

Physical gels from poly(vinyl chloride): behaviour with concentration and temperature of aggregates formed in dilute solutions

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Aggregates formed in dilute poly(vinyl chloride) (PVC) solutions (i.e. below the critical gel concentration) have been studied by static and quasielastic light scattering as well as by viscometry as a function of the polymer concentration and the temperature. From the results, it is concluded that two types of physical links exist in these aggregates: 'strong' links that persist up to 62°C and 'weak' links that progressively break up with temperature. Further, the weak links are absent in aggregates prepared at the lowest concentrations ($C \leq 0.5 \times 10^{-2} \text{ g cm}^{-3}$) but appear at the highest concentrations ($C \geq 1 \times 10^{-2} \text{ g cm}^{-3}$). These results are discussed and the conclusions are extrapolated to the gel state. In particular, it is suggested that the weak links are responsible for the physical ageing of PVC thermoreversible gels.

(Keywords: poly(vinyl chloride); physical gels; aggregates; dilute solutions; elastic and inelastic light scattering; viscometry)

INTRODUCTION

In spite of numerous investigations¹⁻³, the mechanism of formation and the structure of poly(vinyl chloride) (PVC) physical gels have still not been fully elucidated. This situation originates in the lack of techniques of sufficient sensitivity to cope with phenomena near to the limit of detection, such as those involved in PVC physical gelation. In addition, these gels evolve steadily with time^{4,5}, which complicates any study. Under these conditions, the more different the techniques to be used the greater the possibility of finding converging facts that can throw some light on the problem.

Similar difficulties exist with covalently crosslinked gels. The usual way to overcome experimental complications consists of studying the pregel state for which only separated aggregates of small size are formed⁶. As a result, other experimental techniques can be used, such as inelastic light scattering⁷. Furthermore, as the system possesses more degrees of freedom and a lower viscosity, ageing or relaxation times are expected to be shorter.

Quite recently we showed that light scattering (elastic⁸ and quasielastic⁹ combined with birefringence experiments (optical and electrical) can provide information on the pregels and by extension on the gels.

This paper reports on additional experiments to study the effect of both the preparation concentration (but still below the gel formation concentration) and temperature. From the results it is concluded that two types of physical links are present in the aggregates. The extrapolation of these conclusions to the gel state is made and the validity of this view discussed.

EXPERIMENTAL

Materials

A PVC of commercial origin (Rhône-Poulenc S.A.) was used without further purification. This polymer was synthesized at 50°C and was therefore mainly atactic. Tacticity characterization by ¹³C n.m.r. in cyclohexane solutions gave the following results for the triads: $s = 0.33$; $h = 0.49$; $i = 0.18$.

Molecular weight determination was achieved by gel permeation chromatography (g.p.c.) in tetrahydrofuran (THF) with columns calibrated with atactic polystyrene standards according to the universal calibration method, giving $M_w = 1.2 \times 10^5$ and $M_w/M_n = 2.3$.

Freshly distilled diethyl malonate (DEM) was used as the solvent throughout the study.

Sample preparation

Solutions with starting concentrations ranging from $C_s = 5 \times 10^{-3}$ to $2 \times 10^{-2} \text{ g cm}^{-3}$ were prepared under vigorous stirring at 150°C, then cooled down to 23°C. Neither n.m.r. nor infra-red experiments detect any chemical modifications after the above treatment⁸. Light

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scattering experiments carried out on PVC recovered from DEM solutions have shown no significant alteration of the weight-average molecular weight. After quenching, the solution was allowed to remain for three days at room temperature, then diluted at the desired concentration. Such a procedure will be experimentally justified in what follows.

Techniques

Viscometry experiments were carried out with a Sofica automatic capillary viscometer. A capillary diameter of either 0.4 or 0.6 mm was used and values were taken at 25°C.

The correlation time experiments were performed by means of either an argon ion laser ($\lambda=488$ nm) or a helium-neon laser ($\lambda=632.8$ nm) combined with a 72-channel clipped digital autocorrelator. The autocorrelation function was determined in the homodyne regime. The scattering angle was varied from 15 to 135°. The temperature was thermostatically controlled to within $\pm 0.01^\circ\text{C}$.

Intensity correlation data were routinely processed using the method of cumulants, which consists of fitting the data with a distribution of exponentials as follows:

$$C_i(\tau) = \exp(-\langle\Gamma\rangle\tau) \times [1 + v\langle\Gamma\rangle^2\tau^2 + \dots]$$

in which $\langle\Gamma\rangle$ is the average decay rate and v the variance⁸. The latter parameter is a measure of the width of decay rates distribution function and is:

$$v = (\langle\Gamma^2\rangle - \langle\Gamma\rangle^2)$$

For homogeneous particles the diffusion coefficient is given by the first reduced cumulant $\langle\Gamma\rangle/2K^2$. The magnitude of the scattering vector is:

$$K = [4\pi n/\lambda] \times \sin(\theta/2)$$

where θ represents the scattering angle, λ the wavelength of the incident light in a vacuum and n the refractive index of the scattering medium.

RESULTS

Behaviour as a function of starting concentration

Aggregation kinetics. While the gelation process of concentrated PVC solutions is exceedingly rapid, the gel is far from equilibrium. It is known through the mechanical properties^{4,5} that the gel undergoes an apparently never-ending evolution. Accordingly, an investigation of dilute solutions requires a knowledge of the kinetics of aggregate formation. The latter has been determined through the variation of the intensity scattered at $\theta=90^\circ$ as a function of time for solutions heated at 150°C then quenched to 23°C. Results are given in Figure 1 for solutions prepared at $C_s=5 \times 10^{-3}$ and $1.6 \times 10^{-2} \text{ g cm}^{-3}$. As can be seen, chain aggregation is quite rapid in the early stage. For instance, the intensity scattered by a $5 \times 10^{-3} \text{ g cm}^{-3}$ solution after 5 min is about twenty times larger than the intensity expected for isolated PVC chains. The aggregation process seems much slower after 10 min ageing. However, as emphasized by a logarithmic plot (see inset in Figure 1), the aggregation kinetics depend strongly on the starting

concentration. For the $5 \times 10^{-3} \text{ g cm}^{-3}$ solution, the intensity reaches a constant value after 36 h, which indicates that chain aggregation is complete. Conversely, for the $1.6 \times 10^{-2} \text{ g cm}^{-3}$ solution, the intensity increases in a virtually linear fashion, which shows that aggregation has not attained a steady state even after 5 days annealing.

On the basis of the above results, a standard procedure was adopted for all the experiments carried out on these systems. This consisted of ageing the solutions at room temperature for three days prior to any measurements. Under these conditions aggregation still carries on in the most concentrated solutions, but the evolution rate is negligible compared to the measuring time.

Light scattering. The diffusion coefficient determined from quasielastic light scattering reads:

$$D_0(K) = \frac{\sum N_i f_i^2(K)}{\sum f_i^2(K)} \times N_i \quad (1)$$

where $f_i(K)$ is the scattering amplitude of particle i , N_i the number of particles of type i .

Relation (1) only holds when interparticle correlations are either absent or negligible. To overcome this problem, subsequent dilution is usually needed. Dilution of PVC/DEM solutions has virtually no effect on the particle structure as shown by the invariance of the intensity pattern recorded in static light scattering⁸. The anomalous intensity shape may also entail a non-trivial variation of $D_0(K)$ with the scattering angle. However, the form factor becomes molecular weight independent at larger angles, which results in an attenuation of the polydispersity effect on D_0 .

It has been shown in a previous paper⁹ that, while D_0 exhibits an upturn at small angles, its value as determined by extrapolation of the data at largest angles to $K=0$ is in close agreement with that measured by electric birefringence ($R_{\text{Hquels}}=30$ nm, $R_{\text{Heb}}=40$ nm for $C_s=0.5 \times 10^{-2} \text{ g cm}^{-3}$). We shall consider in what follows that this procedure provides a value of the particle hydrodynamic radius R_H close to the actual one.

Figures 2a and 2b show the variation of the first reduced cumulant ($D_0=\langle\Gamma\rangle/2K^2$) and the second reduced cumulant (v =variance) respectively for different solutions. We note that only the solutions for which $C_s \geq 5 \times 10^{-3} \text{ g cm}^{-3}$ have been diluted beforehand.

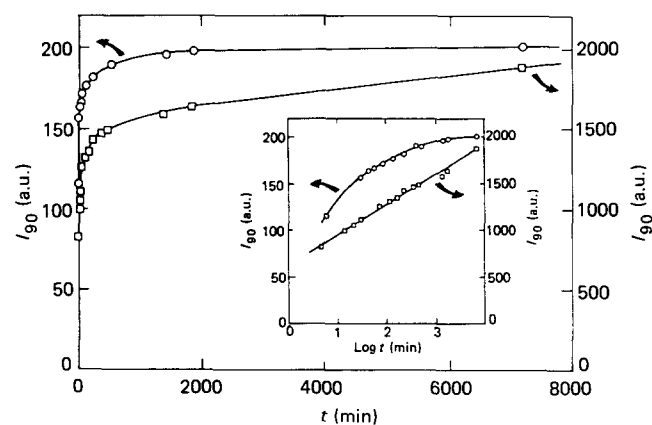


Figure 1 Intensity scattered at 90° , I_{90} , as a function of ageing time t ; \circ , $C_s=5 \times 10^{-3} \text{ g cm}^{-3}$; \square , $C_s=1.6 \times 10^{-2} \text{ g cm}^{-3}$. Inset: I_{90} as a function of $\log t$

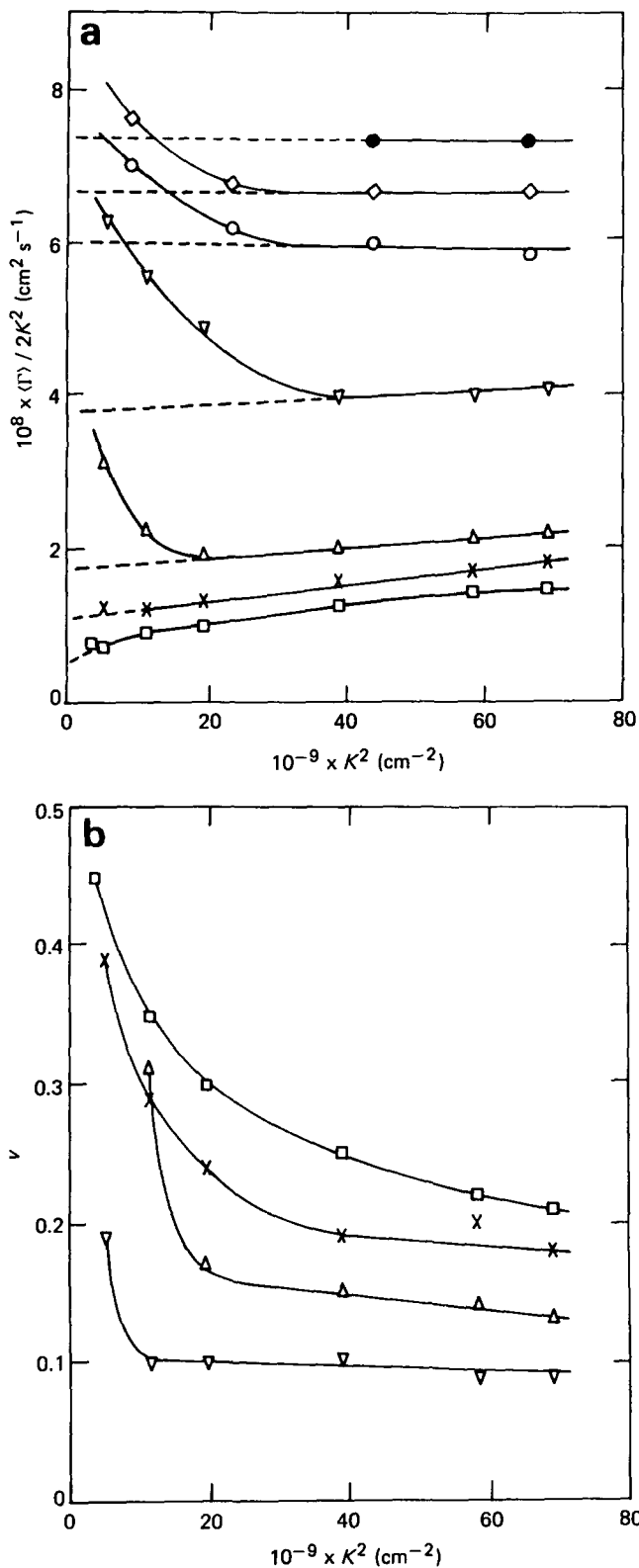


Figure 2 (a) $\langle \Gamma \rangle / 2K^2$ as a function of K^2 . (b) v as a function of K^2 . C_s (g cm^{-3}): \bullet , 2×10^{-4} ; \circ , 5×10^{-4} ; \bigcirc , 1×10^{-3} ; ∇ , 5×10^{-3} diluted to 1×10^{-3} ; \triangle , 1.2×10^{-2} diluted to 1×10^{-3} ; \times , 1.6×10^{-2} diluted to 1×10^{-3} ; \square , 2×10^{-2} diluted to 5×10^{-4}

These results show that both the size and polydispersity of the aggregates increase with concentration. It can be seen from *Figure 2a* that the linear part of the variation of $\langle \Gamma \rangle / 2K^2$ with K^2 , i.e. that obtained in the high K range, has a positive slope. This can be attributed to either the polydispersity effect or the internal modes. The latter

effect has been extensively studied theoretically by Burchard *et al.*¹⁰ These authors established the following relation for $KR_g < 5$:

$$\langle \Gamma \rangle / 2K^2 = D_0(1 + C'K^2R_g^2)$$

where R_g is the particle radius of gyration and C' is a constant which depends on the particle structure. For a hard sphere $C' = 0$ and for a flexible coil $C' \approx 0.15$. It is likely that the gel particles are characterized by a behaviour which is intermediate between that of a hard sphere and that of flexible coils. *Figure 2a* shows that the slope increases with increasing C_s . This can be correlated with the increase of the average particle size which would enhance both the internal modes contribution and the polydispersity effect. In any case, the extrapolation to $K = 0$, which obviously becomes more accurate for the largest values of C_s , eliminates the contributions of both polydispersity and internal modes.

Figure 3 represents R_H and the variance as a function of concentration C_s the hydrodynamic radius and the variance as determined from the largest angles. These values both diverge near the critical gel concentration $C_{\text{gel}} = (2.2 \pm 0.2) \times 10^{-2} \text{ g cm}^{-3}$ as expected (these values are also listed in *Table 1*) (note that C_{gel} is visually estimated as being the concentration under which no macroscopic gel can be formed whatsoever).

Viscometry. *Table 1* gives the values of intrinsic viscosities of solutions prepared at different concentrations, C_s . In a previous paper⁹ it was concluded that the particles can be regarded as swollen spherical objects impenetrable to the flow. For such a model, the viscosity should obey the equation:

$$\eta = \eta_0(1 + 2.5C_v + k_\eta C_v^2) \quad (2)$$

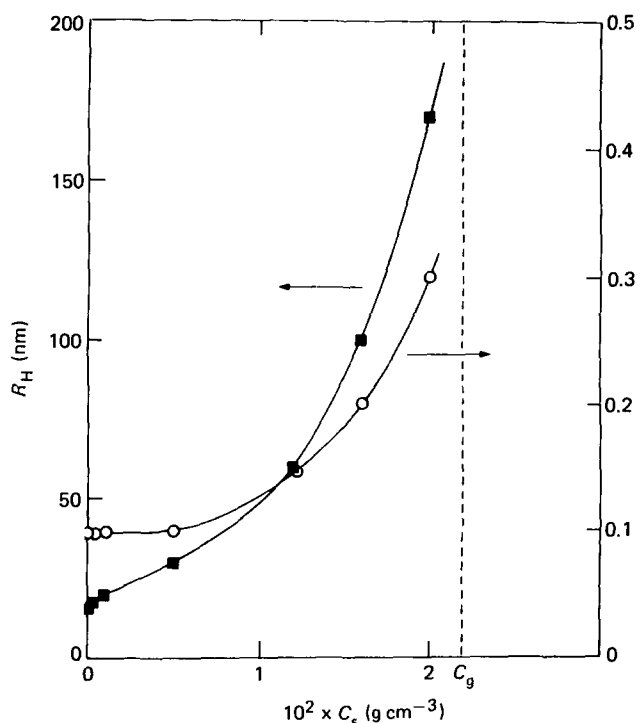
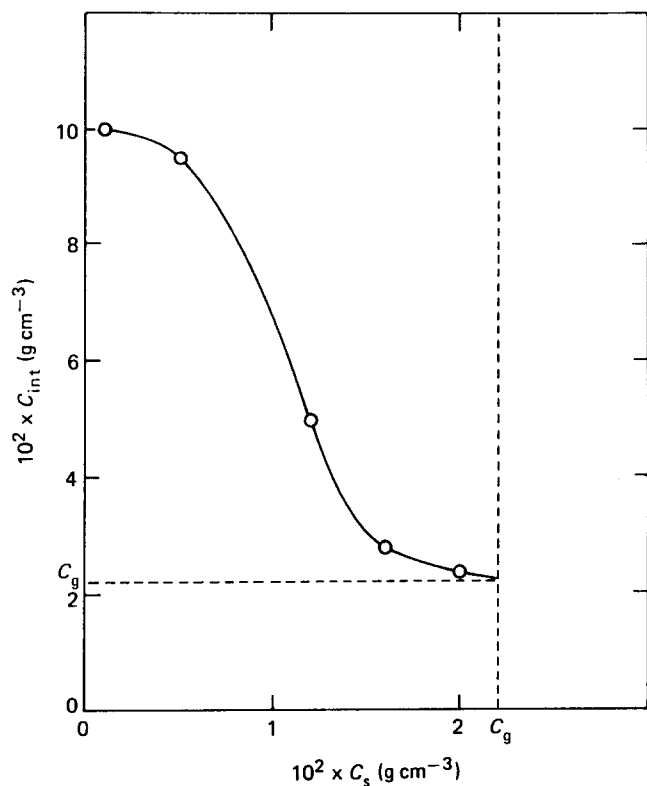


Figure 3 Hydrodynamic radius R_H (\blacksquare) and variance v (\bigcirc) as a function of polymer concentration C_s ; C_g is the critical gel concentration

Table 1 Hydrodynamic characteristics of PVC aggragates

$10^2 \times C_s$ (g cm ⁻³)	0.02	0.05	0.1	0.5	1.2	1.6	2
$10^8 \times D_0$ (cm ² s ⁻¹)	7.2	6.7	5.9	3.9	1.8	1.1	0.65
v	≈ 0.1	0.1	0.1	0.1	0.15	0.2	0.3
$[\eta]$ (cm ³ g ⁻¹)	—	—	25 ± 3	27 ± 1	51 ± 2	88 ± 3	105 ± 5
R_H (nm)	16	18	20	30	60	100	170
$10^2 \times C_{int}$ (g cm ⁻³)	—	—	10	9.5	5	2.8	2.4

**Figure 4** Particle internal concentration C_{int} as determined from viscometry as a function of the polymer starting concentration C_s

where C_v is the volume fraction of the particles and k_η an interaction coefficient whose value is close to 4.8. C_v may be expressed through the polymer concentration C_s and the particle internal concentration C_{int} according to:

$$C_v = C_s / C_{int} \quad (3)$$

Introducing (3) into (2) eventually leads to the following expression for the intrinsic viscosity:

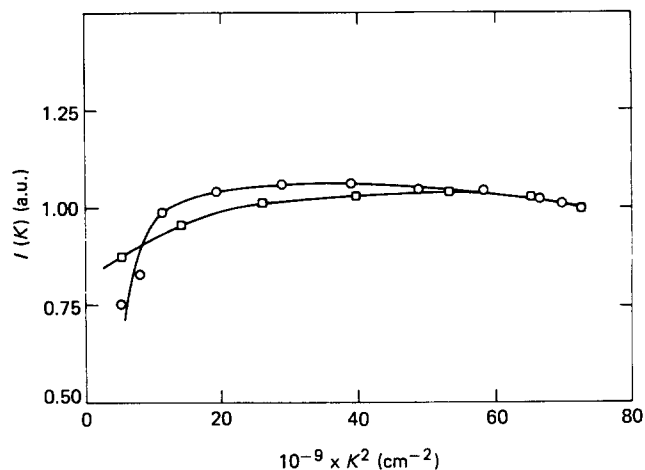
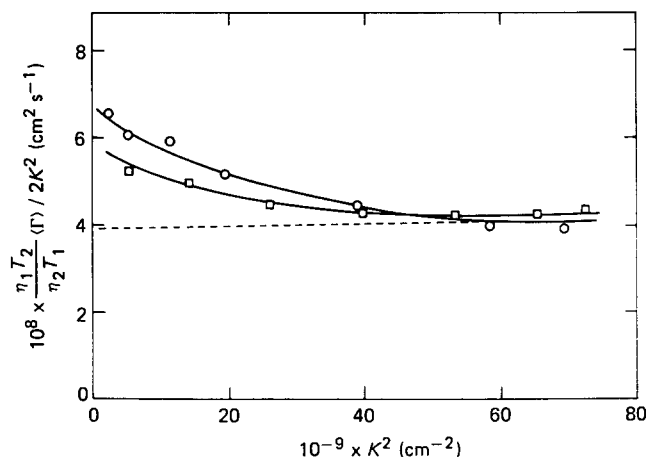
$$[\eta] = 2.5 / C_{int} \quad (4)$$

Values of C_{int} derived from this equation are given in Table 1. We note that the particle internal concentration is quite high at low polymer concentration and decreases with increasing polymer concentration. Figure 4 shows that C_{int} virtually equals the polymer concentration near the critical gel concentration C_{gel} .

Behaviour with temperature

After three days at room temperature, the different samples of differing concentrations were annealed for 24 h at temperatures between 23 and 62°C.

The behaviour of PVC particles as a function of the

**Figure 5** Scattered intensity $I(K)$ as a function of K^2 for $C_s = 5 \times 10^{-3}$ g cm⁻³ for different annealing temperatures. ○, $T = 23^\circ\text{C}$; □, $T = 62^\circ\text{C}$ **Figure 6** Normalized variation of $\langle \Gamma \rangle / 2K^2$ vs. K^2 for $C_s = 5 \times 10^{-3}$ g cm⁻³ for different annealing temperatures. ○, $T = 23^\circ\text{C}$; □, $T = 62^\circ\text{C}$

annealing temperature depends mainly on the starting polymer concentration C_s . Two types of behaviour may thus be schematically distinguished:

(i) For $C_s \leq 5 \times 10^{-3}$. Within experimental uncertainties, the scattered intensity is essentially insensitive to a rise of temperature. Figure 5 shows that results obtained at 23 and 60°C are very similar once normalized. Further, the variations of $\langle \Gamma \rangle / 2K^2$ with K , once normalized by the solvent viscosity and temperature, are quite similar at 23 and 60°C (Figure 6). The wide angle extrapolation almost provides the same value for D_0 .

These results therefore indicate that up to 60°C aggregates formed at these concentrations are practically unaltered.

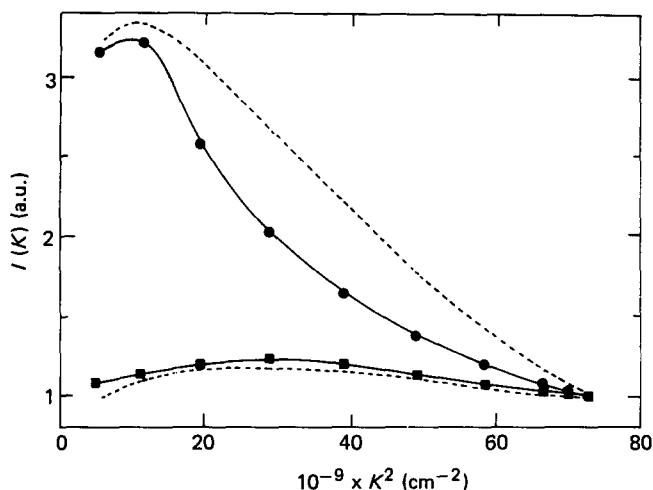


Figure 7 Scattered intensity $I(K)$ vs. K^2 for $C_s = 1.6 \times 10^{-2} \text{ g cm}^{-3}$ diluted to $1 \times 10^{-3} \text{ g cm}^{-3}$ after 24 h annealing at: \bullet , $T = 23^\circ\text{C}$; \blacksquare , $T = 62^\circ\text{C}$. -----, Calculated from relation (7) by using the experimental variation of $I_2(K)$ and the theoretical value of $P_2(K)$ (wherein the value of R is that obtained from quasielastic light scattering of $0.5 \times 10^{-3} \text{ g cm}^{-3}$ solutions). Similarly, the theoretical values of $P_1(K)$ at 23 and 62°C (form factors of the particles in the $1.6 \times 10^{-2} \text{ g cm}^{-3}$ solutions) are derived from the values of the particles hydrodynamic radius

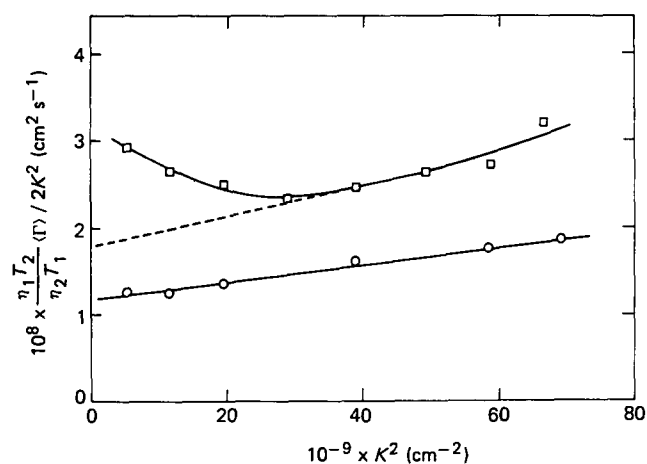


Figure 8 Normalized variation of $\langle \Gamma \rangle / 2K^2$ vs. K^2 for $C_s = 1.6 \times 10^{-2} \text{ g cm}^{-3}$ diluted to $1 \times 10^{-3} \text{ g cm}^{-3}$ after 24 h annealing at: \circ , $T = 23^\circ\text{C}$; \square , $T = 62^\circ\text{C}$

(ii) For $C_s \geq 1 \times 10^{-2}$. The scattered intensity undergoes a drastic change from 23 to 60°C as illustrated in Figure 7. Not only does the absolute value of intensity decrease quite strongly, but also the position of the maximum shifts towards higher K values. Correspondingly, the normalized variations of D_0 as a function of K are totally different at 23°C and 60°C (see Figure 8). In particular, for $T = 60^\circ\text{C}$ the upturn at small angles is again observable as with lower starting polymer concentrations C_s . Hydrodynamic radii calculated from D_0 for $T = 23^\circ\text{C}$ and $T = 60^\circ\text{C}$ show a strong decrease of the particle dimension with temperature (see Table 2). Further, the second reduced cumulant v strongly decreases too, which suggests that particles polydispersity is lower.

Evidently, a rise of temperature at these concentrations leads to a disaggregation of the particles which may find its origin in the melting of certain physical links. Hence,

we come to the conclusion that for $C_s \geq 1 \times 10^{-2} \text{ g cm}^{-3}$ additional links of lower stability are formed.

The same types of results are obtained with a starting concentration of $2 \times 10^{-2} \text{ g cm}^{-3}$, which is near the critical gel concentration (Figures 9 and 10). We further note that for $C_s = 1.6 \times 10^{-2}$ and $2 \times 10^{-2} \text{ g cm}^{-3}$ annealed at 62°C the particles tend to retrieve the characteristics (R_H and C_{int}) they have in $5 \times 10^{-3} \text{ g cm}^{-3}$ solutions.

Table 2 Effect of temperature on the hydrodynamic characteristics of PVC aggregates

$10^2 \times C_s$ (g cm^{-3})	0.5		1.6		2	
Temperature ($^\circ\text{C}$)	23	62	23	62	23	62
$[\eta]$ ($\text{cm}^3 \text{ g}^{-1}$)	27	30	88		105	48
v	0.1	0.1	0.2	0.15	0.3	0.2
R_H (nm)	30	30	100	50	170	65
$10^2 \times C_{int}$ (g cm^{-3})	9.5	8.3	2.8		2.4	5.2

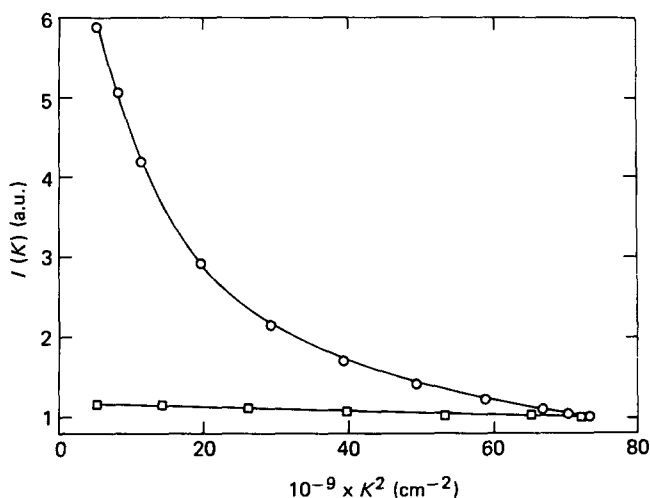


Figure 9 Scattered intensity $I(K)$ vs. K^2 for $C_s = 2 \times 10^{-2} \text{ g cm}^{-3}$ diluted to $1 \times 10^{-3} \text{ g cm}^{-3}$ after 24 h annealing at: \circ , $T = 23^\circ\text{C}$; \square , $T = 62^\circ\text{C}$

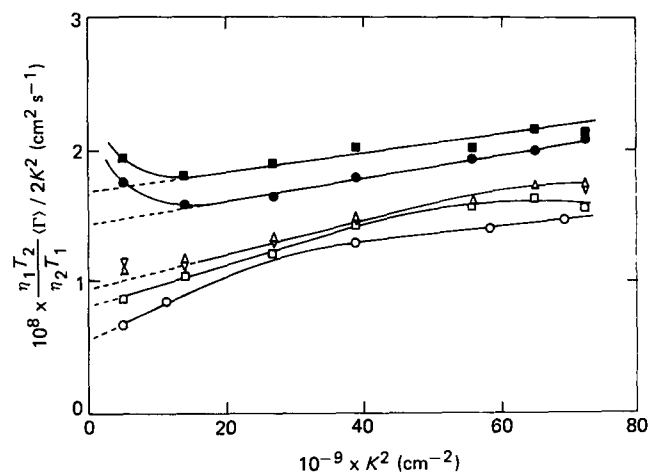


Figure 10 Normalized variation of $\langle \Gamma \rangle / 2K^2$ vs. K^2 for solutions prepared at $C_s = 2 \times 10^{-2} \text{ g cm}^{-3}$ aged for three days at room temperature then annealed 24 h at the following temperatures and diluted to $1 \times 10^{-3} \text{ g cm}^{-3}$: \circ , $T = 23^\circ\text{C}$; \square , $T = 31.5^\circ\text{C}$; \triangle , $T = 41^\circ\text{C}$; ∇ , $T = 51^\circ\text{C}$; \bullet , $T = 58^\circ\text{C}$; \blacksquare , $T = 62^\circ\text{C}$

DISCUSSION

Structure

From viscometry and optical birefringence measurements⁹ it can be concluded that the overall shape of the PVC particles is sphere-like and that they are more or less impenetrable to the flow. In addition, light scattering experiments indicate that the internal structure is optically inhomogeneous^{8,9}. The lack of additional information prevents a precise description of the inhomogeneous features. Yet it is likely that the origin may be found in a 'correlation hole' effect which is known to give rise to a maximum in spite of the absence of any order¹¹. From the position of this maximum no quantitative deductions can be made. This is due to the fact that PVC particles are not of infinite dimensions, which gives the following expression for the intensity:

$$I(K) = P(K) \times S(K) \quad (5)$$

where $P(K)$ is the particle form factor and $S(K)$ is a structure factor of 'correlation hole' type which contains the effect of optical heterogeneities.

As a result, for a given $S(K)$, the position of the maximum actually depends on the form factor $P(K)$. We note that for hard sphere of radius R , $P(K)$ is:

$$P(K) = [3(\sin KR - KR \cos KR)]^2 \times KR^{-6} \quad (6)$$

Using equations (5) and (6), it can be demonstrated that $S(K)$ does not markedly depend on either the starting concentration C_s or the temperature.

If $S(K)$ is independent of the particle size, a simple relation between intensities scattered by particles with form factors $P_1(K)$ and $P_2(K)$ can be derived:

$$I_1(K) = I_2(K) \times P_1(K)/P_2(K) \quad (7)$$

with obvious meaning for the subscripts.

Taking relation (6) for the form factors and using the experimental values of R_{H1} as obtained from the diffusion coefficients, $P_1(K)$ vs. K can be calculated for $1.6 \times 10^{-2} \text{ g cm}^{-3}$ solutions at $T = 23$ and 62°C . From the experimental variation of $I_2(K)$, where $I_2(K)$ is the intensity scattered by the particles in a $0.5 \times 10^{-3} \text{ g cm}^{-3}$ solution at 23°C whose form factor is $P_2(K)$ (calculated in the same way as $P_1(K)$), the theoretical variation of $I_1(K)$ can be calculated through equation (7) for the $1.6 \times 10^{-2} \text{ g cm}^{-3}$ solutions at 23 and 62°C and compared with the experimental values. As can be seen in Figure 7, such an approach enables one to reproduce within experimental uncertainties the intensity shape and, more interestingly, the position of the maximum. As a consequence, $S(K)$ can be regarded as being virtually independent of concentration and temperature in the range 23– 60°C . The same type of analysis can be carried out for different concentrations, giving the same results and conclusions. In particular, the existence of a larger sphere radius for $C_s = 2 \times 10^{-2} \text{ g cm}^{-3}$ results in a shift of the maximum towards lower K values, outside the range of investigation. Such a statement once extrapolated to the gel state may suggest that the gel structure does not resemble a fringed micelle of type A (see Figure 11). In fact, while the intensity scattered by this model should be larger than that of a single chain, its shape is not expected

to exhibit any maximum. Alternatively, the fringed micelle of type B (see Figure 11), which is reminiscent of that found by Yang and Geil³ by electron microscopy, might be an alternative candidate. It is worth emphasizing that this type of structure seems to be quite common in physical gels.

Further experimental results are now needed to elucidate the structure of both the particles and the gel in the wet state.

Aggregation mechanism

Light scattering experiments show unambiguously that the chain aggregation mechanism changes with different starting concentrations, C_s . At lower starting concentrations ($C_s \leq 5 \times 10^{-3} \text{ g cm}^{-3}$), the aggregates are virtually unaltered by a rise of temperature within the range 23– 60°C . Such thermal stability at this dilution suggests that the physical links involved are rather of crystalline origin as opposed to the hydrogen-bond-like type suggested by Yang and Geil³. Indeed, only PVC crystals, which are known to melt at very high temperatures in the bulk state ($T_m \simeq 250$ to 300°C , depending on the amount of syndiotactic sequences¹²), are liable to exhibit such stability at such dilutions. This confirms previous findings on the crystalline nature of the

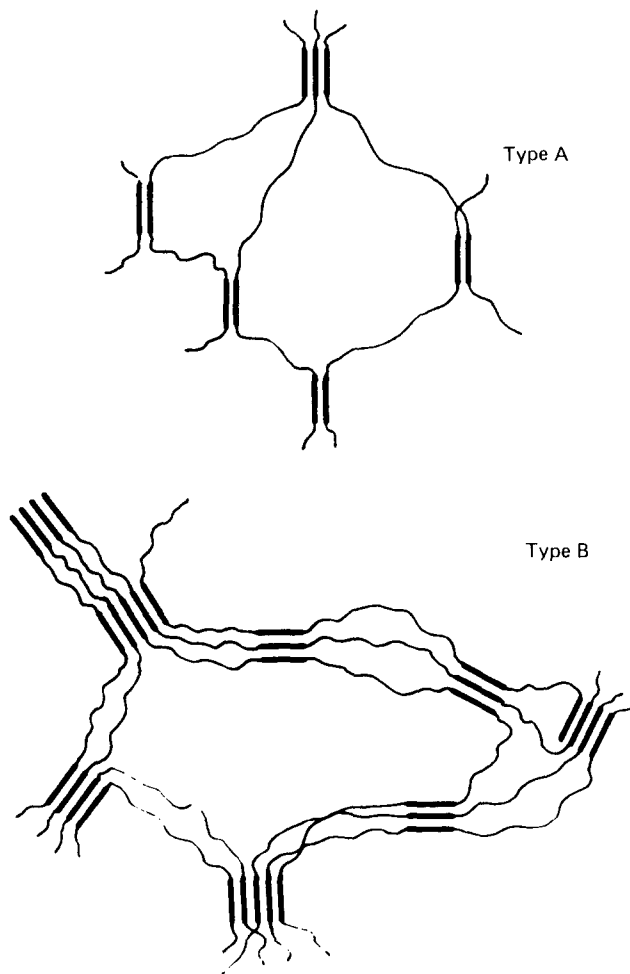


Figure 11 Two schematic types of fringed micellar models: type A is characterized by a short mesh and is thus reminiscent of covalently crosslinked gels. Type B is characterized by a larger mesh due to the fact that two consecutive crystalline knots are linked by several disordered chain portions. This results in the formation of small fibres

physical junctions in these gels¹³. As to hydrogen-bond-like links, one would intuitively expect them to vanish at lower temperatures, as is usually the case for biological systems where such an interaction is considered. These crystalline links will be designated as 'strong links' in the following discussion.

At higher starting concentrations ($C_s \geq 1 \times 10^{-2} \text{ g cm}^{-3}$), another type of physical link evidently appears in the aggregates together with an increase of the particles size, the latter being confirmed by other techniques¹⁵. To measure the particle size by quasielastic light scattering, dilution was employed to remove the interparticle correlations. Evidently, dilution may affect the particle by destroying some of the weaker links. Yet, provided that no additional links are created upon dilution (which would be most surprising), only the amount of the links of the second kind may be altered. Since we are not trying to make any quantitative measurements, this phenomenon can be ignored for the moment.

The size of the aggregates is seen to decrease with temperature, which indicates that these links are weaker than those previously described and will be accordingly designated as 'weak links'. As the single chain behaviour is not recovered at 62°C, but rather the behaviour determined at low starting concentrations, it is inferred that the remaining links at this temperature are nothing but the strong links defined above.

The origin of the weak links may come from slow crystallization of less regular sequences by virtue of their propensity to adopt a rod-like conformation, an idea originally suggested by Juijn *et al.*¹⁴ Alternatively, these weak links may owe their existence to the formation of a phase involving less regular sequences and solvent molecules, whose order would be reminiscent of nematic liquid-crystals (i.e. order in only one direction) as recently proposed for isotactic polystyrene gels¹⁵. It is worth underlining that the appearance of the weak links is correlated with a decrease of the aggregate internal concentration C_{int} , that is, an increase of the particle solvent content.

With the data and hints available so far, any attempt to

locate precisely these links within the PVC particles seems premature. Do they originate in an interaction between two crystals from two different aggregates or do they form in what may be termed the amorphous phase? We cannot yet answer this question. Conversely, it can be stated beyond doubt that these links are responsible for the physical ageing of PVC gels. D.s.c. experiments coupled with compression modulus measurements, which will be reported in due course¹⁶, support such an assumption.

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