Light-Scattering Study of Thermoreversible Aggregates from Chemically Modified PVCs: Outcomes for the Gel State[§]

Helmut Reinecke,[†,‡] **Carmen Mijangos,**[‡] **Daniel Lopez,**[‡] **and Jean-Michel Guenet*,**[†]

Laboratoire de Dynamique des Fluides Complexes, Université Louis Pasteur-CNRS UMR 7506, 4, rue Blaise Pascal, F-67070 Strasbourg Cedex, France, and Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, E−28006 Madrid, Spain

Received September 8, 1999; Revised Manuscript Received December 7, 1999

ABSTRACT: Suspensions in diethyl oxalate (DEO) of aggregates of chemically modified poly(vinyl chloride) (PVC), where a few chlorine atoms are replaced by benzenethiolate groups, have been studied by light scattering. The scattering pattern of the suspensions display a maximum whose intensity decreases while its position, q_m, remains virtually constant as a function of the degree of modification. Diluting further the suspensions with DEO entails a shift of q_{max} toward lower q-values. As has been recently shown with normal PVC, this maximum arises from a liquidlike order between aggregates. At high dilution the weight-average molecular weight and the z-average radius of gyration can be measured. It is found that both parameters decrease with increasing the fraction of benzenethiolate groups, unlike what has been observed with another type of chemical modification (chlorine replaced by hydrogen). These results are interpreted by considering fibrillar aggregates, and the outcomes for the gel state, in particular for its elastic modulus, are discussed.

Introduction

Poly(vinyl chloride) (PVC) forms thermoreversible gels in a large variety of solvents.[1,2] It has been recognized that a study of the finite-sized aggregates formed below the critical gel concentration could bring some useful information for understanding the gel properties.[3,4] In particular, additional experimental techniques such as light scattering, viscometry, etc. have been brought about.[5]

Light-scattering experiments carried out on aggregate suspensions prepared in ester solvents have revealed in the scattering pattern the occurrence of a conspicuous, unexpected maximum (q_{max}).[4−6] This maximum is seen to shift toward the low q-values through subsequent dilution of the suspension with the preparation solvent. At high dilutions it eventually vanishes. This effect has been interpreted as arising from a liquidlike order between impenetrable aggregates, as ascertained by the following expression established experimentally for the scattering maximum:[6]

$$q_{max} \propto (C/M_{agg})^{1/3} \qquad (1)$$

where C is the concentration (g/cm³) and M_{agg} the molecular weight of the aggregates, the latter being determined at very high dilutions. This relation does imply that q_{max} is directly proportional to the reciprocal of the interaggregate distance in the suspensions.

At very high dilutions, both the molecular weight and the z-averaged radius of gyration of the aggregates, R_z, can be determined, and yield the following relation:[6]

$$M_{agg} \propto R_z^{1.5} \qquad (2)$$

The asymptotic behavior determined by investigating the largest aggregates ($qR_z > 1$) yielded typically the same exponent.[6] These results were interpreted by considering fibrillar aggregates whose longitudinal fractal dimension (fractal dimension of the fibril long axis) was $D_f = 1.5$.[6,7]

Although the involvement of the longest syndiotactic sequences in the formation of microcrystallites accounts for the formation of these fibrillar structures,[8,9] previous studies on gels have suggested the existence of PVC−solvent complexes occurring with the less stereoregular sequences.[10−12] This complex is thought to be formed because of electrostatic interactions of the polarized C═O bonds of the solvent and the polarized H−C−Cl bonds of the PVC.[10,11] The occurrence of such complexes has been previously tested by using chemically modified PVCs;[13−15] a few chlorine atoms are replaced either by hydrogen (HPVC samples) or by a thiophenolate group (SPVC samples). This reaction is known to be stereospecific, namely, it does not significantly affect the syndiotactic sequences.[16] Conversely, replacement of chlorine atoms does affect complex formation as shown by a drop in gel elastic modulus.[17,18]

A light-scattering study of the aggregates formed from modified PVCs,[19] samples where the chlorine atoms are replaced by hydrogens, has allowed some light to be thrown on the phenomenon: complex capability vanishes gradually, which is concomitant with a cross-sectional growth of the fibrils (i.e., fibril diameter increases). As a result, the number of fibrils per unit volume (fibril density) decreases. This most probably entails a corresponding decrease of the number of physical junctions per unit volume, which accounts for the drop in modulus.

The drop of modulus in the case of HPVC samples is rather moderate as compared with SPVC samples. For instance, a 5% modification yields a decrease four times larger with SPVC samples than with HPVC samples. The purpose of the present paper is therefore intended to gain more structural information about the SPVC/

* Author for correspondence.
† Université Louis Pasteur.
‡ CSIC.
§ This paper is dedicated to Pr. Karel Dušek on the occasion of his 70th birthday.
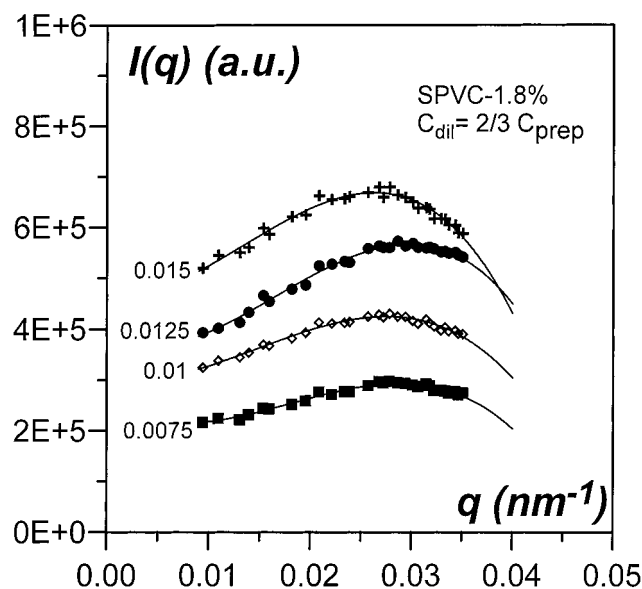
Figure 1. Influence of concentration on the scattering functions of aggregates of S2PVC diluted to $C_{dil} = 2/3\,C_{prep}$. $C_{prep} = 0.015$ g/cm^3 (+), 0.0125 g/cm^3 (●), 0.01 g/cm^3 (◇), and 0.0075 g/cm^3 (■).

Figure 2. Influence of degree of modification on scattering functions of solutions ($C_{prep} = 0.015$ g/cm^3) of S2PVC/DEO (●), S3PVC/DEO (+), S4PVC (◇), and S5PVC/DEO (■).

diethyl oxalate (SPVC/DEO) system to cast some light on the molecular structure differences that exist between HPVC and SPVC systems.

Experimental Section

Materials. The PVC used in the present study was supplied by Rhone Poulenc. The weight-average molecular weight as determined by size exclusion chromatography in tetrahydrofuran was 1.2×10^5 g/mol and the polydispersity index $M_w/M_n = 2.3$. The fraction of triads were obtained by ^{13}C NMR: syndio: 0.33, iso: 0.18, hetero: 0.49.

The chemical modification of the PVC consisted of replacing gradually some chlorine atoms by thiophenolate units using sodium benzenethiolate as the modification agent. This reaction is known to be stereospecific, which means that only iso- and heterotactic triads react, whereas syndiotactic chlorines remain unaffected. More details about the chemical process and the characterization methods of the modified samples are described elsewhere.[13-15,20]

Presently, four modified polymers with various degrees of modification were prepared: 1.8% (S2PVC), 2.6% (S3PVC), 3.9% (S4PVC), and 5.1% (S5PVC).

Solutions were prepared in DEO, which was purchased from Aldrich and was used without further purification.

Sample Preparation. The aggregate samples were prepared by quenching to 20 °C homogeneous solutions of PVC, S2PVC, S3PVC, S4PVC, and S5PVC in DEO after heating to 150 °C. All samples were aged for at least 3 days before the measurements so as to achieve growth of the PVC aggregates to a near-equilibrium size.[5]

Light-Scattering Measurements were performed with an argon Laser Lexel 85 operating at $\lambda_o = 488$ nm, and a BI—PMT goniometer from Brookhaven Instruments. The range of transfer momenta accessible in the light-scattering setup was typically $0.012 < q < 0.034$ (nm^{-1}), where $q = 4\pi n/\lambda_o \sin\theta/2$, with θ the scattering angle, λ_o incident light wavelength, and n the refractive index of the solvent (i.e., DEO in the present case).

The study of the suspensions of aggregates was carried out in cylindrical cells of optical quality, which were kept at 20 °C in a continuously filtered Decalin bath.

Results and Discussion

Structure of Aggregates. In Figure 1 is plotted the scattered intensity for aggregates of S2PVC prepared
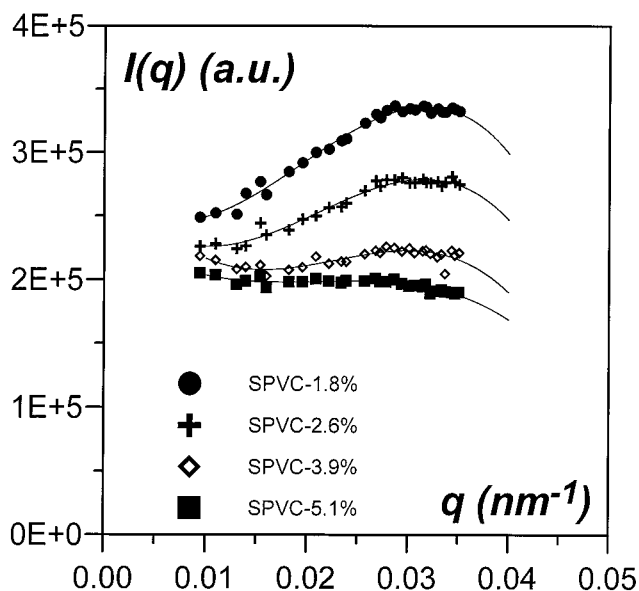
at different concentrations. As expected, scattering maxima are observed in all cases (to have the scattering maxima centered in the q-range explored, results presented in Figure 1 are those obtained after diluting to $C_{dil} = 2/3\,C_{prep}$). Interestingly, the position of these maxima is little dependent upon the preparation concentration. As will be confirmed in what follows, the occurrence of these maxima arises from a liquidlike order between the aggregates.[6] The near-invariance in position therefore implies that the distance between aggregates does not depend strongly upon the preparation concentration. This suggests that the number of aggregates is also nonvariant with preparation concentration. Correspondingly, the number of nuclei from which aggregates grow would also be nonvariant. It is worth mentioning that we observed a similar effect with normal PVC samples but failed to catch its real meaning then.[19] That the number of nuclei be invariant is not unexpected, as PVC gelation and aggregation is primarily a first-order transition due to PVC crystallization. Therefore, the density of nuclei is chiefly dependent upon the preparation temperature, which is a constant in the present experiments.

In Figure 2 is displayed the intensity scattered by solutions of S2PVC, S3PVC, S4PVC, and S5PVC in DEO ($C_{prep} = 0.015$ g/cm^3). As can be seen, all four patterns exhibit maxima that do not markedly depend on the degree of modification. Conversely, the magnitude of these maxima tend to decrease gradually with increasing the degree of modification, and an upturn appears at low angle. Again, the invariance in position is consistent with a constant nuclei density, whereas the upturn may indicate the appearance of nonaggregated chains in the suspensions. We shall further belabor this point below.

Data plotted in Figure 3 highlight that dilution of the aggregate suspensions by the preparation solvent results in a subsequent shift of the scattering maxima, which eventually vanishes for $C_{dil} = C_{prep}/18$. For this concentration, plotting the reciprocal of the intensity as a function of q^2 gives a straight line, which confirms that the Guinier–Zimm approximation holds (see
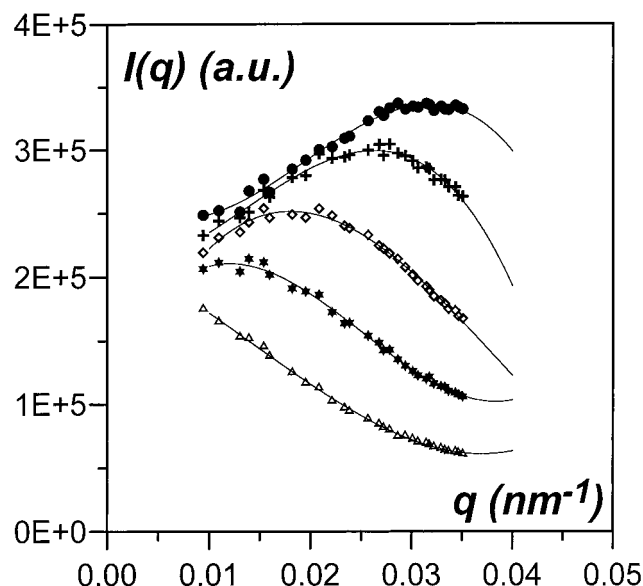
Figure 3. Influence of dilution on scattering functions of aggregates of S2PVC/DEO (C_{prep} = 0.015 g/cm^3) diluted to C_{dil} = C_{prep} (●), C_{dil} = 2/3C_{prep} (+), C_{dil} = 1/3C_{prep} (◇), C_{dil} = 1/6C_{prep} (∗), C_{dil} = 1/18C_{prep} (△).

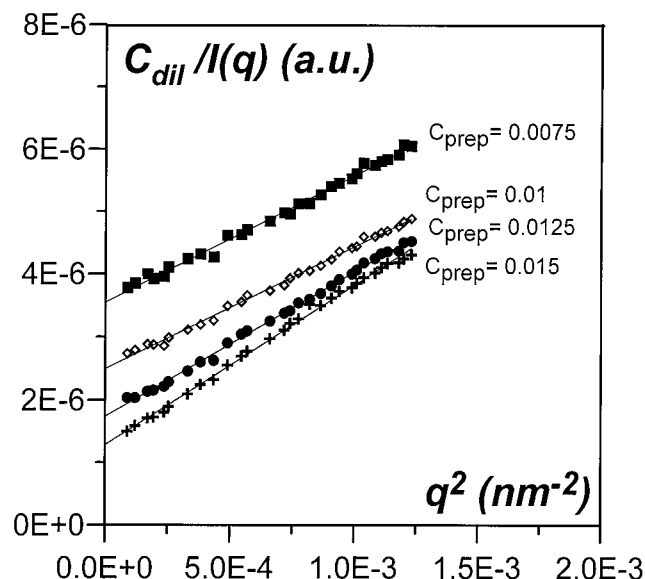**Figure 4.** Zimm plots for S2PVC/DEO solutions of different preparation concentrations C_{prep} diluted to C_{dil} = 1/18C_{prep}; C_{prep} = 0.015 g/cm^3 (+), 0.0125 g/cm^3 (●), 0.01 g/cm^3 (◇), 0.007 g/cm^3 (■).

Figure 4):

$$\frac{C}{I(q)} = \frac{1}{\nu^2 M_{agg}}\left[1 + \frac{q^2 R_z^2}{3} + ...\right] \tag{3}$$

where $C = C_{prep}/18$, M_{agg} the weight-averaged molecular weight, R_z the z-averaged radius of gyration (momentum of third order of the radii distribution function), and ν the refractive index increment. Here, we have assumed ν to be a constant for the three samples. It can be shown that the presence of a low amount of thiophenolate sequences is not liable to alter drastically this parameter.

From these Zimm plots the actual value of R_z can be straightforwardly determined, whereas the molecular weight, M_{agg}, is expressed in arbitrary units. Intensities
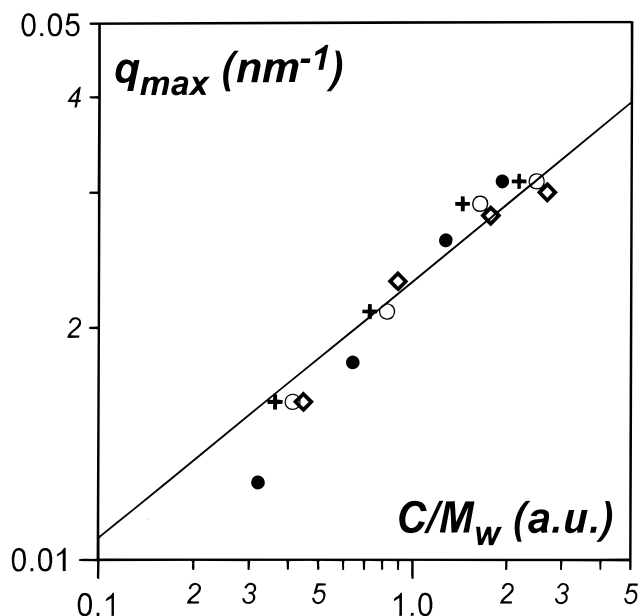

Figure 5. Double logarithmic representation of the variation of q_{max} as a function of C/M_{agg} for PVC/DEO (●), S2PVC/DEO (+), S3PVC/DEO (○), and S4PVC/DEO (◇). Straight line stands for exponent $^1/_3$.

have been obtained, however, always under the same conditions and normalized by the intensity scattered by a toluene reference sample. This procedure is relevant and sufficient for the present purpose. Determination of these structural parameters allows us to plot q_{max} as a function of C/M_{agg} in a double logarithmic representation for all the samples (see Figure 5). Again, the variation given by relation 1 is obeyed, namely, a power law variation with an exponent close to 1/3 is observed.

Note that when a piece of gel prepared from DEO is immersed in an excess of this solvent, no swelling occurs. Also, the results obtained here for normal PVC are the same as those reported by Dahmani et al., although these authors used higher dilutions.[6] Consequently, it is safe to conclude that diluting the aggregates does not affect their shape and size.

The variation of the molecular weight with z-averaged radius of gyration is presented in Figure 6 for the unmodified PVC together with the chemically modified samples. In all cases a power law variation is obtained where:

$$M_w \propto R_z^{1.5 \pm 0.1} \tag{4}$$

Although the chemical modification does not alter significantly the exponent, both the radius of gyration and the molecular weight decrease markedly. This situation differs conspicuously from what we reported on HPVC samples for which the molecular weight increased while the radius of gyration remained virtually constant.

We shall interpret the present results by considering again that the aggregates possess a fibrillar morphology, characterized by a longitudinal fractal dimension D_f = 1.5.[2,7,11,12] Under these conditions, the radius of gyration is written:

$$\langle R^2 \rangle_z = \langle R_L^2 \rangle_z + \langle r_o^2 \rangle_z \tag{5}$$

in which $\langle R_L^2 \rangle_z$ is the z-averaged radius of gyration related to the long axis, and $\langle r_L^2 \rangle_z$ the z-averaged cross-
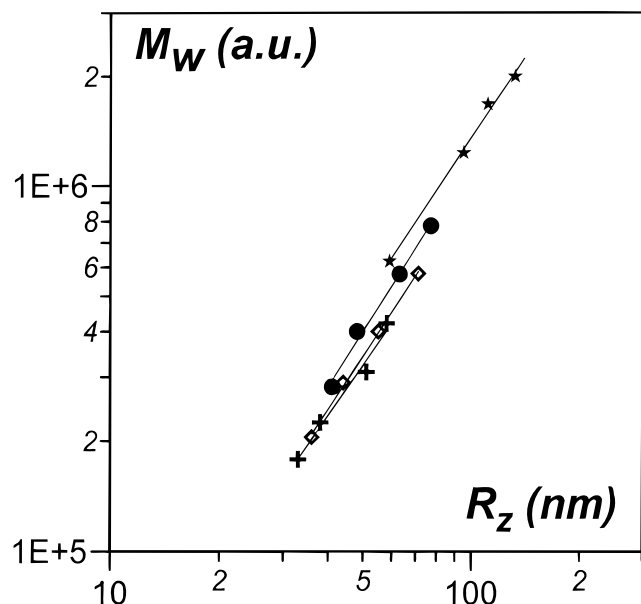
Figure 6. Variation of the molecular weight with z-averaged radius of gyration for aggregates from PVC/DEO ($*$), S2PVC/DEO ($\bullet$), S3PVC/DEO ($\diamond$), and S4PVC/DEO ($+$).

Figure 7. Evolution of the molecular weight with z-averaged radius of gyration for aggregates at constant preparation concentration (0.0075 g/cm^3): PVC/DEO ($\bullet$), S2PVC/DEO ($+$), S3PVC/DEO ($\blacklozenge$), and S4PVC/DEO ($\times$). Dotted line stands for exponent 1.5.

sectional radius of gyration (this relation holds if there is no coupling between the distributions of either type of radius). From neutron-scattering experiments, we know that $\langle R_L^2 \rangle_z \gg \langle r_\sigma^2 \rangle_z$ [$(\langle r_\sigma^2 \rangle_z)^{1/2} \approx 2$ nm] so that the experimental value $\langle R^2 \rangle_z$ essentially reflects the fractal dimension of the fibrils through:[21]

$$\langle R_L^2 \rangle = \frac{L^{2/D_f} l_p^{2-2/D_f}}{2^{(2/D_f-2)}(1+2/D_f)(2+2/D_f)} \qquad (6)$$

in which L and l_p are the contour length and the persistence length of the fibril long axis.

As to the fibril molecular weight it reads:

$$M = \pi r^2 L \rho \qquad (7)$$

in which ρ is the fibril density.

That both R_z and M decrease while increasing the degree of modification definitely implies a shortening of the fibril contour length.

Figure 7 shows the evolution of M_w versus R_z at constant preparation concentration. There appears a noticeable departure from the power law variation $M_w \propto R_z^{1.5}$ expected if only the fibril contour length diminished: the values of M are significantly lower. This may have two origins: presence of nonaggregated chains and decrease of the fibril cross-section. A decrease in cross-section only would then lead to an increase in the number of fibrils per unit volume, and correspondingly to an increase of q_{max}. This is experimentally not the case so that the most likely situation is an increase in the fraction of nonaggregated chains. It is worth emphasizing that the existence of a significant fraction of nonaggregated chains certainly accounts better for the neutron-scattering data gathered on gels from SPVC, especially those obtained at larger angles.

Note that the production of nonaggregated chains without fibril shortening cannot alone explain the decrease of both the radius of gyration and the molecular weight. Indeed, if it were so the experimental
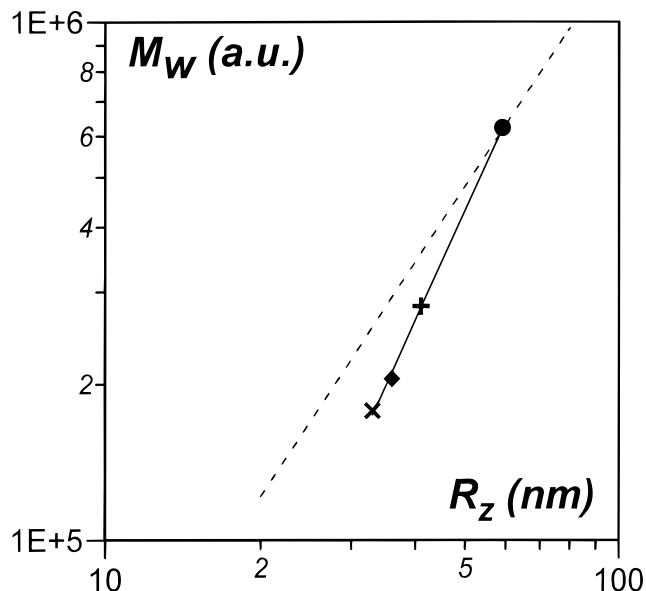
radius of gyration would read:

$$R_{zexp}^2 = X_f R_{zfib}^2 + (1-X_f) R_{zchains}^2 \qquad (8)$$

where R_{zfib} and $R_{zchains}$ are the radii of gyration of the fibrils and of the nonaggregated chains, X_f the volume fraction of fibrils. For instance, for sample S2PVC, the fraction of nonaggregated chains, which should possess a radius of gyration of about 10 nm, should be about 70% to account for the decrease of the radius of gyration from 130 to 75 nm.

Impact on Gel State. To evaluate qualitatively the impact on the gel state of these findings we shall consider a simple model where a gel is formed, that is, an infinite network, when the concentration of fibrils reaches some overlap concentration C_{gel}, namely:

$$C_{gel} \propto \frac{M_{agg}}{R_z^3} \propto R_z^{-1.5} \qquad (9)$$

As has been already observed, R_L is also a function of preparation concentration. In the present approach we shall consider for the sake of simplicity that the evolution of R_L with the preparation concentration does not depend on the type of modification. For the modified HPVCs, for which no change of radius of gyration has been observed,[19] C_{Hgel} is written:

$$C_{Hgel} \propto y_M C_{gel} \qquad (10)$$

in which y_M is the ratio of the modified-PVC fibril molecular weight over the unmodified-PVC one, y_M being larger than 1 as observed experimentally.[19]

For SPVCs, C_{Sgel} reads:

$$C_{Sgel} \propto \frac{1}{X_f} \frac{y_M}{y_z^3} C_{gel} \qquad (11)$$

in which X_f is the volume fraction of fibrils ($1 - X_f$ being

the fraction of nonaggregated chains) and y_z the ratio between the SPVC fibril radius of gyration over the unmodified-PVC one (here y_M must be taken smaller than 1 as reported here).

Relations 9−11 together with the experimental observations indicate that $C_{gel} < C_{Hgel} < C_{Sgel}$. As a result, the mesh size of the gels prepared from unmodified PVC is to be always smaller than that of the modified PVCs at the same polymer concentration. Because the elastic modulus is proportional to the reciprocal of the mesh size,[22] the elastic modulus of gels from unmodified PVC is expected to be always larger than that of the modified PVCs at a given polymer concentration. Similarly, HPVC samples should possess a higher modulus than that of SPVC samples at constant concentration. This is what is effectively observed experimentally.[18]

Concluding Remarks

Light-scattering experiments on the aggregates formed below the critical gelation concentration have allowed us to point out the differences between the molecular structures of two types of chemically modified PVC. Replacing chlorine atoms by hydrogens entails a cross-sectional growth, whereas the use of benzenethiolate results in shortening of the fibrils, together with the appearance of nonaggregated chains. Only a low degree of modification is needed to produce drastic changes at the level of the mesoscopic morphology.

These results allow one to throw some light on and are consistent with the gel properties (systems formed above the critical gelation concentration), and particularly on the evolution of the elastic modulus as a function of the degree and the type of chemical modification.

It is worth emphasizing that the study of aggregates by light scattering proved to be very fruitful for understanding the gel state.[7,19] The conclusions reported here would have been difficult to reach while studying the gel state only.

Appendix

Radius of Gyration of a Solid Fibril with Circular Cross-Section (Demonstration of Relation 3). The radius of gyration of any object is written:

$$R_G^2 = \frac{1}{2N^2}\sum\sum A_i A_j^2 \qquad (A1)$$

in which $A_i A_j$ stands for the mean-square distance between any two points in the objects, N being the number of these points. In the case of a solid fibril with circular cross-section, as represented in Figure 8, the vector $\boldsymbol{A_i A_j}$ can be expressed through:

$$\boldsymbol{A_i A_j} = \boldsymbol{A_i O_m} + \boldsymbol{O_m O_n} + \boldsymbol{O_n A_j} \qquad (A2)$$

in which O_m and O_n are the centers of those cross-sectional areas containing points $\boldsymbol{A_i}$ and $\boldsymbol{A_j}$ and being perpendicular to the fibril long axis (as a result O_m and
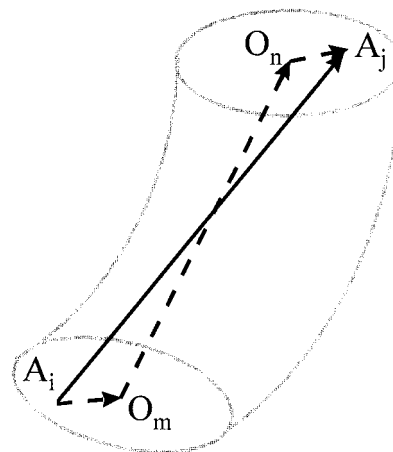

Figure 8. Schematic drawing of a part of a fibril possessing circular cross-section. Vector $\boldsymbol{A_i A_j}$ is shown to be the sum of three vectors, namely $\boldsymbol{A_i O_m} + \boldsymbol{O_m O_n} + \boldsymbol{O_n A_j}$, where points O_m and O_n are the centers of the circular cross-sections, the latter being perpendicular to the fibril's long axis.

O_n are located on the fibril long axis). Squaring expression A2 gives:

$$A_i A_j^2 = A_i O_m^2 + O_m O_n^2 + O_n A_j^2 + 2\boldsymbol{A_i O_m}\cdot\boldsymbol{O_m O_n} + \\ 2\boldsymbol{O_n A_j}\cdot\boldsymbol{O_m O_n} + 2\boldsymbol{A_i O_m}\cdot\boldsymbol{O_n A_j} \qquad (A3)$$

Any vectors $\boldsymbol{A_i O_m}$ and $\boldsymbol{A_j O_n}$ possess an opposite counterpart due to the circular symmetry, so that cross-terms in A3 cancel by pair when the summation over all possible values of $A_i A_j^2$ is performed. Applying A1 therefore leads to:

$$R_G^2 = \frac{1}{2N_L^2\, n_c^2}\sum_m\sum_n\sum_i\sum_j O_m O_n^2 +$$

$$\frac{1}{2N_L^2\, n_c^2}\sum_m\sum_n\sum_i\sum_j A_i O_m^2 + \frac{1}{2N_L^2\, n_c^2}\sum_m\sum_n\sum_i\sum_j A_j O_n^2 \qquad (A4)$$

in which N_L is the number of cross-sectional areas and n_c the number of scatterers per cross-sectional area. A4 is eventually written:

$$R_G^2 = \\ \frac{1}{2N_L^2}\sum_m\sum_n O_m O_n^2 + \frac{1}{2n_c}\sum_i A_i O_m^2 + \frac{1}{2n_c}\sum_j A_j O_n^2 \qquad (A5)$$

The first term is the radius of gyration of the fibril long axis; the sum of the last two terms yields the radius of gyration of the cross-section.

References and Notes

(1) Walters, A. T. *J. Polym. Sci.* **1954**, *13*, 207.
(2) Yang, Y. C.; Geil, P. H. *J. Macromol. Sci.* **1983**, *B22*, 463.
(3) Kratochvil, P.; Petrus, V.; Munk, P.; Bohdanecký, M.; Šolc, K. *J. Polym. Sci. Part C* **1967**, *16*, 1257.
(4) Mutin, P. H.; Guenet, J. M. *Polymer* **1986**, *27*, 1098.
(5) Candau, S. J.; Dormoy, Y.; Mutin, P. H.; Debeauvais, F.; Guenet, J. M. *Polymer* **1987**, *28*, 1334.
(6) Dahmani, M.; Skouri, M.; Much, J. P.; Guenet, J. M. *Europhys. Lett.* **1994**, *26*, 19.
(7) Dahmani, M.; Fazel, N.; Munch, J. P.; Guenet, J. M. *Macromolecules* **1997**, *30*, 1463.
(8) Juijn, J. A.; Gisolf, A.; deJong, W. A. *Kolloid Z. Z. Polym.* **1973**, *251*, 456.
(9) Lemstra, P. J.; Keller, A.; Cudby, M. *J. Polym. Sci. Polym. Phys. Ed.* **1978**, *16*, 1507.

(10) Mutin, P. H.; Guenet, J. M. *Macromolecules* **1989**, *22*, 843.

(11) Abied, H.; Brûlet, A.; Guenet, J. M. *Colloid Polym. Sci.* **1990**, *268*, 403.

(12) López, D.; Dahmani, M.; Mijangos, C.; Brûlet, A.; Guenet, J. M. *Macromolecules* **1994**, *27*, 7415.

(13) Mijangos, C.; Martinez, G.; Millán, A. *Makromol. Chem.* **1988**, *189*, 567.

(14) Mijangos, C.; Gomez-Elvira, J. M.; Martinez, G.; Millán, A. *J. Appl. Polym. Sci.* **1989**, *38*, 1685.

(15) Mijangos, C.; Cassagnau, P.; Michel, A. *J. Appl. Polym. Sci.* **1992**, *44*, 2019.

(16) Mijangos, C.; Lopez, D. *Macromolecules* **1995**, *28*, 1364.

(17) Mijangos, C.; Lopez, D.; Munoz, M. E.; Santamaria, A. *Macromolecules* **1993**, *26*, 5693.

(18) López, D.; Mijangos, C.; Muñoz, M. E.; Santamaria, A. *Macromolecules* **1996**, *29*, 7108.

(19) Reinecke, H.; Fazel, N.; Dosière, M.; Guenet, J. M. *Macromolecules* 1997, *30*,

(20) Pourahmady, N.; Bak, P. I.; Kinsey, R. A. *J. Macromol. Sci.* **1992**, *A29*, 959.

(21) Loucheux, C.; Weill, G.; Benoit, H. *J. Chim. Phys.* **1958**, *2*, 540.

(22) See for instance Jones, J. L.; Marquès, C. M. *J. Phys. (Paris)* **1990**, *51*, 1113.