Physical gels from PVC: A light scattering investigation of dilute solutions

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In order to gain information on the gelation mechanism of PVC in linear esters, dilute solutions have been investigated by the use of light scattering, with unexpected results. Below a given value of solvent refractive index ($n_s \simeq 1.4$) normally-shaped Zimm plots are obtained, although the measured weight average molecular weight is higher (~ 5 times) than the actual one. Above $n_s \simeq 1.4$, hook-shaped Zimm plots are found. Concerning the hook-shaped Zimm plots, all cases known to give rise to such intensity patterns are reviewed. It is found that an aggregate with two types of scatterers characterized by large differences of refractive index may account for the results. This interpretation suggests that clusters resembling fringed-micelle models are not appropriate here. In addition, it is suspected that the structure responsible for such scattering behaviour incorporates solvent, which would imply that the solvent plays an active role. These results suggest that particular structures may be involved in PVC gels prepared from the esters investigated in this paper.

(Keywords: PVC; physical gels; light scattering; esters; two-refractive-index aggregates; solvated structures)

INTRODUCTION

From an intuitive standpoint, physical gelation of polymer solutions should require a crystallization process so as to bridge chains together. While under these conditions only stereoregular polymers should be capable of forming a physical gel, some atactic polymers such as PVC[1] or atactic polystyrene[2] are known to possess the same ability. It has been supposed[3] that there exist in PVC some stereoregular portions (syndiotactic) long enough to permit the formation of tiny crystals acting as junction domains. X-ray diffraction patterns, gathered on stretched and dried gels, undoubtedly show several reflections[3] that are apparently consistent with a gel of crystalline character. Yet, the stereoregular sequences length (syndiotactic) determined from X-ray line broadening is irreconcilable with n.m.r. data. Recently, Yang and Geil[4] have shown by d.s.c. experiments, that while a freshly-prepared PVC gel melts at a well-defined temperature, there is no trace of any melting peak. They conclude that, although crystals may be formed during gel ageing, the early stage of PVC gelation does not necessarily involve a crystallization process. Accordingly, they state that physical gelation of PVC arises from hydrogen-type bondings between chains and, correspondingly, that the junction areas are actually punctual. In doing so, they use an assumption put forward some twenty years ago by Kratochvil *et al.*[5] intended to explain the strong tendency of PVC to form aggregates in dilute solutions. This aggregation phenomenon can be visualized by light scattering that gives Zimm plots with a pronounced downturn at the smallest angles.

From our own studies on PVC gels, we have noticed that three types of solvents can be distinguished: (i) solvents wherein gelation does not occur whatsoever, such as tetrahydrofuran or cyclohexanone; (ii) solvents that give weak gels such as dimethylformamide or diisopropyl ketone; (iii) solvents that produce strong gels, such as bromobenzene or linear esters.

Since a study in dilute solution may provide information on what happens in the gel state, it appeared of interest to investigate by light scattering the solution properties of PVC in linear esters. The results are quite different from those of Kratochvíl *et al.* Particularly, in some esters, hook-shaped Zimm plots are obtained.

EXPERIMENTAL

Materials

PVC of commercial origin (Rhône-Poulenc SA) was used without further purification. This polymer had been synthesized at 50°C and is therefore mainly atactic. Tacticity characterization by ^{13}C n.m.r. in cyclohexanone solutions gave the following values for the triads: $s = 0.33$; $h = 0.49$; $i = 0.18$.

Molecular weight was determined by g.p.c. in tetrahydrofuran at room temperature: the result being $M_w = 1.2 \times 10^5$ g mol^{-1} and $M_w/M_n = 2.3$.

A series of esters of different refractive index was used for this investigation, namely: butyl acetate (1), isoamyl acetate (2), ethyl heptanoate (3), diethyl oxalate (4), diethyl malonate (5), diethyl succinate (6) and diethyl adipate (7).

All were of analytical grade and were systematically freshly distilled before use.

In addition, some experiments were carried out in tetrahydrofuran (THF) and cyclohexanone as reference solvents, since gelation is absent in them.

Preparation of the solutions

Starting solutions ($c = 0.5 \times 10^{-2}$ g cm^{-3}) were prepared under vigorous stirring through heating either at 145°C or just below the boiling point of the solvent until PVC was thoroughly dissolved. In principle, experiments

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for a given polymer–solvent couple were systematically performed with and without stabilizer (tin thioglycolate).

Solutions of lower concentrations were obtained by dilution at room temperature of starting solutions that had been aged approximately 90 min at 20°C. Afterwards, these solutions were centrifuged for 1 h at 14 000 rev min^{-1} to remove dust.

Techniques

Light scattering experiments were carried out with a photogoniodiffusometer from Sofica. The samples were irradiated by a He–Ne laser beam ($\lambda = 632.8$ nm). Scattering glass cells were immersed in *p*-xylene held at 20 ± 0.1°C.

Refractive index increments (d*n*/d*c*) were measured under the same conditions (wavelength and temperature) with a Brice–Phoenix differential refractometer.

RESULTS AND DISCUSSION

Light scattering results

Zimm plots obtained from PVC solutions in THF and cyclohexanone were perfectly classical and provide reasonable weight average molecular weights ($M_w = 1.05 \times 10^5$).

According to the literature[5], poor solvents for PVC, which apparently must be the case for esters, should lead to strong molecular associations. As usual under such conditions, Zimm plots should exhibit pronounced downturns at lower angles. Surprisingly, results reported here do not conform. In some esters, Zimm plots do not present any downturn (*Figure 1a*) and are nearly linear, yet molecular weights are higher than the actual one ($M_w \simeq 5.5 \times 10^5$ instead of 1.05×10^5). In other esters, Zimm plots are characterized by an upturn at lower angles, which gives rise to hook-shaped patterns (see *Figure 1b* and *1c*). Apparently, the main parameter governing the existence or absence of hook-shaped Zimm plots seems to be the refractive index of the solvent. As a rule, for $n_s < 1.4$ normally-shaped plots are found while for $n_s > 1.4$ hook-shaped plots are obtained.

Extrapolation to zero angle and infinite dilution gives values of M_w and A_2 listed in *Table 1*. The values of the second virial coefficient reveal that, as expected, esters are not good solvents of PVC. As no phase separation can be detected visually, even at very low temperatures, it is concluded that esters are marginal rather than theta solvents at room temperature. It should be noted that the determination of A_2 from hook-shaped Zimm plots is questionable.

The weight-average molecular weights measured under these conditions differ considerably from one solvent to another. The general trend is to find higher values for $n_s > 1.4$ than for $n_s < 1.4$, the only exception being diethyl adipate.

Before going further, it is of importance to discover whether any chemical alteration of the original PVC occurred during preparation. The heating process can induce degradation leading to sequences with double bonds as well as to irreversible cross-linking or grafting of solvent molecules on to privileged sites.

Neither infra-red spectroscopy nor n.m.r. detected any chemical alteration of PVC samples recovered from diethyl malonate solutions that had been submitted to the thermal treatment involved. In addition, light scattering experiments performed in THF on these recovered PVC samples do not show any change when compared with the virgin PVC (identical Zimm plot, $M_w = 1.1 \times 10^5$). Another experiment carried out to by-pass the heating process used for solution preparation confirmed the non-chemical origin of the hook-shaped plots. First, a solution was made in THF at 30°C, then diethyl malonate was added and THF extracted by evaporation. The solution, which mainly contained PVC and diethyl malonate, was

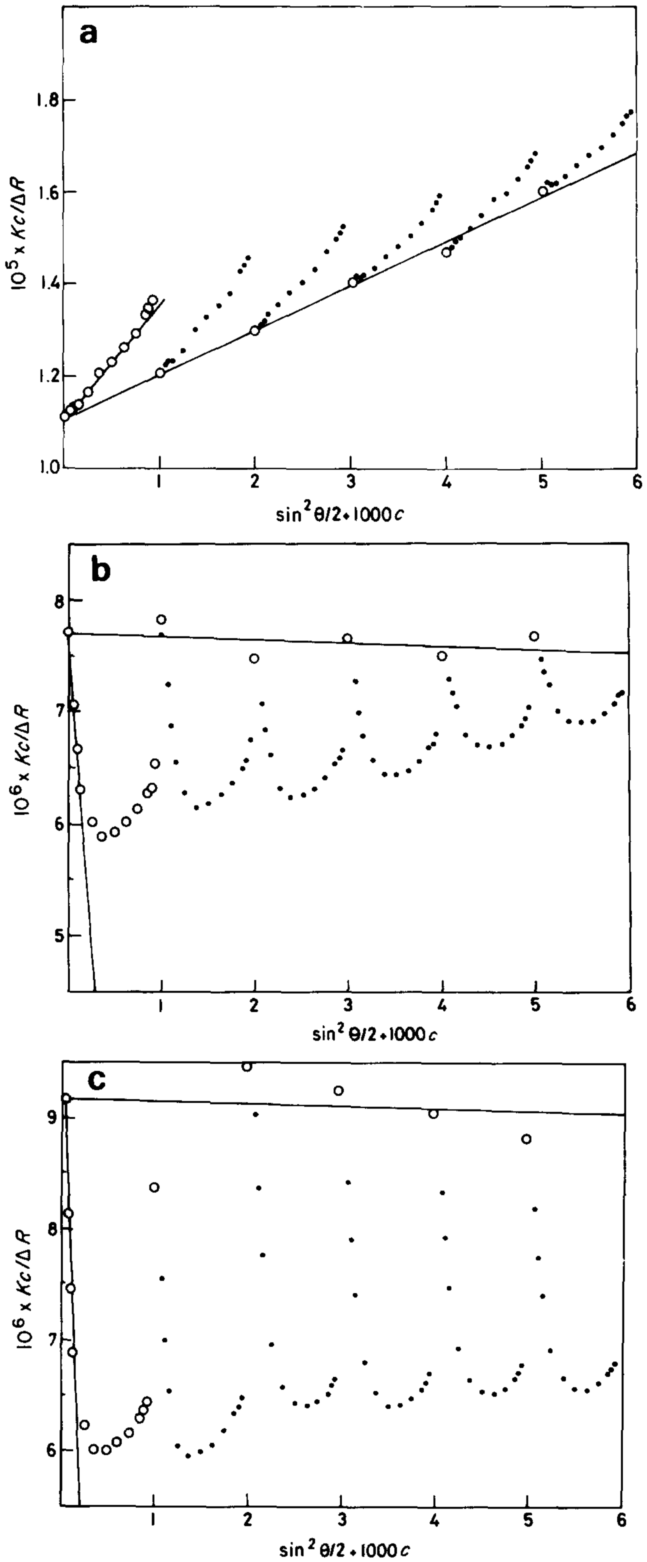

Figure 1 Zimm plots obtained for solutions of PVC in different esters: (a) isoamyl acetate; (b) ethyl heptanoate; (c) diethyl malonate. $c_i = 0.5 \times 10^{-2}$ g cm^{-3}

Table 1 Refractive index, refractive index increment (at 632.8 nm) and results of light-scattering (apparent molecular weight, apparent mean square radius of gyration and second virial coefficient) for different solvents. (A_2 coefficients, being so small, can be considered as effectively zero except for THF and cyclohexanone)

No.[a]	Solvent	n_s ($\lambda = 632.8$ nm)	dn/dc (cm^3 g^{-1})	$10^{-6} \times M_w$	$\langle R^2_{app} \rangle$ (Å^2)	A_2 (cm^3 g^2 mol)
1	Butyl acetate	1.3895	0.112	0.65	$(300)^2$	6×10^{-5}
2	Isoamyl acetate	1.3985	0.098	0.75	$(270)^2$	6×10^{-5}
3	Ethyl heptanoate	1.406	0.102	1.25	$(-700)^2$	-1.4×10^{-6}
4	Diethyl oxalate	1.406	0.103	2.3	$(-600)^2$	1.8×10^{-6}
5	Diethyl malonate	1.411	0.094	2.3	$(-800)^2$	-4×10^{-7}
6	Diethyl succinate	1.416	0.094	2.3	$(-530)^2$	5×10^{-6}
7	Diethyl adipate	1.423	0.085	0.5	$(-560)^2$	-2×10^{-5}
8	Tetrahydrofuran	1.4037	0.1115	0.11	$< \lambda/20$	1.25×10^{-3}
9	Cyclohexanone	1.4468	0.075	0.11	$< \lambda/20$	1.5×10^{-3}

[a] The number which indentifies solvents in *Figures 3* and *4*

again examined by light scattering. The same hook-shaped Zimm plots were found.

Origin of hook-shaped Zimm plots

While hook-shaped Zimm plots are rarely observed from light scattering, their origin is well documented[6]. It corresponds to a few situations only: optical anisotropy, fluorescence, ordering, large spheres, two-refractive index systems. These cases are now reviewed so as to find out which one is most relevant to these results.

Optical anisotropy. Some spurious plots with distorted or hook-shaped patterns can be obtained in solutions of anisotropic molecules that cause depolarization of light. An estimate of depolarization can be achieved by measuring the so-called depolarization ratio: $\rho_v = H_v/V_v$. For the solutions studied here, this ratio has been found to be virtually zero ($\rho_v \simeq 0.015$). Accordingly, depolarization can be discounted.

Fluorescence. In principle, fluorescence is accompanied by strong depolarization of the incident beam. In addition, the use of a high wavelength virtually prevents the appearance of this effect.

Ordering in solution. According to Burchard[7], who found similar results for poly(vinyl carbanilate) in diethyl ketone, the hook-like shape may arise from ordering of the particles, which causes interparticle scattering of Bragg type. The minimum in the Zimm plot is thus assimilated to a maximum of intensity. Light scattering experiments carried out on increasingly diluted systems revealed no change in the intensity pattern, which already renders such an interpretation questionable (*Figure 2*). Also, measurements of particle sizes achieved by inelastic light scattering[8] for solutions of PVC esters have provided hydrodynamic radii of gyration ranging from 300 to 400 Å ($c_{PVC} = 0.5 \times 10^{-2}$ g cm^{-3}). If the average distance between these objects is estimated as with liquid type order with $1.23\ \lambda = 2d \sin\theta m/2$, $d \simeq 4000$ Å. Clearly, this does not correspond to objects being in contact. Under such conditions[9] the Bragg-type maximum should no longer be observed unless long-range interactions exist. However, even in the case of polyelectrolytes such long-range interaction seems out of the question. Ordering does not seem therefore appropriate to account for hook-shaped plots in this case.

Scattering by a sphere. Another possibility would consist of taking into consideration the presence in these solutions of uncorrelated spherical objects. Under these circumstances, the scattered intensity is proportional to the form factor of a sphere $P_s(q)$:

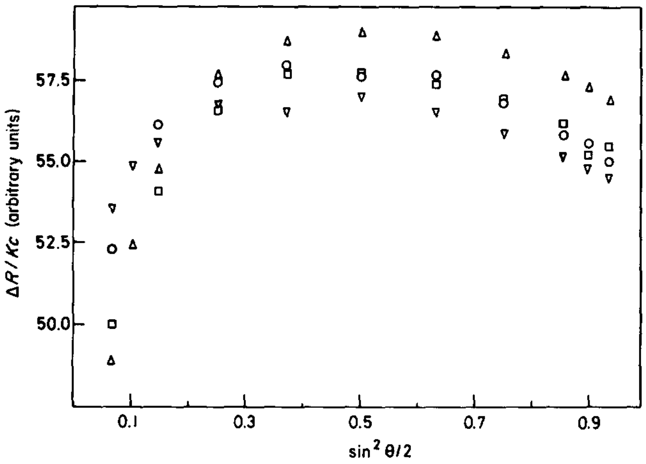

Figure 2 Angular dependence of the normalized scattered intensity. Initial concentration, $c_i = 0.12 \times 10^{-2}$ g cm^{-3}. (△), $c_1 = 2.4 \times 10^{-4}$ g cm^{-3}; (□), $c_2 = 1.91 \times 10^{-4}$ g cm^{-3}; (○), $c_3 = 1.44 \times 10^{-4}$ g cm^{-3}; (▽), $c_4 = 0.96 \times 10^{-4}$ g cm^{-3}

$$P_s(q) = [3(\sin qR - qR\cos qR)]^2 \times (qR)^{-6}$$

where $q\,4\pi/\lambda\ \sin\theta/2$ and R is the radius of the sphere).

It is known that this form factor displays maxima and minima. Accordingly, results reported here may correspond to a domain of q where a maximum of intensity occurs. If such were the case, the size of the sphere could be estimated as it is related to the first maximum by:

$$q_{max}R = 5.765$$

From our experiments, the maximum of intensity generally occurs around $q_{max} \simeq 2 \times 10^{-3}$ Å^{-1}, which leads to $R \simeq 3000$ Å. Considering maxima of higher orders would result in still larger sphere radii. Such a value is irreconcilable with quasi-elastic light scattering (QUELS) data that indicate $R_H \simeq 300$ Å. As a result, this possibility also has to be dismissed.

Aggregates consisting of two types of scatterers. Molecular weights determined in these solvents, although their absolute values are questionable, certainly indicate that aggregation of PVC chains takes place. Accordingly, if it is considered, as is often suggested, that partial crystallization is responsible for this aggregation, two types of scatterers will be present in the cluster, namely, the crystalline part and the disordered domain.

Within this framework, there are two ways of examining the problem: (i) through the theory developed for copolymers; and (ii) through the existence of an intraparticular correlation of the 'correlation hole' type.

Block copolymers. The theory of light scattering by copolymers derived by Benoit *et al.*[10] predicts the occurrence of apparent mean-square radii of gyration with negative values under specific conditions of refractive index increments. Consequently, and as demonstrated experimentally[11], hook-shaped Zimm plots can be obtained. However, it has to be emphasized that such a situation is observed for copolymers made up with few blocks only.

The most obvious and important fact in our experiments is to find above a given value of n_s, $\langle R^2_{app}\rangle < 0$ and below this value $\langle R^2_{app}\rangle > 0$ without any departure from that rule, as would be expected from a two-refractive-index system. In addition, the variation of $\langle R^2_g\rangle$ with n_s is qualitatively in agreement with what would be observed from copolymer solutions[11] (*Figure 3*). The observation of negative apparent mean square radii of gyration implies that the following relation is fulfilled

$$n_B < n_s < n_A \qquad (1)$$

According to the results, it then implies that:

$$n_B \leqslant 1.4$$

Such a value for n_B entails that for $n_s > 1.4$, v_B is either zero or negative.

As a result, the refractive index increment of a copolymer solution given by

$$v = xv_A + (1-x)v_B = x\upsilon_A(n_A - n_s) + (1-x)\upsilon_B(n_B - n_s)$$

(where x is weight composition of species A and υ_A its specific volume) should be lower than that of a solution containing sequence A solely. In the present case sequence A is similar to individual PVC chains. From THF and cyclohexanone solutions in which aggregation is absent v_A can be determined. As apparent in *Figure 4*, v measured for PVC esters solutions is always lower (typically 6% to 16% lower) than v_A measured in THF and cyclohexanone.

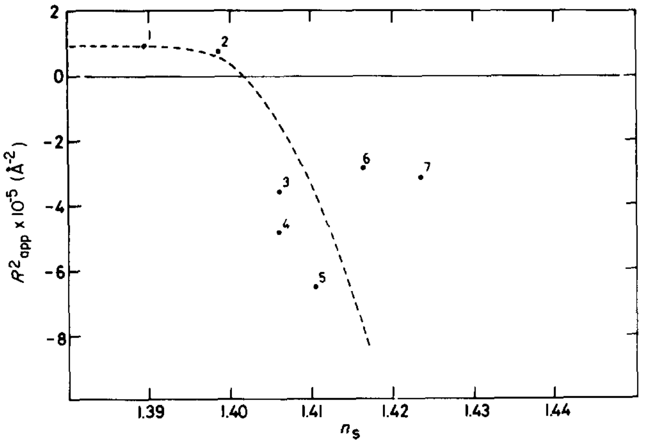

Figure 3 Experimental variation of $\langle R^2_{app}\rangle$ *versus* solvent refractive index (see *Table 1*). Solvents 1 to 7: esters (see text). Initial concentration, $c_i = 0.5 \times 10^{-2}$ g cm^{-3} (dotted lines are guidelines for the eye only)

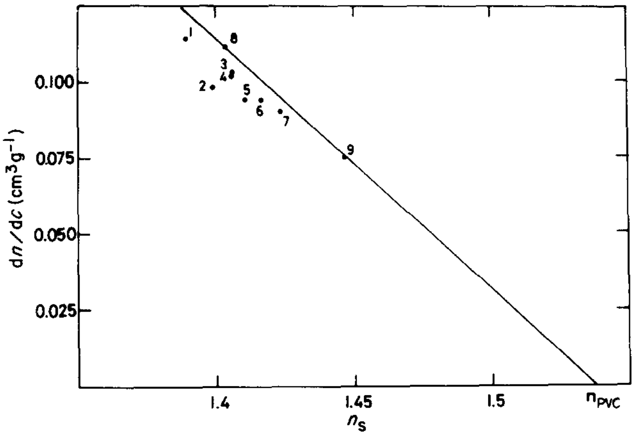

Figure 4 Experimental refractive index increment of PVC solutions (esters 1–7, see text) compared with refractive index increments of respectively THF (8) and cyclohexanone (9) solutions of PVC (see *Table 1*)

Although the discrepancy is not very large, these results are still consistent with a 'copolymer effect'.

However, when it comes to finding out what kind of scatterers are present in these aggregates, the interpretation through a copolymer effect rests on an uncertain basis. If one considers a simple case where the physical cross-links are PVC crystals, the remaining part being amorphous PVC, hook-shaped Zimm plots ought not to be observed. As a matter of fact, these crystals (provided that crystals made up with syndiotactic sequences are dealt with and that they possess the usual orthorhombic cell[12]) should admittedly have an average refractive index n_c slightly larger than 1.54. A rough estimate from density considerations provides $n_c = 1.58$, which ultimately implies that relation (1) cannot be satisfied. Other crystals can be taken into consideration. For instance solvated crystals, which are often reported to exist in several polymers[13–16], may be good candidates. While there is little doubt that such crystals would have a density far lower and correspondingly a smaller refractive index, n_{sc}, calculations made with the relation of Gladstone and Dale indicate that a refractive index of $n_{sc} < 1.4$ for these crystals seems highly unlikely, unless they were void-containing as well. The existence of such crystals cannot be demonstrated so that, although it is premature definitively to dismiss a 'copolymer effect' of physical origin, this case appears too improbable.

Intraparticular correlation or 'correlation hole' type

De Gennes[17] has shown theoretically that partial labelling of a polymer chain in the bulk state entails the appearance of a particular pattern of intensity. If the labelling is not punctual, the scattered intensity displays a maximum, usually related to the radius of gyration ($q_{max} \times R \sim 1$). This effect arises from the so-called 'correlation hole'. The calculation has been extended by Leibler[18] to polymer solutions for which he showed that the maximum should persist down to C^* (overlapping concentration). The only condition required is to have a sufficient difference of refractive indices. Yet, unlike the copolymer effect, relation (1) need not be fulfilled.

In our system, the concentration within an aggregate undoubtedly lies above C^* which means that this type of correlation can be envisaged. However, as already stressed above, a simple fringed micelle model is not expected to possess scatterers with sufficiently large contrast. Apparently, the polymer alone cannot provide such conditions, so that it is suspected that the solvent plays an active role either by promoting the growth of solvated crystals or by specific associations on the amorphous parts so as to alter their refractive index. Such a scheme implies a particular structure which cannot be described solely on the basis of the light scattering results. Further investigations with various techniques are required.

To conclude, a two-refractive-index system seems the most promising way to account for the existence of hook-shaped Zimm plots. However, no model can be derived from these results. The only picture, admittedly a very blurred one, that emerges from this discussion is that the solvent is certainly an active agent of the aggregation process and accordingly of the gelation process, which seems to be a general trend[13,14] so that it is not restricted to PVC. In addition, if these results can be extrapolated in relation to the structure of the gel state, it is quite possible that neither the fringed-micelle model nor the model of Yang and Geil[4] based on hydrogen bonding is appropriate for describing the network in these solvents.

CONCLUSION

Investigations by means of light scattering of dilute PVC solutions in linear esters have provided unexpected results. In particular, above a given value of solvent refractive index hook-shaped Zimm plots were found. After carefully checking the reproducibility of these results and demonstrating the absence of chemical modification it is concluded that these patterns may arise from a two-refractive-index system of physical origin. This means that molecular aggregation of PVC in these solvents leads to the formation of two types of scatterers. It is suspected that the solvent plays a role in this phenomenon and that the structure of these clusters does not resemble a fringed micelle. Accordingly, the same remarks may pertain to the physical gels prepared from these solvents.

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