Low-angle laser light scattering from polystyrene solutions: intensity measurements and photon correlation spectroscopy

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Light scattering measurements have been made on polystyrenes with a range of molecular weights in toluene and for one polystyrene with a range of molecular weights in toluene and for one polystyrene in a range of solvents including a theta solvent. Intensity data were used to calculate second virial coefficients and molecular weights, whilst photon correlation spectroscopy was used to calculate diffusion coefficients. All measurements were made at 30°C and at a scattering angle of *ca.*4°. The data were used to examine current theories of polymer diffusion and the relation between hydrodynamic radius (R_H) and radius of gyration ($\langle s^2\rangle^{1/2}$). The results support accepted theories of polymer diffusion, but suggest that the relation between R_H and $\langle s^2\rangle^{1/2}$ requires further analysis.

Keywords Light scattering; diffusion; viscosity; polystyrene; photon correlation spectroscopy; intensity measurements

INTRODUCTION

Light scattering from dilute solution has been one of the major techniques in the characterization of polymers for some 40 years. Both theory and practice have been reviewed in a number of publications[1-3]. In addition to 'classical' light scattering, i.e., where the average scattered intensity is measured, recent years have seen the development of photon correlation spectroscopy (PCS) which responds to the frequency broadening of the scattered light[4-6]. Classical intensity light scattering data enable the calculation of weight average molecular weight (M_w), second virial coefficient (A_2), and in favourable circumstances the mean square radius of gyration ($\langle s^2\rangle$). Photon correlation spectroscopy observes the dynamics of polymers in solution or swollen gels[7-9]. Descriptions of the theoretical basis of PCS and the apparatus required have been the subject of at least three major conferences over the last 10 years[10-12], and much discussion continues on methods of data analysis and interpretation. The dynamic parameter obtained from PCS depends (in broad terms) on three major factors: (1) the angle of measurement θ *via* the scattering vector $Q=(4\pi n_0/\lambda_0)\sin(\theta/2)$), where n_0 = refractive index of the scattering medium and λ_0 is the wavelength of the incident light *in vacuo*; (2) the concentration of the polymer in solution; (3) the molecular weight. At sufficiently low-angle ($Q<1/\langle s^2\rangle^{1/2}$) in dilute solution the zeroth normal mode of motion of the polymer molecule will be observed and this corresponds to translational diffusion of the whole molecule. At higher angles (0°→180°) and for high molecular weight polymers ($\bar{M}_w \rightarrow 5\times10^6$–$10^7$) higher normal modes (Rouse–Zimm modes) may be observed. As the polymer concentration increases, intermolecular entanglements eventually predominate and a collective mode of many chains will be observed[13]. Consequently, the measurement of the translational diffusion coefficient of a polymer requires extrapolation of data to infinite dilution and zero angle in the case of high molecular weight polymers. Until recently most light scattering goniometers available commercially had a low-angle limit of *ca.* 15° to 30°, below which scattered light intensity values become contaminated by the incident beam. The Chromatix KMX-6 light scattering photometer has an optical system that the angles of scattering are $1°<\theta<7°$, the actual angle being dependent on the refractive index of the scattering medium[14-18]. We report here the use of this instrument in the examination of the diffusion coefficient of polystyrene in solution and an assessment of current theories of this quantity.

EXPERIMENTAL

Materials

Polystyrene, PSN, of molecular weight *ca.* 80×10^3 was prepared in this laboratory by anionic polymerization, g.p.c. gave $\bar{M}_w/\bar{M}_n=1.048$. In addition to this material, four polystyrenes (PSA–PSD) with molecular weights in the range $100\times10^3<M_w<4\times10^6$ were obtained from

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Polymer Labs. Ltd., (Church Stretton, Shropshire, UK) for these materials $\bar{M}_w/\bar{M}_n$ was quoted as less than 1.05. Solvents used were toluene, benzene, carbon tetrachloride, dioxane and cyclohexane. All were dried and distilled before use.

Light scattering

A Chromatix-KMX-6 low-angle laser photometer was used for both classical intensity and PCS measurements. A 2 mW He–Ne laser ($\lambda_0 = 632.8$ nm) was used as a light source, the light being incident on a cell with massive quartz windows, which encloses a volume of *ca.* 0.15 ml. Scattered light is collected at forward angles by a series of annuli at discrete radii from the incident beam direction, and then focused through an aperture onto the photomultiplier. All measurements were made at 30±0.1°C, temperature control being achieved by the integral heaters and proportional controllers in the KMX-6 instrument. For classical intensity measurements, a 0.2 mm diameter aperture was used and the nominal angle of scattering being 6°–7°, the actual value being calculable knowing the refractive index of the scattering medium. This same angle was used for PCS measurements, but in this case the aperture used was 50 μm in diameter. Scattered light intensity levels were recorded on an integral digital meter, whereas for PCS the photomultiplier output was passed *via* a discriminator amplifier to a computer controlled 128 channel Malvern K7025 correlator, where the signal was treated to produce the intensity autocorrelation function which was subsequently analysed to yield a value for the diffusion coefficient.

Complementary measurements

For the calculation of molecular weights the specific refractive index increment (SRII) of polystyrene in each solvent and the solvent refractive index were measured. The latter quantity is also needed to calculate the true angle of scattering. A Brice–Phoenix differential refractometer was used for the measurement of SRII. This instrument had been modified by replacing the mercury lamp with a high intensity tungsten lamp and using a narrow pass 633 nm filter. Thermostatic control was maintained by an external water bath. Refractive indices at 633 nm were obtained by interpolation of a Cauchy plot of data measured, using a Pulfrich refractometer, at wavelengths (nm) of 643.8, 579.1, 546.1 and 435.8[19].

Partial specific volumes of polystyrene in each solvent were measured using a Paar digital densitometer model 602 and solutions with a concentration range of 0.5 to 6 wt.%[20]. Finally, intrinsic viscosities, $[\eta]$, were measured using an Ubbelhohde suspended level viscometer thermostatically controlled at 30±0.1°C.

RESULTS

Light scattering

Intensity measurements. Values of the excess Rayleigh Ratio R_θ were calculated from the observed readings and the known attenuation factors for the Chromatix KMX-6. The values are absolute and independent of any external calibrant. *Figure 1* shows representative plots for $K^* c/R_\theta$ as a function of c, where c = polymer concentration in g ml^{-1} and $K/ = 2\pi^2 n_0^2 v^2/\lambda_0^4$ with $v \equiv$ SRII. Different symbols in *Figure 1* refer to repeated measurements on the same polymer using different solutions and at well separated time intervals varying from a few days to a few weeks, within any one solvent the reproducibility is excellent. Data were analysed by least squares straight line fits, $\bar{M}_w$ being calculated from the intercept and A_2 from the slope. Repeated measurements of $\bar{M}_w$ and A_2 for the same polymer indicate that the uncertainties are ±8% and ±10% respectively. *Tables 1* and *2* give values of $\bar{M}_w$ and A_2 obtained by this means for all polymer solvent combinations examined here.

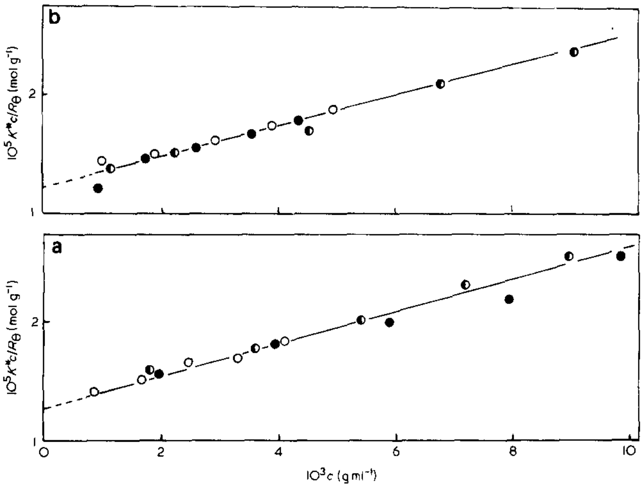

Figure 1 Representative plots of K^*C/R_θ obtained for PSN in toluene (a) and carbon tetrachloride (b). Different symbols refer to measurements made at different times

Photon correlation spectroscopy. A typical intensity autocorrelation function obtained by PCS using the Chromatix KMX-6 is shown in *Figure 2*. Diffusion coefficients were obtained from these type of plot from a cumulants analysis[21] of autocorrelation functions using a procedure outlined by Pusey[10]. Generally, four or five concentrations of polymer were used, with five autocorrelation functions being determined at each concentration the diffusion coefficient, D, being averaged from these five determinations. Diffusion coefficients were plotted as in *Figure 3* and extrapolated to zero concentration of polymer to give the infinite dilution diffusion coefficient, D_0. Such plots can be represented by the equation[22]

$$D(c) = D_0(1 + k_D c) \tag{1}$$

and values of D_0 and k_D are given in *Tables 1* and *2*.

Intrinsic viscosities

Huggins plots of reduced specific viscosity as a function of c were used to obtain $[\eta]$.

DISCUSSION

Concentration dependence of the diffusion coefficient

Diffusion coefficients of polymers in solution at finite (but dilute) concentrations are influenced by both thermodynamic and hydrodynamic factors. These factors are both contained within the parameter k_D of equation (1) which can be formulated as,

$$k_D = 2A_2\bar{M}_w - \bar{V}_2 - k_f \tag{2}$$

Table 1 Experimental data for PSN in various solvents at 30°C

Solvent	$10^{-5}\bar{M}_w$ (g mol^{-1})	10^4A_2 (ml g^{-2} mol)	10^7D_0 (cm^2 s^{-1})	k_D (ml g^{-1})	$[\eta]$ cm^3 g^{-1}
Benzene	0.798	7.1 ± 0.5	5.18 ± 0.2	15.44	39.4
Toluene	0.798	6.5 ± 0.5	6.32 ± 0.2	20.57	36.2
Carbon tetrachloride	0.798	6.85 ± 0.5	3.70 ± 0.2	38.92	38.4
Dioxane	0.798	5.92 ± 0.5	3.10 ± 0.2	13.7	36.5
Cyclohexane (35°C)	0.798	0 ± 0.1	4.61 ± 0.2	−17.62	17.5

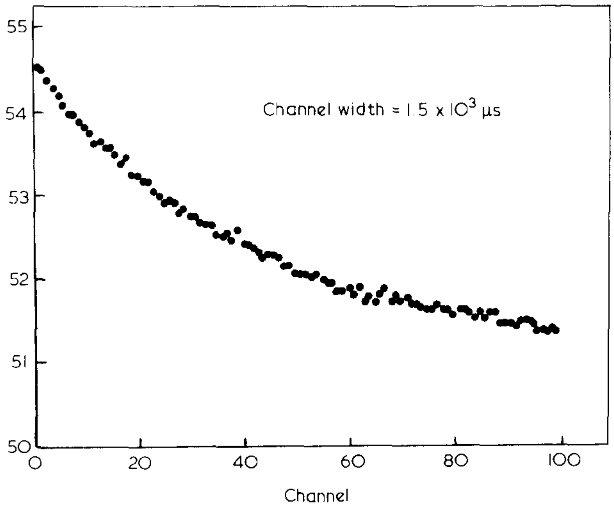

Figure 2 Typical intensity autocorrelation function obtained for PSD in toluene at 30°C

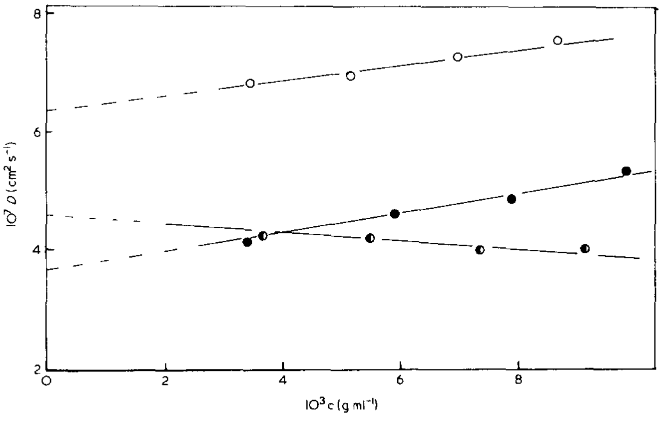

Figure 3 Diffusion coefficients as a function of concentration for PSN in: (○) toluene; (●) carbon tetrachloride (both at 30°C); (◐) cyclohexane at 35°C

where $\bar{V}_2$ = partial specific volume. The term k_f appears as the coefficient in the relation for the concentration dependence of the friction coefficient, f.

$$f = f_0(1 + k_f c + \ldots) \tag{3}$$

The coefficient k_f is dependent on the size and shape of the molecule. Its theoretical calculation involves a summation of long range perturbations and consequently the degree of interpenetration of molecules[23]. Calculations[24] using an equivalent sphere uniform density model have shown that, for soft interpenetrable spheres $k_{f,\phi} = 2.23$, ($k_{f,\phi}$ is the value of k_f when polymer concentration is expressed in volume fraction units). For hard impenetrable spheres Pyun and Fixman[24] calculate $k_{f,\phi}$ as 7.16 whilst an earlier calculation[22] gives 6.88. For polymer solutions the soft interpenetrable sphere limit corresponds to the unperturbed state for infinite molecular weight polymers whilst the hard sphere limit is approximated by infinite molecular weight polymers in good solvents.

Now,

$$k_f = k_{f,\phi}(N_A 4\pi R_H^3 / 3\bar{M}_w) \tag{4}$$

where N_A = Avogadro's Number and R_H = hydrodynamic radius of the molecule in solution.

The diffusion coefficient at infinite dilution is determined by hydrydynamic influences alone,

$$D_0 = k_B T / f_0 \tag{5}$$

using the Stokes–Einstein relation

$$D_0 = k_B T / 6\pi\eta_0 R_H \tag{6}$$

and η_0 is the viscosity of the pure solvent and k_B the Boltzman constant. The calculation of $k_{f,\phi}$ necessitates using equations (2), (4) and (6), and consequently the value of $k_{f,\phi}$ may be subject to considerable error unless the values of the measured quantities have a considerable precision. This is particularly true for the diffusion coefficient, since it enters as a cubic term *via* R_H. The error propagation in the calculation of $k_{f,\phi}$ can be appreciated when the composite equation from equations (2), (4) and

Table 2 Data for varying molecular weight polystyrenes in toluene at 30°C

Polymer	$10^{-5}\bar{M}_w$ (g mol^{-1})	10^4A_2 (ml g^{-2} mol)	10^7D_0 (cm^2 s^{-1})	k_D (ml g^{-1})	$[\eta]$ cm^3 g^{-1}
PSA	0.9346	6.75	5.25 ± 0.2	10.476	49.8
PSB	3.4722	4.98	2.20 ± 0.1	61.36	122.5
PSC	11.3636	3.54	1.20 ± 0.1	173.3	249.5
PSD	38.0228	2.80	0.85 ± 0.05	1552.94	500.0

(6) is written down,

$$k_{f,\phi} = (2A_2\bar{M}_w - \bar{V}_2 - k_D)\bar{M}_w D_0^3 \cdot \frac{3}{N_A 4\pi} \cdot \left(\frac{6\pi\eta_0}{k_B T}\right)^3 \quad (7)$$

Typically in equation (7), $2A_2\bar{M}_w$ is of the same sign and approximate magnitude as k_D and consequently errors in each of these quantities will contribute equally. Since $\bar{V}_2 << k_D$, the error in $\bar{V}_2$ may be disregarded. We estimate the error in $\bar{M}_w$ to be around 10% and that in A_2 to be ~8%. Values of D_0 have errors of *ca.* 10% whilst k_D will also have an error of at least 10%. Evaluation of these errors[25] using typical values for k_D, $\bar{M}_w$ and A_2 indicates that the cumulated error in $k_{f,\phi}$ can be as large as 40% in unfavourable circumstances. Apart from the diffusion coefficient, the major source of error is the product $2A_2\bar{M}_w$. A consideration of the quantities involved in the measurement of these two terms indicates that the major source of error here arises from the measurements of v and n_0 since values of R_θ measured on the Chromatix KMX-6 are accurate to within 2% of the true value. Notwithstanding these possibly large errors in the calculation of $k_{f,\phi}$, the values obtained from our data have reasonably constant values (*Table 3*) which are in excellent agreement with the theoretical prediction of Pyun and Fixman[24]. Values for PSN in a variety of good solvents give an average value for $k_{f,\phi}$ of 7.45, whilst the data for a range of molecular weights in toluene give an average value of 6.54. Additionally, the value obtained for PSN in cyclohexane at theta conditions (35°C) of 2.56 is also in excellent agreement with the theory value of 2.25.

Table 3 Friction factor coefficients obtained for all polymer – solvent combinations

A Polystyrene PSN	$\bar{M}_w = 0.798 \times 10^5$
Solvent	$k_{f,\phi}$
Benzene	6.86
Toluene	8.37
Carbon tetrachloride	5.69
Dioxane	8.86
Cyclohexane (35°C)	2.56

B Polystyrenes PSA–PSD in Toluene at 30°C

Polymer	$10^{-5}\bar{M}_w$	$k_{f,\phi}$
A	0.9346	7.83
B	3.4722	5.29
C	11.3636	6.24
D	38.0228	6.78

Molecular weight dependence of dilute solution parameters

Whilst there appears to be no theoretical basis for a power dependence of A_2 on molecular weight, there has been much discussion on the value of the exponent in such relations. Kurata and Stockmayer[26] state that the largest possible value of γ in

$$A_2 \propto \bar{M}_w^{-\gamma}$$

is 0.15, higher values being attributable to the influence of the third virial coefficient being unaccounted for in the calculation of A_2. Berry and Casassa[27] on the other hand suggest that for polymers in good solvents then γ has a value of *ca.* 0.25. *Figure 4* is a double logarithmic plot of A_2 as a function of $\bar{M}_w$, a least squares straight line through the data yields the following relationship,

$$A_2 = 1.07 \times 10^{-2}\bar{M}_w^{-0.24}$$

with a correlation coefficient of 0.998. To assess the influence of the third virial coefficient, A_3, light scattering data were analysed by an adaptation of the method of Bawn *et al.*[28], by taking pairs of points (i and j) within any one data set and plotting them according to the equation,

$$\left(\frac{K^*c}{R_\theta}\right)_i - \left(\frac{K^*c}{R_\theta}\right)_j = 2A_2(c_i - c_j) + 3A_3(c_i^2 - c_j^2)$$

This analysis showed that although A_3 had finite values in the region of 10^{-4} cm^3 g^{-2} mol, the value of A_2 was not significantly altered from that obtained from the slope of K^*c/R_θ as a function of c and we conclude that the influence of A_3 is negligible here and our data give support to the postulate of Berry and Cassassa[27].

A power law can also be obtained for the dependence of diffusion coefficient on molecular weight. The double logarithmic plot for D_0 of PSA–PSD in toluene at 30°C is shown in *Figure 5*. The linear least squares line drawn has a correlation coefficient of 0.985 with the data and gives,

$$D_0 = 1.35 \times 10^{-4}\bar{M}_w^{-0.49} \quad (8)$$

Since D_0 is related to hydrodynamic radius, R_H, by equation (6), then this relationship suggests that

$$R_H \propto \bar{M}_w^{0.49}$$

The power laws relating R_H and $\langle s^2 \rangle^{1/2}$ to molecular weight and their relation to each other have been much discussed. Theoretically, for polymers of infinite molecular weight in good solvents it is expected from critical theory that[29],

$$\langle s^2 \rangle^{1/2} \propto M^{0.588}$$

which is close to the value of 0.6 obtained for the exponent obtained by Flory[30] some 30 years ago. Experimental results for good solvent systems lie in the region of 0.58 to 0.6. The smaller value of the exponent for the hydrodynamic radius molecular weight dependence found here has been observed by other workers also[31-35]. This

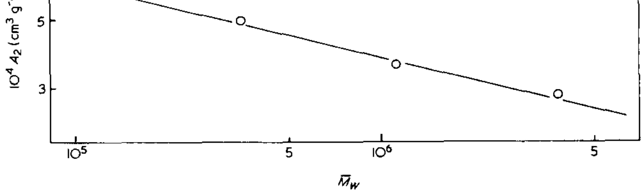

Figure 4 Double logarithmic plot of second virial coefficient of polystyrene in toluene at 30°C as a function of molecular weight

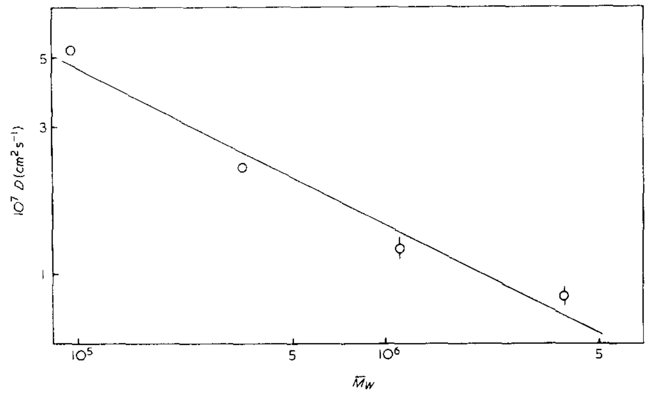

Figure 5 Double logarithmic plot of the diffusion coefficient (at infinite dilution) of polystyrene in toluene at 30°C as a function of molecular weight

smaller exponent has been attributed to the greater sensitivity of the hydrodynamic radius to short range vector distances along the polymer chain[34]. In the limit of infinite molecular weight then both exponents should have the value of 0.588 and consequently it is probable that the value of the exponent in the hydrodynamic radius–molecular weight relation depends on the molecular weight range studied. In this same paper[34] it is suggested that,

$$[\eta]\propto M^{2\nu+\nu_D-1)}$$

where ν and ν_D are the exponents for radius of gyration and hydrodynamic radius respectively. If, for polystyrene in toluene we adopt $\nu=0.588$ as indicated by theory and use the value of 0.49 obtained experimentally here, then this predicts that $[\eta]$ should scale with molecular weight as:

$$[\eta]\propto M_w^{0.67}$$

From the experimental intrinsic viscosities obtained here, a least squares line through the data points gives an exponent of 0.62, in excellent agreement with that predicted by the equation of Weill and des Cloizeaux[34]. It should be borne in mind however that only four molecular weights have been used notwithstanding the almost 40 fold range in the magnitude of molecular weight.

The relation between R_H and $\langle s^2\rangle^{1/2}$ is commonly written as,

$$R_H = X\langle s^2\rangle^{1/2} \qquad (9)$$

and theoretical values of X are 0.537 in a good solvent where the molecule is expanded, and 0.665 in a theta solvent for the unperturbed molecule[35]. In the absence of direct values of $\langle s^2\rangle^{1/2}$ from light scattering data, calculation of X is made *via* an indirect analysis proposed by Kok and Rudin[36], i.e.

$$D_0 = (k_BT/6\pi\eta_0X)(\Phi'/\bar{M}_w[\eta])^{1/3} \qquad (10)$$

where $\Phi'=\Phi 6^{3/2}$ and Φ is the universal viscosity constant defined by Flory. *Figure 6* is a plot of D_0 for PSA to PSD in toluene as a function of $(k_BT/6\pi\eta_0)(\bar{M}_w[\eta])^{-1/3}$. The least squares slope through these data in conjunction with a value of $2.5\times10^{23}\,\mathrm{mol^{-1}}$ for Φ ($[\eta]$ in $\mathrm{cm^3\,g^{-1}}$)

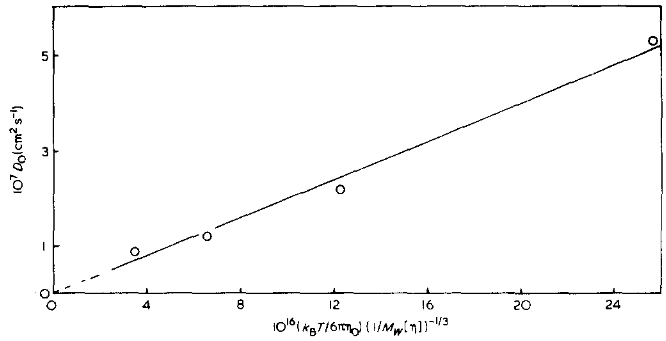

Figure 6 D_0 plotted according to the analysis of Kok and Rudin[36]; $(k_BT/6\pi\eta_0)(\bar{M}_w[\eta])^{-1/3}$ in $\mathrm{cm^2\,s^{-1}\,mol^{1/3}}$

produces a value of 0.779 for X. This value is in excellent agreement with the average value obtained by Kok and Rudin[36] from their survey of existing data and serves to underline the need for further analysis of the relation between R_H and R_g.

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