Study of Thermoreversible Aggregates from Chemically-Modified PVCs

Helmut Reinecke,[†,§,‖,⊥] **Nazir Fazel,**[‡] **Marcel Dosiere,**[‖] **and Jean-Michel Guenet***[,†]

Laboratoire de Dynamique des Fluides Complexes, Université Louis Pasteur-CNRS URA 851, 4, rue Blaise Pascal, F-67070 Strasbourg Cedex, France, Laboratoire de Physique des Liquides et Interfaces, Université de Metz, 1, Bd Arago, F-57070 Metz Cedex, France, Instituto de Ciencia y Tecnología de Polímeros (CSIC), Juan de la Cierva, 3, E-28006 Madrid, Spain, and Laboratoire de Physico-Chimie des Polymères, Université de Mons-Hainault, rue du Parc, 20, B-7000 Mons, Belgium

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ABSTRACT: We report on a light scattering study performed on suspensions of aggregates of PVC and chemically-modified PVCs in diethyloxalate (DEO). The maximum in the scattering function reported by Mutin and Guenet is again observed. Its position, q_m, depends upon the degree of chemical modification at constant polymer concentration: the larger the degree of modification, the lower the value of q_m. The radius of gyration and the weight-averaged molecular weight of the aggregates are determined as a function of the preparation concentration from highly diluted suspensions. The radius of gyration is found to remain virtually unchanged when augmenting the degree of modification while a near 2-fold increase of the weight-averaged molecular weight is observed, the latter being consistent with the variation of q_m. All these results point toward a cross-sectional growth of the fibrillar aggregates with chemical modification while the longitudinal fractal dimension does not vary significantly. Viscometry measurements provide further support to these conclusions.

Introduction

PVC can form thermoreversible gels in a large number of solvents among which diesters.[1−4] Gelation, i.e., formation of an infinite three-dimensional network, occurs above a so-called critical gelation concentration, C_{gel}. Below this concentration, finite aggregates (or clusters) are formed whose size depends upon the preparation concentration, and diverges at C_{gel}.[5] Recent studies on PVC aggregates have provided a simple description of these systems in terms of a longitudinal fractal dimension of the fibers constituting the network,[6,7] and allowed one to account for the exponent of the elastic modulus-concentration relation observed for the gels. Clearly, the molecular morphology of the gel is closely related to that of the aggregates.[8−10]

A recent neutron scattering study on the molecular structure of gels of PVC and of chemically-modified PVCs has given strong support to the occurrence of a PVC-diester complex in the less stereoregular sequences.[9] This complex is thought to arise from electrostatic interactions between the polarized C═O bonds of the diesters and the polarized H−C−Cl bonds of PVC.[8−10] The existence of such a type of complex allows one to account for the high elastic modulii of these gels. Consequently, by replacement of a few chlorine atoms by hydrogen, the electrostatic PVC−diester interaction must eventually vanish which entails a subsequent decrease of the fraction of the complex together with a drop of the elastic modulus, which is experimentally observed.[11] The neutron scattering study further reveals that the basic fibrillar structure is little affected while the number of contacts between fibers is significantly diminished.[10]

The purpose of this paper is to report on light scattering and viscometry experiments on aggregates intended for gaining more information on these systems. As will be shown in what follows, the main effect arising from chemical modification is a cross-sectional growth of the fibers.

Experimental Section

1. Materials. The PVC used in the present study was supplied by Rhone Poulenc SA. The weight average molecular weight as determined by SEC in THF at 25 °C (universal calibration) was $M_w = 1.2 \times 10^5$ and the polydispersity index $M_w/M_n = 2.3$. The fractions of triads were obtained by ^{13}C-NMR:

syndio, 33%; iso, 18%; hetero, 49%

The chemical modification of the PVC sample was achieved by gradually replacing some chlorine atoms by hydrogen using $LiAlH_4$ as the reducing agent.[12] This reaction has been shown to be stereospecific,[13] which means that only iso- and heterotactic triads undergo random modification while "syndiotactic" chlorines remain unaffected. More details about the reaction and the characterization of the polymers are given elsewere.[13]

For the present study modified PVCs with modification degrees (w/w) of 3% (H3PVC) and of 6% (H6PVC), respectively, were produced.

Diethyl oxalate (DEO) was purchased from Aldrich and was used without further purification.

2. Sample Preparation. The samples were prepared by quenching to 20 °C homogeneous solutions of PVC, H3PVC, and H6PVC in DEO that were obtained after heating at 150 °C. All the samples were aged for a minimum of 3 days prior to the measurements so as to achieve the growth of the PVC aggregates to a near-equilibrium size.

3. Light Scattering. Light scattering measurements were performed with an Argon Laser Lexel 85 operating at $\lambda = 488$ 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 $q = (4\pi n/\lambda)(\sin \theta)/2$, with θ the scattering angle, λ the wavelength

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[†] Université Louis Pasteur.

[‡] Université de Metz.

[§] Instituto de Ciencia y Tecnología de Polímeros.

[‖] Université de Mons-Hainault.

[⊥] Permanent address: Instituto de Ciencia y Tecnología de Polímeros (CSIC).

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of light, 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.

4. Viscometry. Determination of the intrinsic viscosity $[\eta]$ of the aggregates suspensions was achieved by means of an Ubbelhodde viscometer immersed in a thermostatic water bath held at 20 ± 0.1 °C. These suspensions were prepared in the same manner as those used for light scattering experiments. The range of concentrations investigated was C_p = 0.0075 to 0.02 g/cm^3. A first dilution to C^o_{dil} = 0.01 g/cm^3 was performed after 3 days of aging for samples of high concentration prior to viscosity measurements. Determination of intrinsic viscosity was achieved by measuring the time of flow of successive dilutions of this diluted concentration. Under these conditions the intrinsic viscosity $[\eta]$ is related to the time of flow through

$$[\eta] + k[\eta]^2\frac{C^o_{dil}}{\delta} = \frac{t - t_o}{t_o} \times \frac{\delta}{C^o_{dil}}$$

wherein t is the time of flow of the suspension diluted to C^o_{dil}/δ (δ varying typically from 1 to 16), t_o is the time of flow of the pure solvent, and k is the so-called Huggins constant.

Results and Discussion

As has been mentioned in the introduction section, previous studies have revealed that light scattering patterns of PVC/DEO solutions ($I(q)$ vs q^2) exhibit a maximum.[4,6] This maximum has been shown to arise from a liquidlike order between clusters,[6] so that its position q^* is related to the average intercluster distance in the solution. Upon dilution of the suspensions the maximum shifts toward lower q-values. This intercluster distance depends upon two parameters: the concentration of the suspension and the aggregates molecular weight M_w. The following relation was experimentally obtained:[6]

$$q^*_m \simeq (C/M_w)^{1/3} \tag{1}$$

This relation indicates merely that the intercluster distance depends upon the cubic root of the reciprocal of the number of clusters per unit volume, as expected for a liquidlike order.

On the basis of neutron scattering, light scattering, and viscometry measurements, Dahamni et al.[7] have come to the conclusion that PVC aggregates can be described as fibrils whose longitudinal fractal dimension is D_F = 1.5 ± 0.1. This means that the fibrils do not resemble straight cylinders, but are askew instead. Here, the longitudinal fractal dimension is defined as

$$\langle S^2\rangle = L^{2/D_F} \tag{2}$$

where $\langle S^2\rangle$ is the mean-square end-to-end distance of the long axis of the fibril and L its contour length (in other words D_F is the fractal dimension with respect to the long axis).

In Figure 1 the scattering functions of solutions of PVC, H3PVC, and H6PVC in DEO are compared at the same polymer concentration (C = 1.2%). As can be seen, maxima in the scattering patterns are observed for all the samples, yet their positions are dependent upon the degree of modification: the maximum is shifted toward lower q values with an increase in the degree of modification. Relation 1 therefore implies that, in order to be so, the molecular weight of the clusters must increase with an increase in the degree of modification. Typically, the ratio between the values found for q_m in the case of PVC and of H6PVC is about 1.3. In view of relation 1, a nearly 2-fold increase in molecular weight of the fibrils at constant polymer concentration is expected.

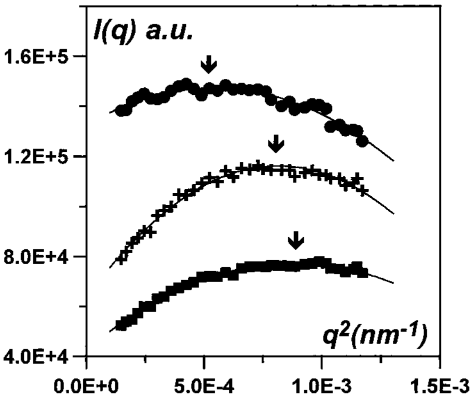

Figure 1. Scattering functions ($I(q)$ vs q^2) for solutions of PVC/DEO(■), H3PVC/DEO (+), and H6PVC/DEO (●) prepared at C = 1.2% (w/w). Solid lines represent a fit with a parabola. This fit has no theoretical meaning but is simply a convenient way of determining the maxima (indicated by arrows).

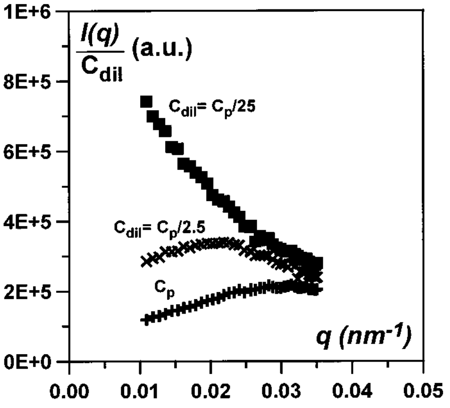

Figure 2. Effect of dilution on the scattering functions. C_{dil} as indicated. C_p = 1%.

Further information can be gained by diluting the suspensions of aggregates. As has been shown in previous papers,[6,7] dilution with DEO does not alter significantly the cluster size while it allows one to get rid of the maximum in the scattering curve and therefore to have access to the size and molecular weight by using the Zimm relation

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

where C is the actual concentration, M_w 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 appearance of a low amount of "polyethylene-like" sequences is not liable to alter drastically this parameter. This assumption is further borne out by what follows.

As can be observed in Figure 2, dilution does entail vanishing of the maximum. The Zimm plots for the unmodified PVC are shown in Figure 3. The values of

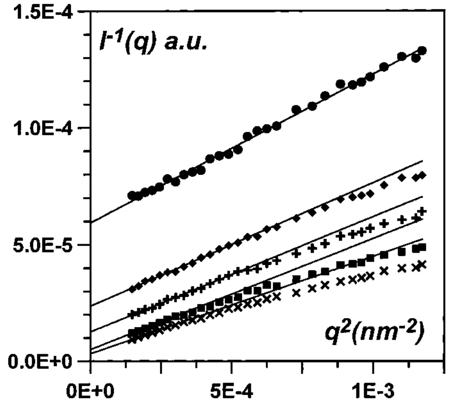

Figure 3. Zimm plot of PVC/DEO solutions from different preparation concentrations C diluted to $C_{\mathrm{dil}} = {}^{1}/_{25}C$: C = 1.7% (×), 1.5% (■), 1.2% (+), 1.0% (◆), and 0.7% (●).

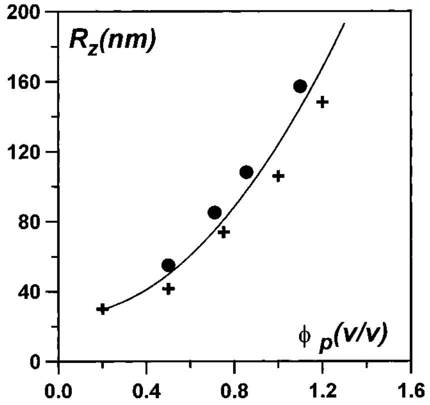

Figure 4. Comparison between the values of R_z reported by Dahmani et al. (+) and those determined in this work (●). The solid line is a guideline for the eyes.

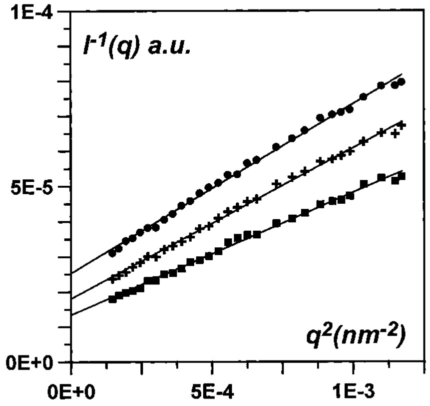

Figure 5. Zimm plots for solutions prepared at $C = 1.0\%$ and diluted to $C_{\mathrm{dil}} = {}^{1}/_{25}C$: PVC/DEO (●), H3PVC/DEO (+), and H6PVC/DEO (■).

R_z are in good agreement with those obtained by Dahmani et al.,[6,7] within experimental uncertainties (see Figure 4).

A comparison between the unmodified PVC and the chemically-modified samples is presented in Figure 5. From these Zimm plots the actual value of R_z can be straightforwardly determined while a reduced molecular weight, M_r, has only been measured. Intensities are always obtained under the same conditions and normalized by the intensity scattered by a toluene reference sample. For the present purpose, which consists in determining the exponent of a power law variation, M_r is a relevant and sufficient quantity. In the three cases under study the following power law is obtained (Figure 6):

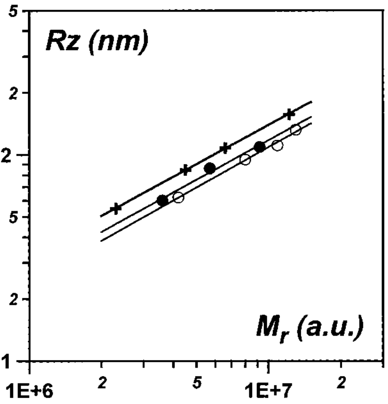

Figure 6. Double logarithmic representation of the variation of the radius of gyration as a function of the relative weight-average molecular weights as determined from the light scattering experiments. PVC/DEO (+), H3PVC/DEO (●), and H6PVC/DEO (○).

$$R_z = M_r^{1.5\pm0.1} \tag{4}$$

While R_z is virtually unchanged with the degree of chemical modification (an increase of only about 10% is seen), the molecular weight is seen to increase markedly by a factor of about 2. This result is consistent with the conclusions drawn from the displacement of the maximum observed in the scattering pattern under nondiluted conditions. Chemical modification affects significantly the molecular weight of the aggregates whereas their mean size is virtually unaffected.

The molecular weight of a fibril that possesses cylindrical symmetry is written

$$M = \pi\rho r^2 L \tag{5}$$

where r is the cross section radius, L the contour length of the long axis, and ρ the fiber density.

The mean-square radius of gyration of the same object is written:

$$\langle R^2\rangle = \langle R_L^{\,2}\rangle + \langle r_\sigma^{\,2}\rangle \tag{6}$$

R_L is the radius of gyration associated with the long-axis which is written[14]

$$\langle R_L^{\,2}\rangle = \frac{L^{2/D_F} l_p^{\,2-(2/D_F)}}{2((2/D_F) - 2)(1 + 2/D_F)\,(2 + 2/D_F)} \tag{7}$$

where l_p is the persistence length with respect to the long axis.

r_σ is the cross-sectional radius of gyration which reads in the case of a circular cross section of radius r_c

$$\langle r_\sigma^{\,2}\rangle = \frac{r_c^{\,2}}{2} \tag{8}$$

In the case of a polydisperse system, assuming no correlation between the length and the cross-section distribution functions, relation 6 becomes simply

$$\langle R^2\rangle_z = \langle R_L^{\,2}\rangle_z + \langle r_c^{\,2}/2\rangle_z \tag{9}$$

where the subscript z denotes a z-average.

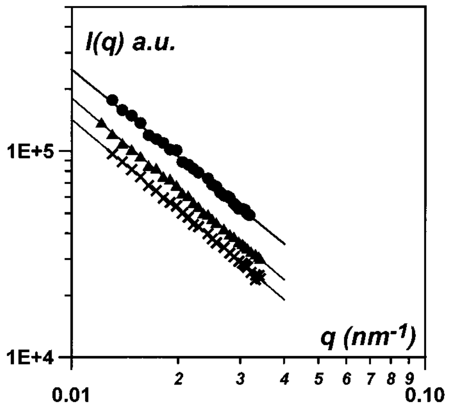

Figure 7. Log−log representation of the scattering functions in dilute regime for highly-concentrated samples (preparation concentration $C = 1.7\%$) diluted to $C_{\mathrm{dil}} = {}^{1}/_{25}C$: PVC/DEO (●), H3PVC/DEO (▲), and H6PVC/DEO (×).

Small-angle neutron scattering studies on PVC gels and aggregates in DEO have shown that PVC fiber cross sections are characterized by a distribution function $w(r) \sim r^{-1}$ with two cutoff radii, $r_{\min} \approx 1.9$ nm and $r_{\max} \approx 11$ nm,[9] which yield $\langle r_c^2\rangle_z^{1/2} \approx 8.8$ nm. Clearly, the dominant term in relation 9 is $\langle R_L^2\rangle_z$ so that doubling $\langle r_c^2\rangle_z^{1/2}$ will not significantly affect the value of the mean radius of gyration of the fibers. Conversely, relation 5 implies a 4-fold increase of the molecular weight. A 2-fold increase of the molecular weight as observed here therefore corresponds to a 40% increase of the average cross section. It is worth mentioning that Lopez et al.[10] observed a 20% increase on 5% PVC gels in DEO for similar samples.

These results altogether suggest that significant growth of the fiber cross sections occurs with chemical modification while preserving the longitudinal fractal dimension. The invariance of this dimension can be further checked by studying aggregates for which $qR_z > 1$. Under these conditions, provided that $ql_p < 1$, the intensity should be written

$$I(q) \sim q^{-D_F} \tag{10}$$

This can be experimentally achieved by investigating suspensions of PVC, H3PVC, and H6PVC prepared in DEO at $C = 0.017$ g/cm^3 and diluted 25 times. As is apparent from Figure 7 a straight line is obtained by means of a double logarithmic representation which yields $D_F = 1.45 \pm 0.05$, a value in close agreement with that derived from relation 4.

The cross-sectional growth of the fiber with chemical modification is borne out by the viscometry investigation. The evolution of $[\eta]$ as a function of the preparation concentration is shown in Figure 8. The intrinsic viscosity of the aggregates prepared from chemically-modified PVC is significantly lower than that of the unmodified PVC. The following relation allows one to account qualitatively for these results[15]

$$[\eta] \sim \frac{R_H R_G^{\,2}}{M} \tag{11}$$

where R_H is the hydrodynamic radius, R_G the radius of gyration, and M the molecular weight.

As above, increasing the fiber average cross-section will essentially result in increasing the molecular weight without significantly affecting R_H and R_G. Consequently, the intrinsic viscosity is expected to be lower as is experimentally observed. The occurrence of two regimes in PVC/DEO suspensions is related to the presence of weak links between fibers and ultimately to the formation of the PVC−DEO complex. This effect has been discussed in detail in ref 7.

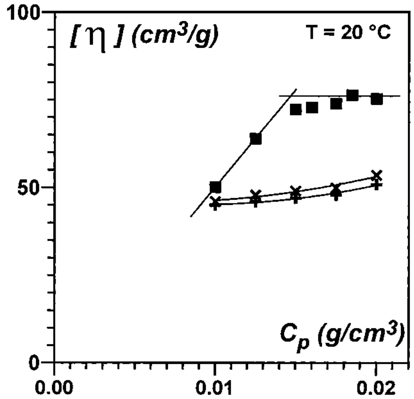

Figure 8. Intrinsic viscosity as a function of preparation concentration C_p for PVC/DEO (■), H3PVC (×), H6PVC/DEO (+).

Concluding Remarks

The light scattering investigation reported here highlights the cross-sectional growth of the fibrils prepared from chemically-modified PVCs. Although a previous study by small-angle neutron scattering had already pointed out such an effect,[10] the investigation reported here on the aggregates allows one to be definite about this point.

As was already discussed in previous papers, the PVC fibrils are thought to be composed of three types of domains: (1) tiny crystallites made up with the highly syndiotactic sequences, (2) organized domains build up from the PVC-DEO complex, and (3) disordered domains.[8−10] Due to constraints that inevitably exist at the interfaces between the *crystal-complex* domains or the *crystal-disordered* domains, and that essentially arise from solvent occlusion, the cross-sectional growth of the fibrils is limited. The chemical modification has been shown to impede the formation of a PVC-DEO complex, which most probably results in the formation of “polyethylene-like” interactions. Expulsion of solvent molecules from this domain is therefore expected, which should diminish the stress imposed upon the aforementioned interfaces. As a result, fibrils are liable to grow larger in cross section. The cross-sectional growth appears therefore to be consistent with the disappearance of the PVC−DEO complex. As fibrils grow larger in the gel at constant polymer concentration the number of contacts between them inevitably decreases. This explains why the elastic modulus decreases with increasing the degree of chemical modification as its magnitude is directly related to the number of junctions per unit volume.

Investigating the structure of aggregates prepared below the critical gelation concentration therefore provides information that has a direct bearing upon the gel properties, including the rheological properties.

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