Quasielastic light scattering from polystyrene/poly(methyl methacrylate)/toluene solutions*

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Quasielastic light scattering was used in an investigation of solutions of mixtures of polystyrene and poly(methyl methacrylate) (1:1 by weight) in toluene, in which poly(methyl methacrylate) is not 'visible'. Bimodal distributions of decay times observed with semidilute solutions, i.e. above the cross-over concentration, were interpreted as cooperative and interdiffusion processes. Experimental results were in good agreement with the recent theory of Benmouna *et al.*

INTRODUCTION

In recent years, the dynamic properties of ternary solutions of homopolymers, i.e. polymer 1/polymer 2/solvent systems, have been investigated with increased attention[1-11]. Most papers deal with compatible (e.g. poly(vinyl methyl ether)/polystyrene[1-4]) or partly incompatible (e.g. polystyrene/poly(methyl methacrylate)[5-10]) polymer mixtures in solvents that are isorefractive with one of the polymers and provide sufficient optical contrast for the other polymer. Under such conditions, by using quasielastic light scattering (QELS), it is possible to observe directly the dynamics of only the 'visible' polymer in a solution containing another 'invisible' polymer. At low concentrations of the 'visible' polymer (the so-called probe polymer), it is possible, by using QELS measurements, to determine its self-diffusion coefficient, for example in semidilute solutions of the other polymer, i.e. in the polymeric matrix of the 'invisible' polymer.

Recent QELS measurements of the dynamics of poly(methyl methacrylate) (PMMA) molecules in a polystyrene matrix in a mixed solvent (toluene/chloronaphthalene), isorefractive for polystyrene, have proved the existence of two diffusion modes[6]. The slow mode was identified as a translational movement of the centre of gravity of the chain of the probe polymer (PMMA), while the fast mode was interpreted as a coupling of the movement of PMMA molecules with the cooperative motion of the polystyrene matrix.

The existence of such bimodal time correlation functions in three-component solutions containing two types of interacting particles and a solvent was predicted earlier by Phillies[12,13] and Pusey[14]. Their theory, employing bound linear diffusion equations, was successfully applied to the interpretation of QELS measurements in systems of strongly interacting

particles[12,14], but appeared to be unsuitable for ternary semidilute solutions of homopolymers[6]. Recently, a theory of quasielastic light scattering in mixtures of homopolymers in solutions has been reported, based on the random-phase approximation[15,16]. The main result of the theory is the prediction of the existence of two dynamic processes in QELS spectra, which were interpreted as cooperative and interdiffusion modes. In particular, the dependence of scattering amplitudes and decay times on the composition of the mixture and on the polymer concentration in solution was discussed there. Since it was difficult to obtain physical implications from general relations, only two special cases were discussed in detail: (i) a mixture of two polymers having the same molecular weights and dimensions, but differing in the refractive index increment; and (ii) a mixture of two chemically identical polymers having different molecular weights. Systems of both types were also investigated in dilute solutions[17] and in the absence of solvent[18]. Some implications of the theory were experimentally checked by QELS measurements using ternary mixtures of two homopolymers (namely polystyrene/poly(methyl methacrylate)[9] and polystyrene/poly(dimethylsiloxane)[11]) having the same molecular weight (corresponds to case (i)). The latter case (ii) was experimentally studied using ternary solutions of two polyisobutylenes in chloroform, in which one of the polymers was present each time in semidilute concentration (matrix polymer), while the other was the probe polymer[19,20]. It appeared that also in this case two diffusion processes are operative. The fast process corresponds to the collective diffusion mode of the matrix of the semidilute polymer, while the slower process reflects the interdiffusion mode of the probe polymer. It is of importance that, with trace quantities of probe molecules, this procedure can be used in determining the self-diffusion coefficient in the matrix of the other polymer.

In this study solutions of two mixtures of polystyrene

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and poly(methyl methacrylate) (1:1 by weight) in toluene, differing in the molecular weights of the components, were investigated by QELS spectroscopy within a broad concentration range. The objective of the study was to investigate and discuss cooperative and interdiffusion processes under conditions more general than those considered so far. The experimental results thus obtained are in a good agreement with the implications of the theory of Benmouna *et al.*[15].

EXPERIMENTAL

Polymers and solvent

Two poly(methyl methacrylate) (PMMA) polymers prepared by radical polymerization, $M_w = 5 \times 10^4$ and 1.3×10^6, were fractionated in the system *m*-cresol/heptane. The middle fractions (~ 20 wt% of the total mass for both samples), PMMA-1 and PMMA-2, as well as two polystyrene (PS) standards (Pressure Chemicals, number 3b (PS-1) and 7b (PS-2)) were used in our study. Relevant characteristics of these samples are shown in *Table 1*.

Toluene (isorefractive solvent for PMMA), reagent grade (Lachema, Czechoslovakia), was purified and dried before use. *Table 2* shows the refractive index increments, (dn/dc), for the PS and PMMA in toluene[21].

Sample preparation

Two PS/PMMA mixtures (1:1 by weight) were used for the measurements: I, PS-1/PMMA-1; II, PS-2/PMMA-2. The samples were prepared by direct dissolution at elevated temperature (80°C) and optically cleaned by filtration through a glass bacterial filter G5 (Jena, GDR) into cylindrical cells, which could be sealed. The total polymer concentration ranged from $c = 5 \times 10^{-4}$ to 5×10^{-2} g cm^{-3}.

Apparatus

QELS measurements were made with a photon correlation spectrometer described elsewhere[22]. The light source was a He–Ne laser or, in some cases, an Ar-ion laser. A sample was placed in a compartment allowing the temperature to be controlled between 0 and 100°C with an accuracy of ±0.05°C. The homodyne spectrometer equipped with a 96-channel digital correlator enabled us to measure the multi-time correlation function (*MTCF*) covering 3.5 decades of decay time. The correlator operated with three simultaneous sampling times.

Data treatment

Laplace transform inversion of *MTCF*s was performed using a constrained regularization calculation REPES[23], similar to Provencher's CONTIN[24], to obtain the decay time distribution $A(\tau)$. As, in some cases (semidilute solutions), the distribution function consisted of two well separated narrow bands (bimodal distribution), correlation functions were also fitted by a double-exponential forced fit.

RESULTS AND DISCUSSION

The dynamic behaviour of ternary polymer solutions (mixtures I and II) in toluene was investigated as a function of the total polymer concentration, c_T. *Figure 1*

Table 1 Polymer characteristics

Sample	$M_w \times 10^3$	$\dfrac{A_2 \times 10^{4\ a}}{(\text{cm}^3\ \text{g}^{-2}\ \text{mol})}$	M_w/M_n
PS-1	390[b]	4.5[c]	1.10[b]
PS-2	37[b]	7.7[c]	1.06[b]
PMMA-1	47[c]	4.8[d]	1.2[e]
PMMA-2	1190[c]	2.3[d]	1.5[e]

[a] At 25°C
[b] Values given by the manufacturer
[c] Static light scattering in toluene
[d] Membrane osmometry in toluene
[e] QELS in methyl ethyl ketone

Table 2 Refractive index increments (cm^3 g^{-1}) of PS and PMMA in toluene (436 nm)

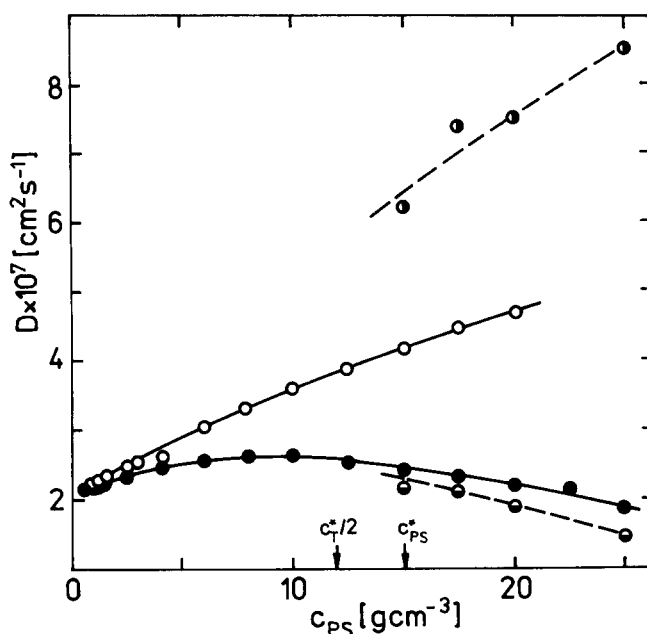| Sample	Temperature (°C)			
	15	20	25	30
PS	0.113	0.115	0.117	0.118
PMMA	−0.003	0.0012	0.0028	0.0039

Figure 1 Concentration dependences of the diffusion coefficients obtained from QELS measurements of solutions of the polymer mixture I and polystyrene in toluene: (●) D_{app}, (○) D_c, (◐) D_s, (◑) D_f. Arrows indicate cross-over concentrations of the mixture, c_T^*, and of polystyrene, c_{PS}^*

shows the dependence of the apparent diffusion coefficient D_{app} of mixture I obtained by the forced single-exponential fit of experimental time correlation curves on the PS concentration (c_{PS}) in a ternary solution ($c_T = 2c_{PS}$). For the sake of comparison, values of the collective diffusion coefficient, D_c, of PS present alone in toluene are also plotted in *Figure 1*. Arrows mark cross-over concentrations, which represent the boundary between the domains of dilute and semidilute solutions. The concentrations were obtained by a viscosity measurement, from a change in the slope of the concentration dependences of η/c, where η is the viscosity of the polymer solution under investigation[25].

In dilute solutions interactions between the individual polymer coils can be neglected, which in *Figure 1* is demonstrated by the fact that in dilute solutions D_{app} virtually does not differ from D_c. With increasing PS concentration both diffusion coefficients increase, with the difference that the increase in D_{app} is much slower than that in D_c. Such a slower rise in D_{app} is obviously due to a decrease in the second virial coefficient, A_2, caused by the impaired quality of the solvent as a result of the presence of incompatible PMMA[26,27]. Recently, the problem has been investigated, both theoretically and experimentally, by Akcasu *et al.*[17]. Unfortunately, the results obtained can be applied only to a mixture of two chemically identical polymers having different molecular weights. A more general application of the theory is impeded, in particular, by the fact that the first and second moments of the pair correlation function remain unknown.

The increase in D_{app} stops near c_T^*; above that region, D_{app} (unlike D_c) begins to decrease with increasing concentration. The basic difference in the concentration dependences of D_{app} and D_c for $c_T > c_T^*$ suggests that the measured diffusion coefficients correspond to different diffusion processes. Since no structural anomalies, e.g. polystyrene aggregation, were detected by static light scattering experiments in the polymer mixture solutions
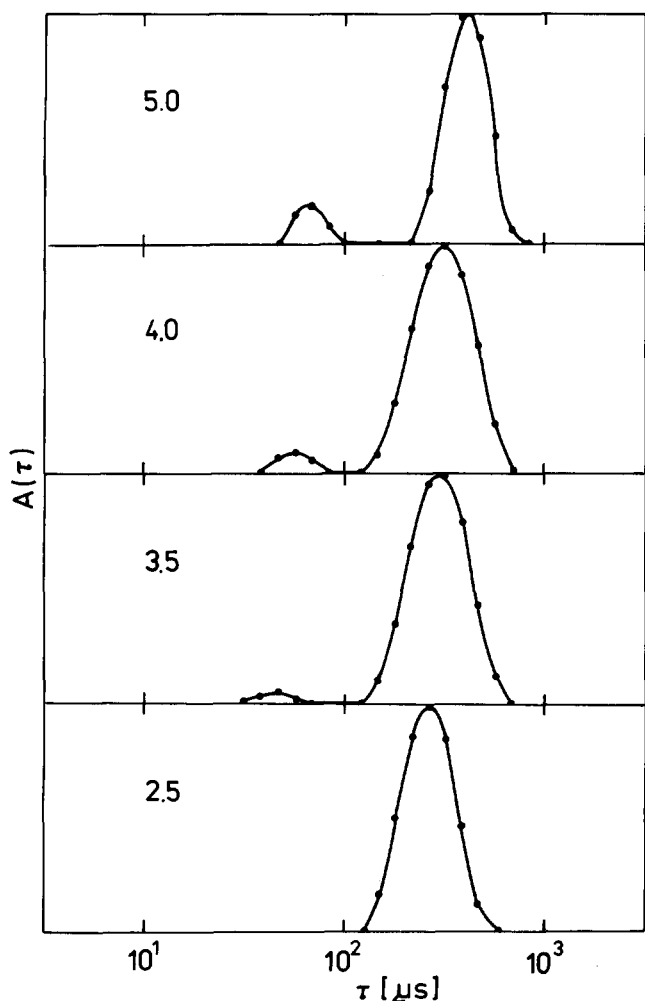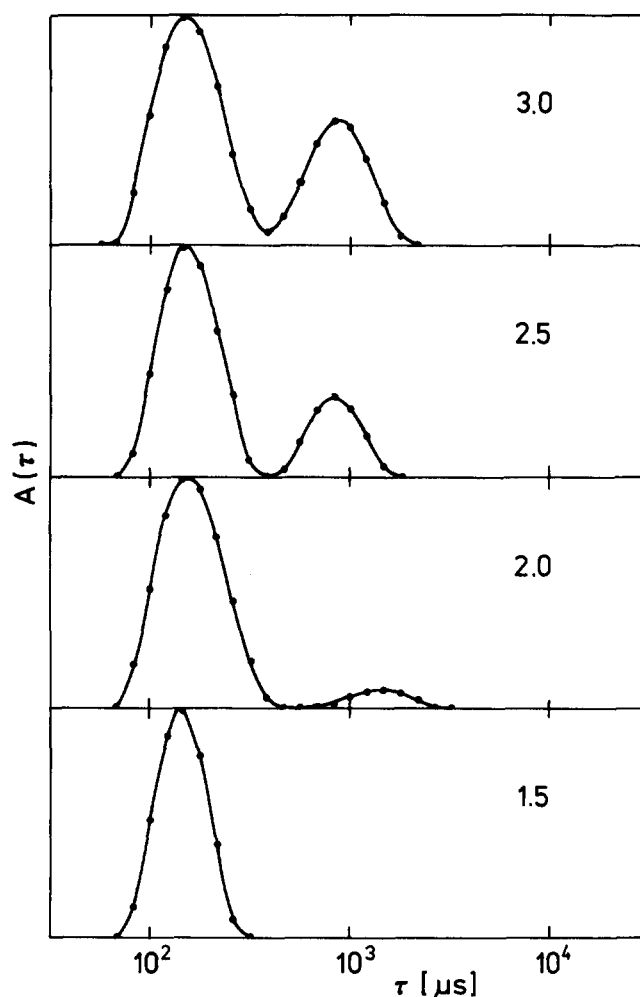

Figure 3 Distribution functions of decay time $A(\tau)$ of the mixture of polymers II (Ar-ion laser, scattering angle $\theta = 30°$). Numbers in the right-hand part of the figure are the respective concentrations c_T (10^{-2} g cm^{-3}) of the polymer in the mixture

Figure 2 Distribution functions of decay time $A(\tau)$ of the polymer mixture I (He–Ne laser, scattering angle $\theta = 45°$). Numbers in the left-hand part of the figure represent the respective concentrations c_T (10^{-2} g cm^{-3}) in the mixture

under study, we suppose that, according to theoretical results of Benmouna *et al.*[15], the slow diffusion process should be interdiffusion, with the corresponding diffusion coefficient D_I being much lower compared with the expected value of D_c (this is discussed in greater detail below).

Since the quality of single-exponential fits was very low for $c_T > c_T^*$, the corresponding *MTCF*s were analysed by employing the REPES program. The distribution functions of decay times $A(\tau)$ are shown in *Figures 2* and *3* for mixtures I and II. Since in all cases these distribution functions consist of two well separated narrow bands (bimodal distributions), experimental time correlation functions were further fitted using a two-exponential fit, which in this concrete case gave more reliable and more exact values of fast and slow decay times, τ_f and τ_s, respectively, and of relative scattering amplitudes than the inverse Laplace transform program REPES. Values of the decay rates Γ_f ($= 1/\tau_f$) and Γ_s ($= 1/\tau_s$) and of the ratio of the corresponding amplitudes A_f/A_s for mixtures I and II are summarized in *Tables 3* and *4*. Both these decay times have a diffusion character (i.e. $\Gamma_i \approx K^2$, where $i = f, s$, and K is the length of the scattering vector); hence, it is possible to introduce and calculate two corresponding diffusion coefficients D_f ($= \Gamma_f/K^2$) and D_s ($= \Gamma_s/K^2$). The D_f and D_s values calculated from the Γ_f and Γ_s values of

Table 3 Values of decay rates pertaining to fast and slow processes, Γ_f and Γ_s, respectively, and ratios of corresponding scattering amplitudes, A_f/A_s, for mixture I at 25°C

$c_T \times 10^2$ (g cm^{-3})	$2A_2M_w c_T$	$\Gamma_f \times 10^{-4}$ (s^{-1})	$\Gamma_s \times 10^{-3}$ (s^{-1})	Γ_f/Γ_s (exp)	A_f/A_s (exp)	A_f/A_s (theor)
3.0	1.35	0.799	2.78	2.87	0.28	0.080
3.5	1.58	0.954	2.75	3.47	0.17	0.084
4.0	1.80	0.969	2.46	3.94	0.23	0.088
5.0	2.26	1.097	1.94	5.65	0.18	0.094

Table 4 Values of decay rates, Γ_f and Γ_s, and ratios of corresponding scattering amplitudes, A_f/A_s, for mixture II at 25°C

$c_T \times 10^2$ (g cm^{-3})	$2A_2M_w c_T$	$\Gamma_f \times 10^3$ (s^{-1})	$\Gamma_s \times 10^2$ (s^{-1})	Γ_f/Γ_s (exp)	A_f/A_s (exp)	A_f/A_s (theor)
2.0	10.9	7.21	1.18	6.09	3.27	5.20
2.5	13.7	7.28	1.25	5.81	1.70	3.76
3.0	16.4	7.18	1.05	6.85	1.30	2.90

mixture I are plotted in *Figure 1* for the sake of comparison. One can see immediately that the D_s values do not differ too much from the D_{app} values, while the D_f values in the mixture are higher than the D_c values in a PS solution; also, that both the D_c and D_f values increase slightly with increasing polymer concentration in solution.

To rule out the possibility that the observed fast mode (D_f) is due to the diffusion of macromolecules of the not completely 'invisible' PMMA, the following experiments were performed:

(i) QELS measurements in a ternary solution ($c = 5.0 \times 10^{-2}$ g cm^{-3}) in the temperature range 15–25°C, i.e. near the temperature of 18.5°C at which PMMA should be completely isorefractive with toluene (cf. *Table 2*). We checked and confirmed the assumption that A_f/A_s (*Table 5*) is virtually temperature-independent within the limits of experimental error. If the fast mode were due directly to the diffusion of macromolecules of PMMA, the scattering amplitude A_f, and thus also A_f/A_s, should be strongly temperature-dependent.

(ii) QELS measurement in a toluene solution of PMMA ($c = 2.5 \times 10^{-2}$ g cm^{-3}) at 30°C. However, even after a period of measurement longer by an order of magnitude than that used in measurements with ternary solutions, no time correlation function allowing a sufficiently exact and reproducible determination of D_c of PMMA molecules in toluene could be obtained.

Both experiments suggest that the direct diffusion mode of PMMA molecules cannot affect the QELS measurements in ternary solutions sufficiently, and thus it cannot be responsible for the observed fast relaxation decay time (τ_f). According to a recently reported theory of dynamic light scattering in solutions of mixtures of homopolymers based on the random-phase approximation, D_s and D_f should correspond to the cooperative diffusion mode and interdiffusion mode, respectively[15]. The higher D_f values compared with the D_c values of a PS solution can be explained by the fact that D_f corresponds to an effectively higher polymer concentration in a ternary solution than in the PS solution.

To check quantitatively the results of the theory of Benmouna *et al.*[15], we compared the calculated Γ_c/Γ_I and A_c/A_I values with experimental ones. We applied

Benmouna's general theory to a case of two chemically different polymers, one of which has no optical contrast with the solvent. Assuming that the quality of the solvent is the same for both polymers (which holds comparatively well for the system PS/PMMA/toluene), we have[28]:

$$\frac{\Gamma_c}{\Gamma_I} = \frac{A + \frac{1}{2}\sqrt{B}}{A - \frac{1}{2}\sqrt{B}} \tag{1}$$

where

$$A = \frac{1}{2}\left(\frac{1}{yP_1} + \frac{1}{P_2} + v\varphi N_2\right)$$

$$B = \left(v\varphi N_2 + \frac{1}{P_2} - \frac{1}{yP_1}\right)^2 - 4xv\varphi N_2\left(\frac{1}{P_2} - \frac{1}{yP_1}\right)$$

$$+ 8x(1-x)(v\varphi N_2)^2(\chi/v)$$

v is the familiar excluded-volume parameter for a pair of monomers, φ is the total number segmental concentration in the system, x is the fraction of polymer 1 in the system, χ is the Flory–Huggins interaction parameter, N_i is the degree of polymerization of the ith polymer, P_i is the form factor of a coil of the ith polymer and $y = N_1/N_2$.

For A_c/A_I we then obtain:

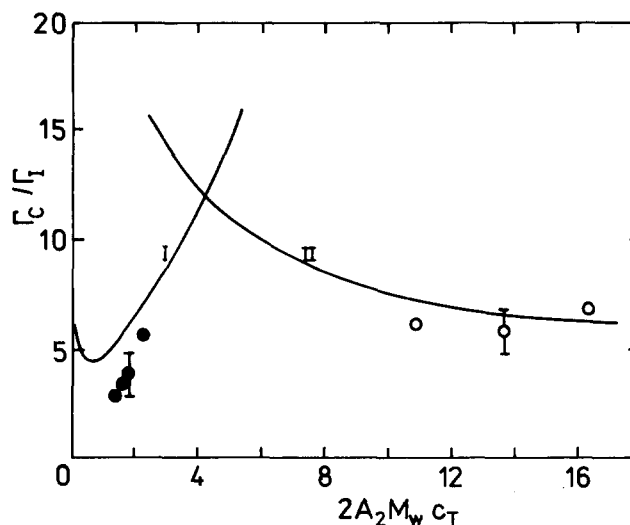$$\frac{A_c}{A_I} = -\frac{A + \frac{1}{2}\sqrt{B} - C}{A - \frac{1}{2}\sqrt{B} - C} \tag{2}$$

where

$$C = \frac{(1-x)xP_2(v\varphi N_2)^2 + [1 + (1-x)v\varphi N_2]^2}{1 + (1-x)P_2 v\varphi N_2}$$

The values of Γ_c/Γ_I calculated from equation (1) are illustrated in *Figure 1* (solid lines) for both polymer

Table 5 Temperature dependence of the ratio of scattering amplitudes, A_f/A_s (mixture I, $c_T = 5.0 \times 10^{-2}$ g cm^{-3})

Temperature (°C)	$(dn/dc)_{c \to 0}$	A_f/A_s
15	−0.003	0.20
17	−0.0013	0.19
20	0.0012	0.20
25	0.0028	0.18

Figure 4 Theoretical concentration dependence of Γ_c/Γ_I calculated from equation (1) for mixtures I and II (———). The points represent experimental values of Γ_f/Γ_s: (●) mixture I, (○) mixture II

systems. In the calculations it was assumed that $P_1 = P_2 = 1$, $x = 0.49$ and $\chi/v = 5 \times 10^{-2}$ (cf. ref. 15). It should be pointed out here that, in standard notation, $v\varphi N = 2A_2 M_w c_T$ where A_2 is the second virial coefficient, c_T is the concentration in g cm^{-3} and M_w is the molecular weight of the polymer. The experimental values of Γ_f/Γ_s (*Figure 4*, points) are systematically lower than the calculated ones for both polymer systems under study. In spite of this, however, with respect to the approximations used the agreement between the calculated and experimental values should be regarded as very satisfactory.

The agreement between the calculated and experimental values of A_c/A_l is somewhat poorer (cf. *Tables 3* and *4*). The theory predicts quite correctly, however, that A_c/A_l changes from values below unity for system I to those higher than unity for system II.

CONCLUSIONS

It should be said, in conclusion, that the existence of a bimodal distribution of relaxation times observed in semidilute ternary solutions (PS/PMMA/toluene) under study can be explained using the theory of Benmouna *et al.*[15]. The theory satisfactorily predicts the ratio of decay rates of the fast and slow modes Γ_f/Γ_s, and also predicts, within an order of magnitude, the ratio of the corresponding scattering amplitudes A_f/A_s.

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