariance of $r_{\min}$ possibly conveys the notion of a minimum cross section for a fiber to be stable, and there is no obvious reason why $r_{\min}$ should vary in the same way as $r_{\max}$.

2. Chain Conformation. The determination of the chain conformation within the network can be achieved by incorporation of a few labeled PVC chains within the gel matrix. In the present case the labeled species is hydrogenous PVC imbedded in a gel matrix composed of deuterated PVC and a binary mixture of DEOD and DEOH. The isotopic composition of the binary solvent is calculated so as to match the coherent scattering per unit volume of the deuterated chains. The only remaining coherent scattering arises therefore from the hydrogenous chains.

The results are drawn in Figure 4 by means of a Kratky plot [$q^2 I_A(q)$ vs q] for gels of total polymer concentration 0.15 g/cm^3. Two salient features are apparent: (i) there is a noticeable upturn at small angle the magnitude of which decreases with decreasing the concentration of labeled species, (ii) the terminal behavior shows significant departure from a plateau regime while varying linearly with q.

The upturn at small angle indicates that intermolecular scattering cannot be neglected. In many instances the importance of intermolecular scattering terms originates in isotopic segregation. Here, it is believed that it may arise from a high degree of chain alignments in the fibers. Under these circumstances, intermolecular scattering terms between highly parallel, rod-like objects are very strong for $qd_r \sim 1$, in which d_r is the averaged distance between labeled chains.[19] When this distance is increased either by diminishing the content of labeled species or by increasing the polymer total concentration, the intermolecular scattering should gradually vanish, as is observed experimentally.

The significant departure from the plateau regime in a Kratky plot is consistent with the existence of rodlike sections in the chains. A totally extended conformation or a wormlike conformation should, however, produce in this q range a straight line extrapolating very close to the origin for $q = 0$, unlike what is seen here.[19,20] A copolymer-like model containing rodlike sections alternating with disordered, Gaussian-like sections is certainly a better model to account for the scattering curve at large q. In the q range where the cross-terms between the different sections of the chain can be ignored, the intensity is written as

$$q^2 I_A(q) = KC_H \mu_L \left[X^2 \pi q + (1 - X)^2 \frac{12}{b} + ...\right] \quad (8)$$

in which μ_L is the mass per unit length, X is the fraction of rodlike sections, and b is the length of the statistical segment in the disordered sections. Since $\mu_L = 250$ g/nm mol and $b \approx 1.5$ nm for hydrogenous PVC chains, X amounts to $X = 0.41 \pm 0.03$. Whether calculated from the slope or from the intercept, nearly the same value for X is derived, which highlights the self-consistency of the analysis. The value of X, although lower than what had been deduced elsewhere[16] (X ≈ 0.57), still indicates too large a fraction of rodlike sections as could be accounted for by those rodlike sequences in the "syndiotactic" microcristallites. This, again, strongly favors the existence of another type of organized domains, namely PVC−DEO complex domains. The model used here meets conclusions drawn by Abied et al.,[6] who have considered the presence of three types of domains in a PVC gel fiber: "syndiotactic" crystallites (probably below 10%[4]), organized domains of the PVC−solvent complex (somewhere between 40% to 60%) and disordered domains (between 30% and 50%).

Here, it is worthwhile emphasizing that the PVC−DEO complex domains must percolate throughout the fiber in order to make it rigid, which could not be achieved if these domains were separated one another by disordered, flexible domains.

3. The PVC−DEO Complex. The short-range structure of the gel, together with the chain trajectory, strongly suggests but does not demonstrate the existence of a PVC−DEO complex. Neutron diffraction is a convenient tool for settling this point conclusively.[21,22]

The intensity diffracted by a two-component system can be written under its general form:

$$I(q) = \langle A_P(q)\rangle^2 S_P(q) + \langle A_S(q)\rangle^2 S_S(q) + 2\langle A_P(q)\rangle\langle A_S(q)\rangle S_{PS}(q) \quad (9)$$

in which $A_P(q)$ and $A_s(q)$ 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:

$$\langle A(q)\rangle = v_{\mathrm{m}}^{-1}\langle\sum_{1}^{N} a_i \exp(iq\rho_i)\rangle \tag{10}$$

In which a_i is the scattering length of atom i located at a distance ρ_i from the center of mass of the molecule or of the monomer unit and v_{m} is the molar volume of the species. (note that scattering amplitudes reach constant values for low q).

When the polymer and the solvent form a complex together, the use of deuterated instead of hydrogenated solvent must alter the diffraction pattern, as the labeling modifies the cross-term in relation 10.[21,22] Conversely, if the polymer crystallizes on its own without incorporation of solvent molecules, then the diffracted intensity reduces to

$$I(q) = \langle A_{\mathrm{P}}(q)\rangle^2 S_{\mathrm{P}}(q) + \langle A_{\mathrm{S}}(q)\rangle^2 S_{\mathrm{S}}(q) \tag{11}$$

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

As can be seen in Figure 5, two different diffraction patterns are produced whether DEOD or DEOH is used. A diffraction peak can be seen at $q = 9$ nm^{-1} in PVCD/DEOH gels which is absent in PVCD/DEOD gels. The appearance of a new reflection by simply modifying the labeling of the solvent while using in both cases PVCD gives decisive support to the existence of a PVC−DEO complex. It is worth noting that the two other reflections at $q = 1.5-2.93$ nm^{-1} correspond to the liquidlike diffraction pattern of the free solvent. This is the reason why the peak at 1.5 nm^{-1} 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 Bragg's law. This distance is not something known for crystallites constituted of syndiotactic sequences[23] and is therefore due beyond doubt to the PVC−DEO complex structure. Recent results obtained from small-angle neutron scattering have assigned a sheet-like structure to the PVC−DEO complex.[16] In this structure, which is thought to be stabilized through electrostatic interactions,[6,16] rows of PVC molecules alternate with rows of solvent molecules. This reflection, which vanishes when using deuterated diethyl oxalate, is likely to correspond to the diffraction caused by rows of PVC. This is rather consistent with the proposed structure 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[16] suggested, however, that the distance between PVC rows should be about 1.5 nm, approximately twice the value found here. The fact that this reflection is rather broad may account for that apparent discrepancy. Clearly, further investigation will be needed to resolve with more detail the structure of the PVC−DEO complex.

PVC/Dibutyl Oxalate Gels (PVC−DBO). As was commented above, HTPVC−DBO gels swell considerably when immersed in an excess of preparation solvent, unlike HTPVC−DEO gels.[7] The experiments reported here have been carried out on nonswollen samples. The large-scale gel structure of a 2% system (aggregates) differs from that of a 10% gel (see Figure 6). For a 2% system a linear variation is found in a $q^4I_{\mathrm{A}}(q)$ vs q representation in the transitional domain as with HTPVC−DEO gels and aggregates. For a 10% gel this is no longer the case. Considering the theoretical analysis by Guenet,[15] one has to interpret these data with the equation derived for the general case where $w(r) \sim r^{-\lambda}$:

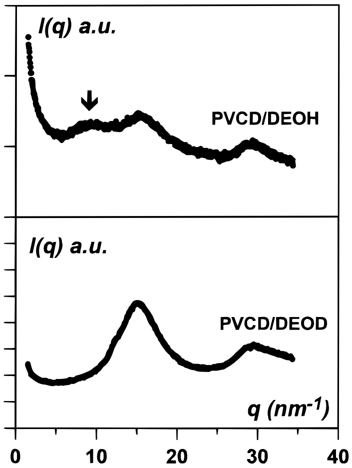

Figure 5. Diffracted intensity (in arbitrary units) as a function of q: upper curve = PVCD−DEOH gel; lower curve = PVCD−DEOD gel. The arrow highlights the reflection at 9 nm^{-1}.

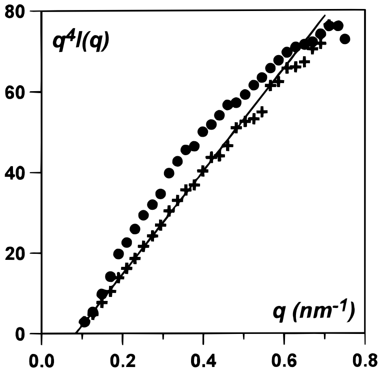

Figure 6. $q^4I_{\mathrm{A}}(q)$ vs q for HTPVC1−DBO gels in the low-q range: (●) $C_{\mathrm{PVC}} = 0.093$ g/cm^3, (+) $C_{\mathrm{PVC}} = 0.02$ g/cm^3. For the latter case the intensity has been multiplied by 4.65.

$$q^4I_{\mathrm{A}}(q) \sim A(\lambda)q^{\nu} - \frac{1}{\lambda\pi r_{\max}^{\lambda}} \tag{12}$$

In the present case it is found that $\lambda = {}^1/_3$. $A(\lambda)$ is a constant (see ref 15 for further details).

Extrapolation to $q^4I_{\mathrm{A}}(q) = 0$ gives a value of q_0 related to $r_{\max}$ through the following relation:

$$r_{\max} = \frac{1}{q_0[\lambda\pi A(\lambda)]^{1/\lambda}} \tag{13}$$

It turns out that the constant term depends very little upon λ (for $\lambda = 0.33$, $A(\lambda) = 1.15$). Similarly, $r_{\min}$ is here expressed as

$$r_{\min} = \frac{1}{q[\lambda\pi A(\lambda)]^{1/\lambda}} \tag{14}$$

Although further investigations will be needed to understand fully the implications of the value of λ, it is likely that this discrepancy originates in a swelling equilibrium problem. While, as has been stressed above, the structures in the 2% system can be considered at swelling equilibrium, this is not the case in the 10% gel. Rheological data bear out this view: HTPVC-DEO and HTPVC-DBO gels exhibit virtually the same

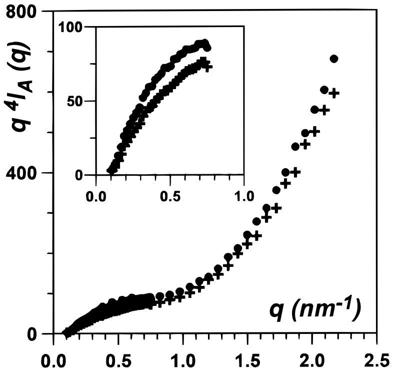

Figure 7. $q^4I_A(q)$ vs q for PVC–DBO gels, $C_{PVC} = 0.093$ g/cm^3: (●) HTPVC2, (+) HTPVC1. Inset shows enlargement of the low-q range.

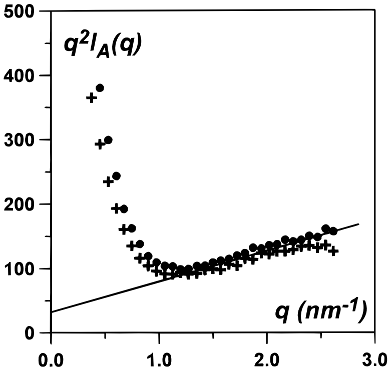

Figure 8. $q^2I_A(q)$ vs q for PVC–DBO gels in the high-q range; $C_{PVC} = 0.093$ g/cm^3: (●) HTPVC2, (+) HTPVC1. The straight line correspond to the asymptotic behavior.

modulus–concentration relation only when swollen to equilibrium.[11]

Interestingly, whereas the value for r_{max} in the HTPVC–DBO 2% system ($r_{max} = 7.5 \pm 0.5$ nm) is found to be about 2 times lower than in the 2% system HTPVC–DEO ($r_{max} = 13.5 \pm 0.1$ nm), r_{min} invariably is virtually the same ($r_{min} = 1.8 \pm 0.2$ nm). This suggests that r_{min} is an intrinsic property of this type of PVC fibers while r_{max} is solvent-dependent. That r_{max} is smaller in the case of DBO, a solvent of larger molecular volume than DEO, is not surprising within the framework of a polymer–solvent complex. As will be detailed in what follows, the short-range structure illustrates this point clearly.

In Figure 7 are drawn the results in the whole q range for 10% gels produced from HTPVC1 and HTPVC2. The same comments as those expressed for HTPVC–DEO gels hold here. HTPVC2 gels possess more junctions than HTPVC1 gels for the same reason as discussed in the previous section. On the other hand, the large q range behavior turns out to differ markedly from that seen in HTPVC–DEO gels in that no q^{-2} behavior is observed but rather a q^{-1} dependence (see Figure 8). This implies that chains are no longer arranged in a sheetlike fashion, so the structure of the complex definitely differs from that in DEO. Again, no significant discrepancy is seen in this q range whether HTPVC1 or HTPVC2 is used.

That the chains are more spaced than in DEO arises most probably from the fact already mentioned above that the molecular volume of DBO is larger than that of DEO. This inevitably influences both the gel structure and the short-range molecular arrangement of the HTPVC–DBO complex within the fiber. The fiber model proposed by Abied et al.[6] implies that the more the chains are separated in the "nonsyndiotactic" crystals, the thinner the "syndiotactic" crystals must be for achieving fiber stability;[24] hence, a lower value is found for r_{max} in DBO than in DEO.

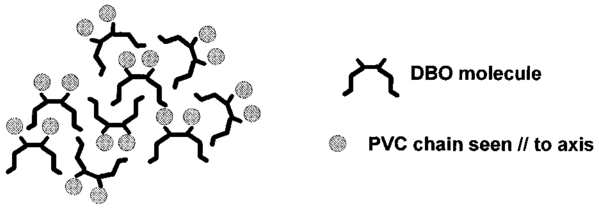

Figure 9. Schematic representation of a possible structure for the PVC–DBO complex as seen parallel to the chain axis, which highlights the chain pairing through solvent complexation.

As to the short-range arrangement, the observation of a q^{-1} behavior would suggest offhand that the chains are locally isolated from one another by a shell of solvent molecules. Here we shall tone down this view and rather propose another structure which consists of chains assembled by pair through solvent molecules (Figure 9). The relevancy of this structure relies upon the assumption put forward in previous articles as to which a diester molecule is capable of "bridging" two chains together through electrostatic interactions.[6,7] Since polarization of the C=O bond is enhanced when increasing the size of the alcohol group of the diester, so must be this type of electrostatic bridging with DBO. Admittedly, pairing does not necessarily extend throughout the fibers between the same two chains.

As is shown below, this structure does not conflict with the q^{-1} behavior. A rodlike aggregate of two chains should scatter as

$$q^2 I_A(q) \sim 2\mu_L q\pi \exp[-q^2 r_s^2/2] \qquad (15)$$

in which r_s is the cross section radius of gyration of the object. A rough estimate of the cross section radius of gyration can be obtained by considering a rectangular cross section in which two PVC chains are separated by about the same distance, as in a "syndiotactic" crystal.[23] This gives a length of about $L_s \approx 0.9$ nm and a width $w_s \approx 0.4$ nm. The cross section radius of gyration is written as

$$r_s^2 = \frac{L_s^2}{12} + \frac{w_s^2}{12} \qquad (16)$$

Relation 16 gives $r_s \approx 0.28$ nm, a value low enough to have virtually no effect on the pure q^{-1} behavior in the investigated q range. The same type of analysis as developed in relation 8 for labeled chains in a gel matrix therefore holds in this q range. In particular, assuming two chains per rodlike object allows calculation of X, that is the proportion of extended sections, and correspondingly of HTPVC–DBO complex. The value of X amounts to about 0.56 in the present case, which is consistent with previous analyses.[16] Clearly, the structure model considering two chains bridged by DBO molecules can account for the data, yet other model structures may possibly work as well, which calls for additional investigations in an attempt to settle this issue.

PVC/Bromobenzene Gels (PVC–BrBz). Gels prepared from bromobenzene show considerable swelling when immersed in an excess of preparation solvent. The

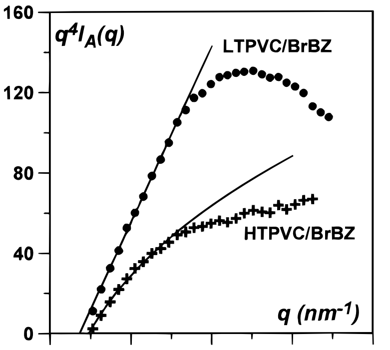

Figure 10. $q^4I_A(q)$ vs q for PVC–bromobenzene gels in the low-q range, C_{PVC} = 0.093 g/cm^3. (●) LTPVC, (+) HTPVC1.

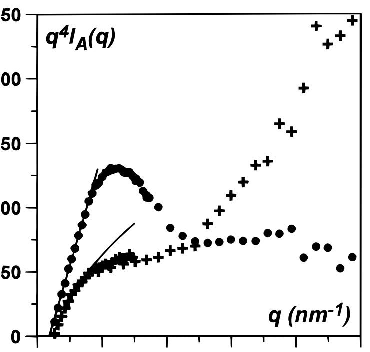

Figure 11. $q^4I_A(q)$ vs q for PVC–bromobenzene gels in the whole q range, C_{PVC} = 0.093 g/cm^3: (●) LTPVC, (+) HTPVC1.

elastic modulus in the case of HTPVC is significantly lower than in HTPVC–DBO gels.[17] On the other hand, the elastic modulus is increased drastically by using LTPVC instead.

In bromobenzene the effect of polymer tacticity on the gel molecular structure has been examined by comparing HTPVC1–BrBz gels and LTPVC–BrBz gels. In Figure 10 are drawn typical results obtained in the transitional q range for both systems. As can be seen, the scattering curves differ quite markedly. For HTPVC1–BrBz gels, a behavior of the type given in relation 12 is observed with an exponent $\lambda \simeq 0.34$. Calculation of r_{max} by means of relation 13 yields r_{max} = 6.7 ± 0.05 nm. Conversely, for LTPVC–BrBz gels the behavior is linear and can be fitted by means of eq 3. The value of r_{max} amounts to r_{max} = 8.8 ± 0.08 nm, a value about 1.3 larger than that found for HTPVC1–BrBz gels.

Interestingly, the scattering curve by LTPVC–BrBz gels in the low q range is similar to that by HTPVC–DEO gels (see Figure 1), which hints at a similar large-scale structure in both solvents in spite of the differing PVC tacticities. Using PVC of higher syndiotacticity in bromobenzene or using atactic PVC with diethyl oxalate produce, therefore, the same effect: there exists an equivalence between solvent type and polymer tacticity. Mutin and Guenet[9] had already come to this conclusion from the study of the gel elastic modulus. The modulus was shown to increase by altering either PVC syndiotacticity or solvent type. Clearly, in both systems this equivalence originates in the formation of additional links: "syndiotactic" crystals when increasing syndiotacticity or complex formation when using diethyl oxalate. This suggests that the local structure should differ in either system, as is effectively revealed by experiments carried out at larger q. HTPVC–DEO gels exhibit a q^{-2} behavior related to the sheetlike arrangement of the complex while LTPVC–BrBz gels display a q^{-4} behavior (Figure 11) due to compact objects such as nonsolvated crystals.

Increasing the fraction of "syndiotactic" crystals should entail rejection of the solvent from the fibers. The fiber grown under such conditions is then composed of "syndiotactic" domains and highly concentrated disordered domains. From q^* and from the height of the plateau r_{min} and ρ can be determined, provided that the structure is correctly described by Guenet's model.[15] The following values are obtained: r_{min} = 2 ± 0.2 nm and ρ = 250 ± 25 g/nm mol. As the theoretical density of "syndiotactic" crystals is ρ_c = 940 g/nm mol,[23] the value found here suggests that the polymer concentration within the fiber amounts to about 27%, that is approximately 3 times larger than the overall polymer concentration. Worth noticing is that the fiber density is about the same in HTPVC–DEO gels but is due to the structure of the HTPVC–DEO complex.[16]

Another feature of interest in Figure 11 is the importance of q^{-6} terms for LTPVC–BrBz gels, which hints at the existence of a large number of junctions between fibers, as expected from the increase in the number of "syndiotactic" crystals. This is also consistent with the high elastic moduli measured for these gels.[9,17]

Finally, the scattering curve of HTPVC1–BrBz gels differ totally from that of LTPVC–BrBz gels in this q range as well (Figure 11). The behavior seems to reach a q^{-2} asymptote, although the signal/noise ratio is too low to allow definite conclusions to be drawn on this point. Studies at higher concentrations can settle this point.

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