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Poly(vinyl chloride) Thermoreversible Gels: A Fractal Approach to the Relation between Structure and Mechanical Properties[†]

Mohammed Dahmani,[‡] Nazir Fazel,[§] Jean-Pierre Munch,[‡] and Jean-Michel Guenet*,[‡]

Laboratoire d'Ultrasons et de Dynamique des Fluides Complexes, Université Louis Pasteur, CNRS URA 851, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France, and Laboratoire de Physique des Liquides et Interfaces, Université de Metz, F-57070 Metz Cedex, France

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ABSTRACT: Poly(vinyl chloride) aggregates have been studied by static light scattering in diesters and monoesters. By considering a fibrillar structure, it has been assumed that these experiments provide one with the longitudinal fractal dimension of the fibers, which equals $D_f = 1.5 \pm 0.1$ independent of the solvent type. Relations established between the elastic modulus and the polymer concentration for the same solvents have been accounted for in most cases by using both a theory developed by Jones and Marques for rigid networks and the fractal dimension as deduced from light scattering. The mechanisms promoting fiber rigidity in these gels are discussed.

Introduction

In most poly(vinyl chloride) (PVC) thermoreversible gels, the exponent found for the modulus−concentration relation[1] is usually close to or even larger than 3. The fringed-micelle structure which has been often contemplated to model these gels fails to account for these values.[2] This model depicts the network as small crystallite domains, *the junctions*, connected by flexible chains with a typical mesh size of a few nanometers. Such a model implies that elasticity must be chiefly entropic as in usual chemical gels, yet theories developed for these systems cannot predict the experimental exponents. Alternatively, on the basis of electron microscopy investigations[3] and neutron scattering experiments,[4] a new network structure is now considered: *an array of fibers* (with cross-sections of a few nanometers) possessing a mesh size of a few tenths of a micron. Also, Najeh et al.[5] have suggested on the basis of previous findings by Mutin et al.[6,7] that elasticity may be *enthalpic* as opposed to *entropic* as would be if the fringed-micelle model were relevant. Clearly, these findings call for a reappraisal of the structure−property relationship in PVC thermoreversible gels.

In many thermoreversible gels composed of an array of straight or nearly-straight fibers, the elastic modulus−concentration relation follows a square power law[8] which can be accounted for in the framework of a theory developed by Jones and Marques[9] for rigid gels (enthalpic elasticity) through the fractal dimension D_f of the objects connecting at the junctions. In the case of fibrillar thermoreversible gels, it suffices to consider the *longitudinal fractal dimension* of the fibers ($D_f \approx 1$) to derive the right exponent.[8] Recently, Dahmani et al.[10] have studied PVC aggregates by light scattering and have concluded that some fractal dimension was obtained through this method. As aggregates are nothing but small gel particles, the fractal dimension derived from light scattering may have a direct bearing upon the gel mechanical properties. The purpose of this paper is to report on light scattering and viscometry measurements on aggregates together with the determination of modulus−concentration relations on gels in selected solvents so as to test the relevance of this new approach.

Experimental Section

(1) Samples. The atactic PVC sample used in this study is of industrial origin (Rhovyl SA) and was synthesized at 50 °C by radical polymerization. Characterization by GPC in THF gave the following weight-averaged molecular weight and polydispersity: $M_w = 1.23 \times 10^5$, $M_w/M_n = 2.3$. NMR characterization provided the following proportions for the triads: iso = 0.19, syndio = 0.32, hetero = 0.49.

Four different solvents were used: diethyl oxalate (DEO), dibutyl oxalate (DBO), ethyl pelargonate (EPL), and ethyl valerate (EVA). They were purchased from Aldrich Chemical Co. and used without further purification.

(2) Light Scattering. Suspensions of PVC aggregates were obtained from homogeneous solutions prepared at 150 °C in closed test tubes and quenched at room temperature. These samples were transferred into light scattering cells of 1 cm diameter and aged therein for a minimum of 72 h at 20 °C. In what follows, C_p will designate the concentration at which these suspensions were prepared while C_{dil} will specify the concentration after subsequent dilution by the preparation solvent.

Light scattering experiments were carried out with a laser source tuned to a wavelength of $\lambda = 488$ nm. The q range accessible in the light scattering setup was $5 \times 10^{-3} \leq q$ (nm^{-1}) $\leq 3 \times 10^{-2}$, where $q = 4\pi n/\lambda \sin(\theta/2)$, n = the solvent refractive index, and θ = the scattering angle. This q range corresponds to distances ranging from 200 down to 33 nm. Light scattering cells containing the aggregate suspensions were kept in a toluene bath held at 20 °C during data collection.

(3) Viscometry. Determination of the intrinsic viscosity $[\eta]$ of the aggregate suspensions was achieved by means of an Ubbelohde viscometer immersed in a thermostatic water bath held at 20 ± 0.1 °C or 60 ± 0.2 °C. These suspensions were prepared in the same manner as those used for light scattering experiments. The range of concentrations investigated was $C_p = 0.0075-0.02$ g/cm^3. A first dilution to $C_{dil}^0 = 0.01$ 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.

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* To whom correspondence should be addressed.

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[‡] Université Louis Pasteur.

[§] Université de Metz.

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Under these conditions, the intrinsic viscosity $[\eta]$ is related to the time of flow through

$$[\eta] + k[\eta]^2 \frac{C^0_{\mathrm{dil}}}{\delta} = \frac{t - t_0}{t_0}\frac{\delta}{C^0_{\mathrm{dil}}} \qquad (1)$$

wherein t is the time of flow of the suspension diluted to $C^0_{\mathrm{dil}}/\delta$ (δ varying typically from 1 to 16), t_0 is the time of flow of the pure solvent, and k is the so-called Huggins constant.

For the study of the suspensions at 60 °C, the samples were prepared and aged as above at 20 °C and then heated to 60 °C. The different dilution procedures were performed at this temperature.

(4) Rheology. Determination of the elastic modulus was carried out by compressing cylindrically shaped samples by means of a compressive device described elsewhere.[11] The elastic modulus is then written

$$E = \frac{F}{A_0(\lambda - 1/\lambda^2)} \qquad (2)$$

where F is the force resulting from a deformation λ and A_0 is the initial area of the flat faces of the gel. The cylindrically shaped gel samples were obtained by injection molding, which provided highly parallel faces.[5] The gels were then aged in an excess of preparation solvent until swelling equilibrium was reached. Typical aging times were about 20 days. For each polymer concentration, a minimum of three samples were tested so as to estimate the experimental scatter.

Results and Discussion

The choice of the solvents used in this study relies upon a recent study by Najeh et al.[5] in which they determined the evolution of the elastic modulus as a function of the swelling degree, the latter parameter being monitored through the use of different preparation solvents. Najeh et al. observed that gels prepared from diesters could be described by the same modulus—swelling relation, which differed markedly from that obtained for monoesters. According to these authors, diesters, whatever the swelling degree of the gels may be, are said to promote the formation of the so-called weak links in the PVC fiber domains constituted of the less stereoregular sequences (for further details, see refs 6, 7, and 12). The effect of the existence of these weak links is twofold: (1) stiffening of the fibers and (2) promoting fiber aggregation. The main outcome is that in diesters gel elasticity is thought to be enthalpic.

Conversely, a plasticization process is thought to occur for gels prepared from monoesters. For low swelling degrees, DSC traces indicate that the less stereoregular domains remain below their glass transition, therefore promoting fiber stiffening. As a result, enthalpic elasticity is also expected for EPL, yet for different reasons than in diesters. When the swelling power is increased by using monoesters of increasing solvent quality, these less stereoregular domains are then swollen by monoester molecules, which results in a substantial drop of their glass transition temperature well below room temperature. Elasticity should then be of an entropic origin.

Gels prepared from DEO or EPL do not show any significant swelling when immersed in an excess of preparation solvent unlike what happens in DBO and EVA. Aggregates and gels have therefore been studied in these solvents to assess the effect of solvent quality. This will allow one to determine whether the solvent quality or the nature of the esters (di or mono) governs the rheological properties.

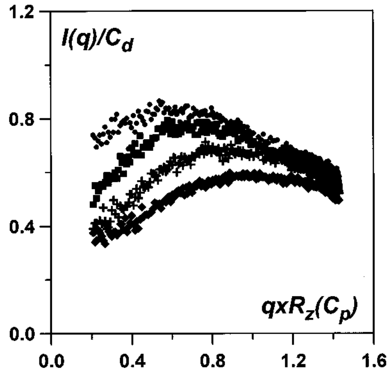

Figure 1. Effect of dilution on the normalized scattering function ($KI(q)/C_\mathrm{p}$) for a sample quenched at 20 °C and prepared at $C_\mathrm{p} = 0.005$ g/cm^3: (◆) $\delta_{\mathrm{dil}} = 2$; (+) $\delta_{\mathrm{dil}} = 4$; (■) $\delta_{\mathrm{dil}} = 8$; (●) $\delta_{\mathrm{dil}} = 16$.

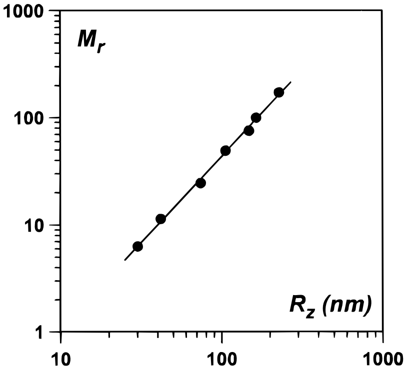

Figure 2. Variation of the relative molecular weight of the aggregates prepared in DEO as a function of the z-averaged radius of gyration. Both values have been determined after dilution to $C_{\mathrm{dil}} = 10^{-4}$ g/cm^3.

(A) Structure of the Aggregates. (1) Light Scattering. Typical light scattering patterns of PVC suspensions in DEO display a maximum (see Figure 1). As has been discussed in a former article,[10] this maximum is due to a liquid-like order between the aggregates. As a result, by diluting the suspension with the preparation solvent, this maximum is gradually shifted toward smaller angles. At high dilution the assumption has been made that the intensity arises only from the scattering by a population of clusters in the dilute regime. As no swelling occurs for the gel state, it has been further assumed that dilution does not entail the breaking up of the aggregates. One can thereby measure their mean radius of gyration together with their molecular weight through the relation

$$I(q) \sim M_\mathrm{w}\left[1 - \frac{q^2 {R_z}^2}{3}\right] \qquad (3)$$

where M_w is the weight-averaged molecular weight and R_z the z-averaged radius of gyration (${R_z}^2 = \sum C_i M_i {R_i}^2 / \sum C_i M_i$, where C_i is the concentration of particles with mass M_i and radius R_i). This relation holds provided that $qR_z < 1$.

It is of interest to establish whether there exists a power law relation between R_z and M_w, and, should it be the case, the meaning of the exponent. As only the value of the exponent is of interest, all the experiments have been calibrated by means of the extrapolated intensity at $q = 0$ of a very dilute sample prepared as described above ($C_\mathrm{p} = 10^{-4}$ g/cm^3). Such a sample shows minimum aggregation (about 4 molecules per aggregate as determined from the refractive index increment).

As can be seen from Figure 2, a power law relation is indeed obtained between the reduced mass M_r (see ref 10 for details) and the z-averaged radius of gyration for

PVC aggregates in DEO:

$$M_r \sim Rz^{1.6\pm0.06} \tag{4}$$

The meaning of the above exponent deserves to be discussed in light of the fiber model considered by several authors.[3,4,12] According to this model, PVC aggregates consist of solid fibers of cylindrical symmetry displaying a polydispersity in cross-section.[12] This polydispersity is characterized by a distribution function of the type $w(r) \sim r^{-1}$ with two cutoff radii $r_{\min}$ and $r_{\max}$.[13] From small-angle neutron scattering experiments it has been found that in DEO and for concentrations lower than 0.02 g/cm^3 these two radii are constant and equal to $r_{\min} = 1.9$ nm and $r_{\max} = 13.5$ nm.[14] Due to the nature of the distribution, fibers of small cross-section predominate.

So far there are no reasons to consider perfectly straight fibers. Previous neutron scattering investigations only require that the fibers be straight over distances of about 20 nm.

For objects with cylindrical symmetry, it can be shown that the radius of gyration is written

$$R_g^{\,2} = R_L^{\,2} + r_\sigma^{\,2} \tag{5}$$

where R_L^2 is the *longitudinal radius of gyration* and r_σ^2 the *transverse radius of gyration*. If one assumes that no correlation exists between the fiber's length distribution and the fiber's cross-section distribution, then any average value for the radius of gyration is simply given by

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

Clearly, in light of the measured values of $r_{\min}$ and $r_{\max}$ the dominant term in relation 6 is $\langle R_L^2\rangle$ so that the radius of gyration determined from light scattering experiments should be directly related to the *longitudinal length L* (or contour length) of the fibers.

As for the fiber's molecular weight, it can be expressed as

$$M_{ij} = \rho\pi r_i^{\,2} L_j \tag{7}$$

where ρ is the fiber density. The weight-averaged molecular weight reads

$$M_w = \frac{\sum_i^n\sum_j^N C_{ij}M_{ij}}{\sum_i^n\sum_j^N C_{ij}} \tag{8}$$

where C_{ij} is the concentration of those fibers of mass M_{ij}. Again, if the fiber's length distribution and the fiber's cross-section distribution are uncorrelated, then $C_{ij} = C_iC_j$ and M_w is eventually written

$$M_w = \rho\pi\frac{\sum_i^n C_i r_i^{\,2}}{\sum_i^n C_i}\,\frac{\sum_j^N C_j L_j}{\sum_j^N C_j} \tag{9}$$

As the term depending upon fiber cross-section should be nearly a constant, M_w will chiefly depend upon the fiber's contour length. Consequently, both R_z and M_w will mainly depend upon the fiber's contour length. The approach developed here therefore suggests that the exponent 1.6 found in relation 4 might well stand for the fractal dimension of the fibers' contour length L. Here the fractal dimension will be defined in a broad sense as

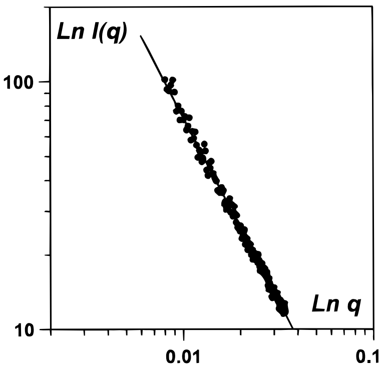

Figure 3. Representation by means of a double-logarithmic scale of the intensity scattered by aggregates prepared at $C_p = 1.6 \times 10^{-2}$ g/cm^3 and diluted to $C_{dil} = 10^{-4}$ g/cm^3. The slope of the straight line is 1.5.

$$S^2 \sim L^{2/D_f} \tag{10}$$

where S^2 is the mean-square distance between the fiber's ends. (The term *longitudinal fractal dimension of the fiber* is purposefully used to highlight that it differs from the fractal dimension of the fibers, the latter being obviously equal to 3).

It is worth emphasizing that this analysis is only valid if the fibers are unbranched in the concentration domain where the relation between R_z and M_w has been established. As will be established below, the viscosity studies will support this assumption.

Also, if the length polydispersity of the fibers is too high, there should be a significant discrepancy between the measured exponent and the actual longitudinal fractal dimension. Another way of estimating this fractal dimension, which is far less sensitive to length polydispersity, consists in investigating PVC suspensions for $qR > 1$. Under these conditions, provided $qr < 1$ (r = average fiber cross-section radius), the scattered intensity reduces to[15]

$$I(q) = q^{-D_f} \tag{11}$$

In Figure 3 is shown a typical result obtained with PVC suspensions prepared in DEO at $C_p = 0.016$ g/cm^3 and diluted to $C_{dil} = 10^{-4}$ g/cm^3. As can be seen, $I(q)$ does vary as predicted in relation 11 with an exponent close to $D_f = 1.5 \pm 0.05$, a value consistent with that found from the variation of R_z vs M_w, which therefore indicates that polydispersity effects can be ignored.

Similar investigations were carried out with the three other solvents, that is EPL, DBO, and EVA. The same exponent was found, which indicates no effect of solvent type or of solvent quality.

(2) Viscometry. The variation of the intrinsic viscosity $[\eta]$ as a function of the preparation concentration C_p is shown in Figure 4. Diesters and monoesters exhibit different types of behavior. In diesters, the intrinsic viscosity reaches a plateau for $C_p \approx 0.015$ g/cm^3 unlike what is seen in monoesters. Conversely, for $C_p < 0.015$ g/cm^3 in all solvents the intrinsic viscosity is seen to vary linearly with increasing polymer concentration. That the intrinsic viscosity levels off in diesters

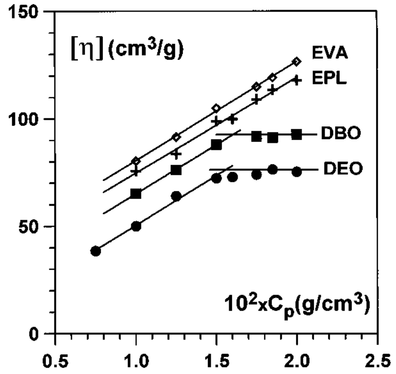

Figure 4. Intrinsic viscosity as a function of the preparation concentration C_p. As can be seen, this parameter levels off from $C_p = 1.5 \times 10^{-2}$ g/cm³ onward in DEO and DBO.

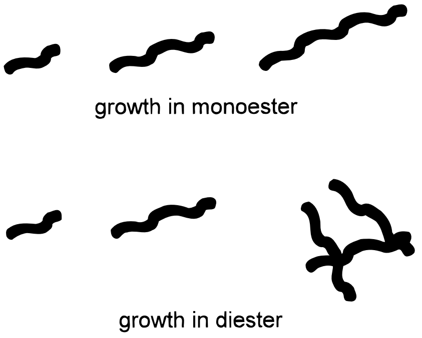

Figure 5. Schematic representation of the structure of aggregates in monoesters and diesters for different preparation concentrations (concentration increases from left to right). Superaggregation between fibrillar aggregates is thought to occur in diesters but not in monoesters.

at higher concentrations can be accounted for by the appearance of the so-called weak links[4,5,7] between fibers. The following equation,[16] which relates intrinsic viscosity to the particle's characteristics, namely the hydrodynamic radius, R_H, the mean-square radius of gyration, $R_G{}^2$, and the molecular weight, M, clarifies this point:

$$[\eta] \sim \frac{R_H R_G{}^2}{M} \qquad (12)$$

This equation holds in the present case provided that the length of the particle is much larger than its cross-section (otherwise more appropriate equations should be used, which will not, however, modify the following reasoning). If we consider the appearance of fibers branching through the weak links as has been proposed in several papers[6,7,12,14] (see Figure 5), then the molecular weight of the aggregates ought to increase more rapidly than their size. For instance, two fibers of identical molecular weight randomly branched will form a composite object with twice their molecular weight but having a size of only $1.225R_G$. Branching results in diminishing drastically the rate of increase of the intrinsic viscosity.

Interestingly, the same type of investigation carried out at 60 °C shows an identical behavior for monoesters and diesters (Figure 6). Again, this gives strong support to the above interpretation since the weak links are known to melt at 55 ± 5 °C.[9] As a result, fiber branching through weak links cannot occur any longer in diesters at this temperature.

This set of results suggests three comments:

(i) At low concentrations or at temperatures above 60 °C, the behavior of the intrinsic viscosity is essentially the same independent of the solvent used.

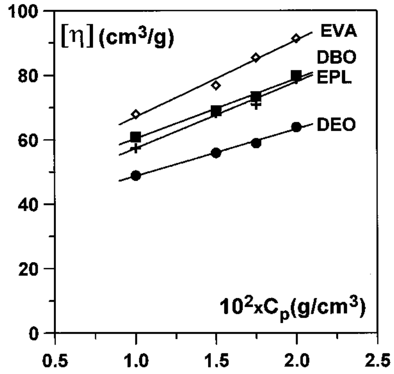

Figure 6. Intrinsic viscosity as a function of the preparation concentration C_p measured at 60 °C. As can be seen, in the four solvents this parameter increases continuously. No crossover is seen for diesters, unlike what was observed at 20 °C.

(ii) This in turn suggests a similar basic structure in all the solvents studied, which is consistent with the same "fractal" dimension deduced from the scattering curves for $qR_z > 1$. Note that these curves have been obtained for DEO and DBO in a concentration domain where fiber aggregation exists. Yet, the range of distances explored (typically smaller than 100 nm) makes that the actual value of the fractal dimension is little affected by a low degree of branching.

(iii) The existence of a similar basic structure in all solvents investigated again gives support to the hypothesis as to which the fibrillar structure arises primarily from the crystallization of the most syndiotactic sequences.

While the behavior is virtually the same at low concentrations or high temperatures in all solvents studied, the absolute values of the viscosities differ markedly. This means in the light of relation 12 that the fiber contour lengths and/or the molecular weights differ. There is no strong argument to favor a difference in fibers contour length. Conversely, fiber cross-section may vary from one solvent to another, thus altering the molecular weight. Accordingly, one would expect to obtain fibers with cross-sections smaller in DBO than in DEO. Recent neutron scattering results[14] bear out this conclusion as it is found that in DBO $r_{max} = 7.5 \pm 0.5$ nm against $r_{max} = 13.5 \pm 1.0$ nm in DEO while $r_{min} = 1.8 \pm 0.1$ nm in both solvents and the cross-section radius distribution is of the same type ($w(r) \sim r^{-1}$). As a result, the average cross-section associated with the intrinsic viscosity must be smaller in DBO than in DEO. If this interpretation is correct, then fibers produced in EPL and in EVA should possess cross-sections smaller than those obtained in DBO.

Finally, it is of interest to plot on a double-logarithmic scale the intrinsic viscosity as a function of the reduced molecular weight as deduced from light scattering on PVC/DEO suspensions for $C_p \leq 0.015$ g/cm³. As can be seen in Figure 7, a power law variation is observed:

$$[\eta] \sim M_r{}^{1.12\pm0.03} \qquad (13)$$

If one assumes that R_H and R_G vary in the same way, that is $R_H \sim R_G \sim M^{1/D_f}$, then a fractal dimension can also be derived through relation 12:

$$[\eta] \sim M_r{}^{(3-D_f)/D_f} \qquad (14)$$

The fractal dimension derived through (13) and (14) equals $D_f = 1.42$. It is worth noting that this dimension may be closer to the true fractal dimension of the objects as the exponent of relation 13 is close to 1. As a matter

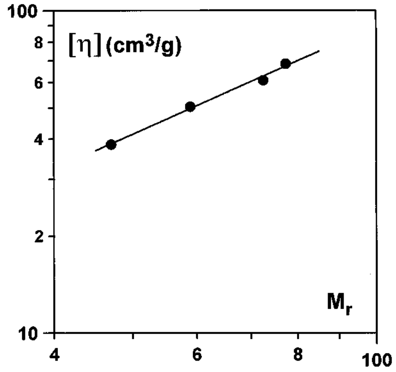

Figure 7. Variation of the intrinsic viscosity as a function of the relative molecular weight for aggregates prepared in DEO.

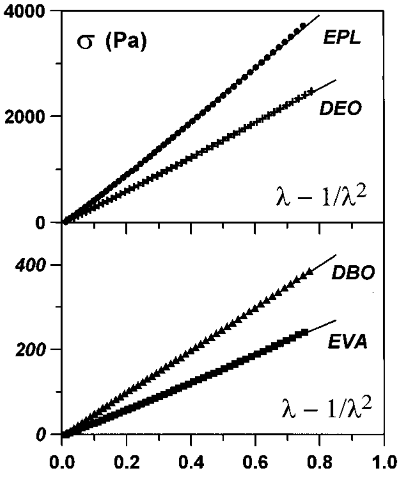

Figure 8. Typical Mooney–Rivlin plots (σ vs $\lambda - 1/\lambda^2$) for different samples swollen to equilibrium in an excess of preparation solvent (solvent as indicated).

of fact, the average molecular weight associated with the intrinsic viscosity is

$$M_v = \left[\frac{\sum_i^N N_i M_i^{a+1}}{\sum_i^N N_i M_i} \right]^{1/a} \tag{15}$$

where a is the exponent of the power law $[\eta] \sim M^a$ and N_i is the number of polymer molecules of mass M_i. Under the present conditions, M_v is very close to M_w, which is nearly an ideal condition for determining the fractal dimension as the same moments of the distribution are used for both parameters.

In any case the three approaches used yield a fractal dimension D_f in the range 1.42–1.6, that is, 1.51 ± 0.09.

Finally, it is worth noting that the molecular weight of the fibers, and most probably their length, grows nearly linearly with the preparation concentration.

(B) Rheology of the Gels. The rheological study consisted in determining the elastic modulus after allowing the gel to swell to equilibrium in an excess of preparation solvent. As the relaxation rate of PVC gels is usually very low[5] (1% or less per decade), the moduli have been measured by displacing the piston of the compressive device to new positions every 30 s and by recording the corresponding stress. A typical plot using relation 2 is shown in Figure 8. As can be seen, a straight line is obtained which nearly goes through the origin thanks to the highly parallel faces obtained by compression molding.

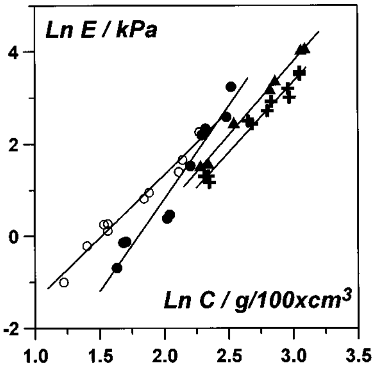

Figure 9. Variation of the elastic modulus for samples swollen to equilibrium as a function of the equilibrium concentration (double logarithmic scale): (○) = PVC/DBO; (●) PVC/EVA; (▲) PVC/EPL; (+) PVC/DEO.

In Figure 9 are plotted the moduli for the different solvents as a function of the equilibrium concentration. The latter is calculated by assuming that the gel swells without escape of any chains into the surrounding liquid phase. The results show a linear variation, which points to the existence of power law relations. The relations are (the concentrations are expressed in g/cm³):

$$E_{\mathrm{DEO}} = 4 \times 10^3 C^{3.06 \pm 0.2}\ \mathrm{kPa}$$

$$E_{\mathrm{DBO}} = 4.8 \times 10^3 C^{2.74 \pm 0.1}\ \mathrm{kPa}$$

$$E_{\mathrm{EPL}} = 7.4 \times 10^3 C^{3.19 \pm 0.2}\ \mathrm{kPa}$$

$$E_{\mathrm{EVA}} = 8 \times 10^4 C^{4.02 \pm 0.3}\ \mathrm{kPa}$$

In what follows we shall examine these results in the light of Jones and Marques' theory[9] which considers the fractal dimension of self-similar objects connecting at the junction of the network together with the type of elasticity (*entropic* and *enthalpic*). Although the theory was primarily developed for chemical gels, it can be used in the present case by assuming that the size of the physical junctions does not exceed the cross-sections of the fibers.

In the case of *entropic elasticity*, flexible objects, such as flexible chains, are involved. This particularly means that an angle between two objects connecting at the same junction can fluctuate.

The modulus is then written

$$E \sim C^{3/(3-D_f)} \tag{16}$$

where D_f is the fractal dimension of the objects connecting at the junctions.

In the case of *enthalpic elasticity*, rigid objects are dealt with, which means that, unlike what was postulated above, any angle defined between two objects connecting at the same junction cannot fluctuate. Considering again the fractal dimension of the objects, the modulus is now written

$$E \sim C^{(3+D_f)/(3-D_f)} \tag{17}$$

From relations 16 and 17 fractal dimensions can be deduced and compared to those determined from the study on the aggregates. These values are gathered in Table 1.

As is apparent from this table, there is good agreement between the fractal dimension derived from light scattering and that calculated by considering *enthalpic elasticity* for gels prepared from DEO, DBO, and EPL.

Table 1. Fractal Dimensions As Determined by Light Scattering and As Calculated from the Modulus−Concentration Relations Using Jones and Marques' Equations for Enthalpic Elasticity and Entropic Elasticity

	D_f	
solvent	light scattering	modulus−concentration
DEO	1.49 ± 0.09	1.52 ± 0.06 (enthalpic) 2.02 ± 0.06 (entropic)
DBO	1.48 ± 0.1	1.4 ± 0.04 (enthalpic) *1.91* ± 0.04 (entropic)
EPL	1.52 ± 0.1	1.57 ± 0.06 (enthalpic) *2.06* ± 0.06 (entropic)
EVA	1.54 ± 0.1	1.81 ± 0.06 (enthalpic) *2.25* ± 0.06 (entropic)

This gives therefore a simple description of these gels and supports the conclusions drawn by Najeh et al. as to the different processes involved in stiffening PVC fibers. Apart from the stiffening due to the crystallization of the syndiotactic sequences, either complex formation or vitrification within the less stereoregular domains is also liable to produce a totally rigid fiber. It ought to be noted that in their description of PVC fibers when complexation occurs Abied et al.[4] consider three types of domains: *"syndiotactic" crystals, organized domains of PVC−solvent complex*, and *disorganized domains*. Clearly, for achieving rigidity the first two types of domains must percolate throughout the fibers. Otherwise, if flexible, disorganized domains interrupted this "rigidity continuum", then the resulting elasticity would certainly be entropic.

Conversely, PVC/EVA gels cannot be described in the same way. Neither the dimensions derived by considering enthalpic elasticity nor those calculated for entropic elasticity agree with the light scattering results. Here, the theory fails to account for the experimental results, which implies that the simple description through the notion of a fractal dimension is not appropriate. In fact, Jones and Marques' theory relies upon the self-similarity of the connecting objects, a notion not fulfilled in the case of PVC/EVA fibers for which one expects rigid domains (syndiotactic crystals) alternating with flexible domains. PVC/EVA may be better described by regarding the PVC chains as multiblock copolymers in which crystallizable sequences alternate with noncrystallizable ones. It turns out that similar results were obtained by He et al.[16] on multiblock copolymers of which one sequence was flexible and the other one crystallizable. An exponent of about 4.5 was found, which they interpreted by assuming that the modulus should vary in the same way as the osmotic pressure. Possibly, this type of approach may be more appropriate here.

Concluding Remarks

In this paper it has been shown that in some solvents the exponent of the power law relating the elastic modulus to the concentration of PVC gels can be accounted for in a simple way through a single parameter, i.e. the *longitudinal fractal dimension* of the gel fibers, that can be determined independently by means of light scattering on the aggregates formed below the critical gelation concentration. For the first time the quite common exponent of approximately 3 found for PVC gels, and which has long puzzled scientists involved in this area, can be given a consistent explanation.

PVC gels differ from most physical gels in that the latter are usually composed of straight or nearly-straight fibers, which have a longitudinal fractal dimension $D_f \approx 1$. In the case of PVC, it is likely that, while fiber rigidity can be locally achieved, the absence of long-range order prevents the formation of straight fibers as those seen in other systems. The origin of a fractal dimension of $D_f \approx 1.5$ is probably due to this poor long-range order.

Finally, solvent quality has little impact upon the fractal dimension, which again highlights that this property is not necessarily the driving effect in PVC thermoreversible gelation. Unlike what is commonly stated, a good solvent can promote gelation as efficiently as a poor solvent. In the case of diesters what matters most is the formation of PVC−solvent complexes.

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