Dynamics and structure of an amphiphilic triblock copolymer of styrene and 5-(*N*,*N*-diethylamino) isoprene in selective solvents*

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Abstract: Solution properties of a highly asymmetric aminofunctionalized triblock copolymer of 5-(*N*,*N*-diethylamino)isoprene and styrene were investigated in dilute regime. Toluene, THF, 1,4-dioxane, or DMF were used to prepare the solutions. It was found that the solvent selectivity for one or both block affects the copolymer solution behavior as reflected by the calculated parameters through light-scattering techniques: weight-averaged, molecular-weight $\bar{M}_w$, radius of gyration R_g, translational diffusion coefficient D_0, and hydrodynamic radius R_h. According to what was determined, the quality of the polymer–solvent interactions decreases in the order: toluene, THF, 1,4-dioxane, and DMF. After quaternization with dimethyl sulfate, the triblock copolymer consisted of a polystyrene (PS) block with short poly[5-(*N*,*N*,*N*-diethylmethylammonium)isoprene][methyl sulfate] block at both chain ends, shows a better solvation in polar solvents. Transmission electron microscopy (TEM) was used to characterize the crew-cut aggregates prepared from the quaternized copolymer.

INTRODUCTION

5-(*N*,*N*-dialkylamino)isoprenes constitute a class of polar monomers [1] that can be attached to apolar monomers, via anionic polymerization, to form interesting amphiphilic block copolymers with specific architectures and well-defined, molecular-weight distributions. In addition, upon quaternization of the tertiary amino groups, positively charged ionic block can be obtained [2].

In dilute solutions of selective solvents (i.e., good for one block, but poor with respect to the other), block copolymers can intermolecularly associate to form aggregates. Solution properties of amphiphilic block copolymers as well as their aggregation behavior have long been investigated and have attracted much attention from both theoretical and experimental viewpoints [3]. The knowledge of their solution behavior is of utmost importance due to the several applications of this class of copolymers. Drug delivery, catalysis, colloid science, separation, and microencapsulation, among others, are fields where these materials find potential application [4].

In this paper, a highly asymmetric triblock copolymer of the type polybase-neutral block-polybase (i.e., ASA, where A stands for aminoisoprene and S for styrene) was anionically synthesized.

Subsequently to the synthesis, the copolymer tertiary amino groups were quaternized to produce positively charged block at both chain ends. The positively charged block(s) are expected to be fully ionized and, therefore, not subjected to pH change effects. Because of their composition, of ca. 90 mol % of polystyrene, the quaternized triblock copolymer is not directly soluble in water. An indirect method of preparation of the aggregates in aqueous solution is required [5]; all the obtained structures could be classified as crew-cut aggregates [6].

The scope of the present paper is to first investigate the solution properties in different solvents (toluene, THF 1,4-dioxane, or DMF) of this material through static and dynamic light scattering. The copolymer behavior revealed to be sensitive to the solvent quality for one or both blocks. In highly polar solvent (DMF), the copolymer was found to intermolecularly associate. However, the quaternization of the copolymer amino blocks favors the solvation in this solvent.

Aggregates in aqueous solution were then prepared and their morphologies determined via transmission electron microscopy (TEM) to better elucidate the solvent–polymer interactions.

EXPERIMENTAL SECTION

Polymer synthesis and quaternization

The triblock copolymer was synthesized via sequential anionic polymerization of 5-(*N,N*-diethylamino)isoprene followed by styrene and again by 5-(*N,N*-diethylamino)isoprene, giving rise to the copolymer ASA. The polymerization occurs exclusively by a 4,1-addition of the monomer to the end of anionic chain. The polymerization reaction was carried out in benzene at 10 °C, using *sec*-butyllithium as initiator. More details on the synthesis procedure can be found elsewhere [7]. The copolymer polydispersity and degree of polymerization were determined by size exclusion chromatography (SEC), and the composition was determined by ^{1}H NMR. The calculus of the degree of polymerization of the polystyrene relative to the poly[5-(*N,N*-diethylamino)isoprene] was performed according to what was previously described [1]. The copolymer characterization is summarized in Table 1.

After synthesis, the copolymers were quaternized with dimethyl sulfate, in a mixture of solvents (methanol/benzene), according to a method already described in the literature [2], in order to obtain positively charged blocks at both chain ends. The quaternized triblock species are designated as poly[5-(*N,N,N*-diethylmethylammonium)isoprene][methyl sulfate]-*b*-polystyrene-*b*-poly[5-(*N,N,N*-diethylmethylammonium)isoprene][methyl sulfate], which, for the sake of convenience, is presently designated as ASAq.

The styrene homopolymer was synthesized following established methods [8] via anionic polymerization under an ultrapure nitrogen atmosphere (Matheson) in flame-dried glassware. The reaction was carried out in freshly distilled THF. The polymer was characterized (molecular weight and polydispersity) through SEC on a Waters® instrument interfaced to a computer running Millenium® software using THF as eluent. A calibration curve was constructed using polystyrene standards (Aldrich). The data are given in Table 1.

Table 1 Molecular characteristics of the block copolymer of styrene and 5-(*N,N*-diethylamino)isoprene.

	PAI content[b] (mol %)	M_n (g/mol)[c]	M_n/M_w[c]
PAI$_{11}$-*b*-PS$_{228}$-*b*-PAI$_{11}$ (ASA)[a]	8.8	26 800	1.20
PS	0	21 300	1.13

[a]The numbers indicate the number average degrees of polymerization of each block.
[b]The PAI content was determined by ^{1}H NMR relative to that of the PS block.
[c]Parameters determined by SEC.

Light-scattering measurements

Static and dynamic light-scattering measurements (SLS and DLS) were performed at 20 °C on an automatic BI-200M goniometer and a BI-9000 AT digital correlator (Brookhaven Instruments). A Spectra Physics (model 127) He-Ne laser (λ = 632.8 nm) was used as light source. Intensity time-correlation functions were obtained in multiple-τ mode in the angular range from 45° to 145°.

The polymer/solvent solutions were filtered through a millipore filter of nominal pore size of 0.22 μm into dust-free cylindrical scintillation vials.

The refractive index increments *dn/dc,* corresponding to each polymer/solvent system, were determined by a modified Abbe refractometer at 20 °C. These values are given in Table 2.

Table 2 Refractive index increments *dn/dc* (mL/g) of the various polymer/solvent systems.

	Toluene	THF	Dioxane	DMF
ASA	0.13	0.18	0.15	0.14
PS	–	–	–	0.16

The intensity time-correlation functions were recorded for each resulting solution, from 45° to 145°, in steps of 5° or 10°. The scattering volume was minimized using a 400-nm aperture. Hydrodynamic radius values were obtained with the help of the CONTIN algorithm, which was used to determine the relaxation rates Γ and apparent diffusion coefficients D_{app}.

Self-assembly procedure and transmission electron microscopy

Because the copolymer core-forming block (polystyrene) is much longer than the corona one (quaternized amino polymer) the aggregates were prepared by an indirect method; the copolymer was first dissolved in a good solvent for both blocks and then water was added as a precipitant to induce the segregation of the hydrophobic blocks.

Among the solvents used in the LS experiments, only DMF, THF, and 1,4-dioxane are useful in preparing the aggregates because they are water-soluble. The copolymers were first dissolved in the organic solvent (DMF, THF, or dioxane) to desired concentrations, and let stir overnight at room temperature. After that, deionized water (Milli-Q) was added at a rate of 0.5 wt % per minute, until predetermined contents. At very low concentrations of water, isolated chains are dispersed in the solution. As the addition of water progresses, the quality of the solvent for the longer block (polystyrene) gradually decreases and the aggregates are formed. The solution was then dialyzed against water for three days to remove the organic solvents.

Transmission electron microscopy (TEM) experiments were carried out on a JEM2000-FX microscope operating at 80 kV. Aqueous aggregate solutions free of organic solvents were used to prepare the TEM samples. A drop of the dilute solution (10–20 times dilution) was placed onto copper grids precoated with Formvar and carbon and let evaporate at room temperature.

RESULTS AND DISCUSSION

Light scattering

Static light-scattering data were analyzed according to the method proposed by Zimm [9]. The averaged intensities were extrapolated to zero angle and to zero concentration, obtaining the following parameters for each polymer/solvent system: weight-averaged, molecular-weight $\bar{M}_w$, radius of gyration R_g, and second virial coefficient A_2.

The intensity time-correlation functions were obtained by photon-correlation spectroscopy (DLS) for each individual solution. Relaxation rates, Γ, and apparent diffusion coefficients $D_{app} = \Gamma/q^2$, where q stands for the magnitude of the wave vector, were evaluated by CONTIN algorithm. D_{app} values were extrapolated to zero angle to give the diffusion coefficient D_c corresponding to each concentration c. Through the linear extrapolation of D_c to zero concentration, the diffusion coefficient D_0 was obtained by the equation:

$$D_c = D_0 \, (1 + k_D \, c). \tag{1}$$

Finally, the Stokes–Einstein equation,

$$D_0 = \frac{k_B T}{6\pi\eta_o R_h} \, , \tag{2}$$

was applied to evaluate the hydrodynamic radius, R_h. The ρ parameter, which is related to the chain conformation in solution, was obtained by the relation:

$$\rho = R_g/R_h. \tag{3}$$

Solutions of ASA in either toluene, THF, or 1,4-dioxane could be analyzed according to the Zimm method (Table 3). However, solutions of ASA in DMF showed a strong angular dependence of the normalized light-scattering intensity (Fig. 1), suggesting the formation of aggregates, which has prevented the calculus of the static parameters.

In order to better understand the solution behavior in DMF, besides ASA, we also investigated the solution behavior of ASAq/DMF and PS/DMF (PS with approximately the same degree of polymerization of the PS-block of the copolymer). The PS solutions demonstrated virtually the same behavior as the one shown by ASA/DMF, i.e., strong angular dependence of the normalized light-scattering intensity (Fig. 2). However, when the analyzed system was ASAq/DMF, the results suggested an improvement of the polymer–solvent interactions, as evidenced by the results in Table 4 and Fig. 3. Berry plot was used to evaluate the static parameters because it has shown a better fit.
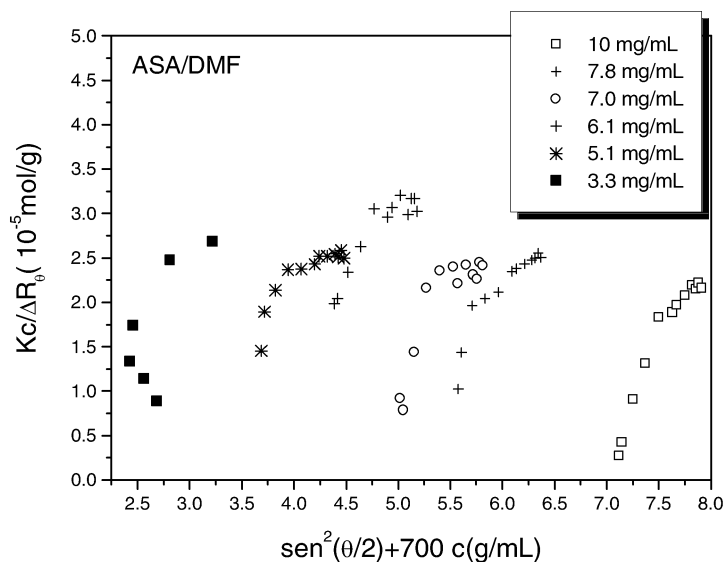

Fig. 1 Zimm plot of ASA in DMF.

In order to better understand the solution behavior in DMF, besides ASA the solution behavior of ASAq/DMF and PS/DMF (PS with approximately the same degree of polymerization of the PS-block of the copolymer) was also investigated . The PS solutions demonstrated virtually the same behavior as the one shown by ASA/DMF, i.e., strong angular dependence of the normalized light scattering intensity (Fig. 2). However, when the analyzed system was ASAq/DMF, the results suggested an improvement of the polymer–solvent interactions, as evidenced by the results in Table 4 and Fig. 3. Berry plot was used to evaluate the static parameters because it has shown a better fit.

The analysis of the time-correlation function of all investigated systems (ASA, ASAq, and PS in various solvents) depicted only one relaxation rate, indicating the presence of only one molecular
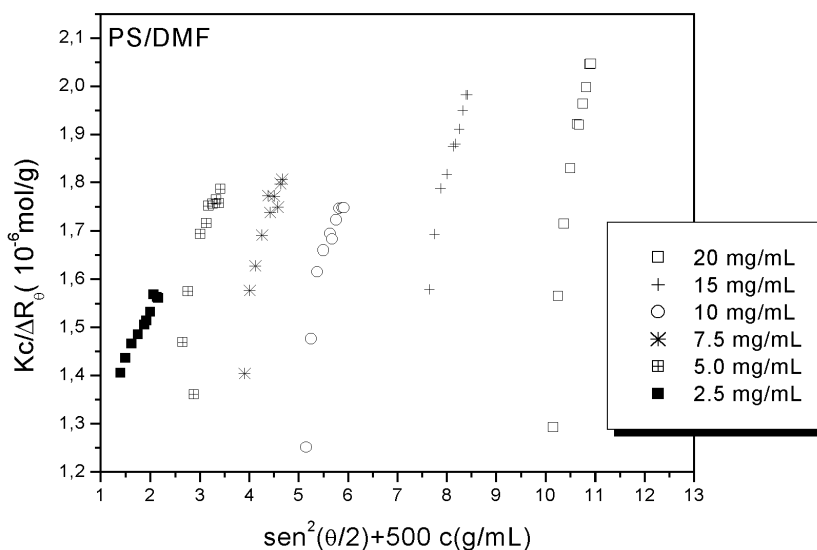

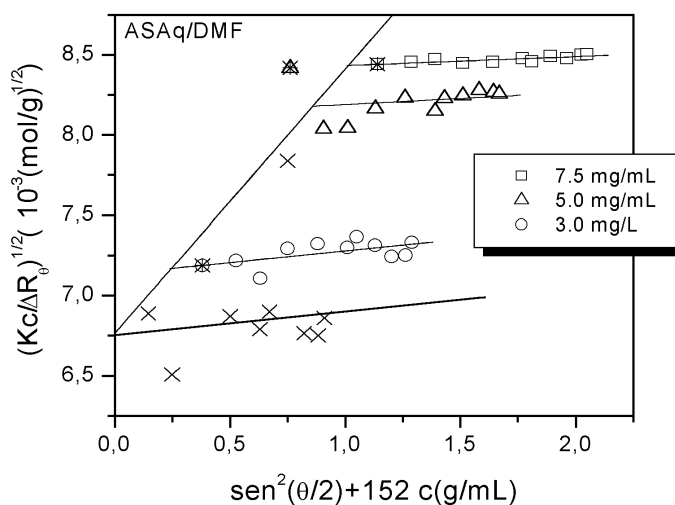**Fig. 2** Zimm plot of PS in DMF.

Fig. 3 Berry plot of ASAq in DMF.

species in solution and leading to the calculus of one R_h corresponding to each polymer–solvent system. The calculated values of the dynamic parameters are given in Tables 3 and 4. Whenever possible, the ρ parameter was also calculated. The R_h values obtained for the ASA triblock in toluene, THF, and 1,4-dioxane are similar to the observed for the ASAq/DMF system, however, the ASA triblock and PS in DMF show a higher R_h value due to aggregates formation.

Table 3 Static and dynamic light-scattering parameters from ASA in various solvents.

	Toluene	THF	1,4-Dioxane
$\bar{M}_w$ (g/mol)	33 300	49 000	26 900
A_2 (cm^3 mol g^{-2})	2.09×10^{-3}	8.55×10^{-4}	1.16×10^{-4}
R_g (nm)	10.6	30.0	22.3
R_h (nm)	3.9	3.9	2.9
D_0 (cm^2 s^{-1} 10^{-7})	9.46	10.08	5.46
k_D (cm^3 mg^{-1})	360	10	22
ρ	2.7	7.7	7.7

Table 4 Static and dynamic light-scattering parameters from solutions of ASA, ASAq, and PS in DMF.

	ASA	ASAq	PS
$\bar{M}_w$ (g/mol)	–	22 800	–
A_2 (cm^3 mol g^{-2})	–	1.66×10^{-3}	–
R_g (nm)	–	17.2	–
R_h (nm)	8.9	2.0	6.6
D_0 (cm^2 s^{-1} 10^{-7})	3.08	18.26	4.12
k_D (cm^3 mg^{-1})	60	17.8	–8.8
ρ	–	8.7	–

It is well known that the solvent interactions with respect to one or both blocks constitute a determinant factor on the solution behavior of such macromolecules.

Since PS is a nonpolar polymer, its interaction with the solvents can be predicted from some parameters, named the solubility parameter δ and the dielectric constant ε. These two parameters are related to the parameter χ, which reflects the strength of the interaction between the polymer and the solvent. According to what was discussed in a previous paper [10], the polystyrene–solvent interaction should be stronger in THF, followed by dioxane and DMF, since the solubility parameter of the THF is the closer to that of homo-PS when compared to dioxane and DMF. Although the parameter χ is not available for the quaternized homopoly(aminoisoprene); it is not soluble in dioxane nor in DMF, but it is soluble in THF. Besides, it is known that DMF is not a good solvent for PS. Therefore, within this simple approach it was expected that the solubility of the copolymers would be higher in THF, than in dioxane or DMF. Regarding toluene, since it is a nonpolar solvent, it is a better solvent for PS.

Table 5 Solubility parameters δ, viscosities η, and refractive index, n [11].

	Toluene	THF	1,4-Dioxane	DMF	PS
δ (MPa$^{1/2}$)[a]	18.2	18.6	20.5	24.8	16.6–20.2
$\eta_{20\,°C}$ (cP)	0.59	0.55	1.26	0.79	–
$n_{20\,°C}$	1.4969	1.4070	1.4224	1.4321	–

[a]These numbers are not available for the poly(aminoisoprene).

This conclusion can also be drawn from the analysis of the second virial parameter A_2 for ASA-triblock in different solvents. The systems ASA/toluene and ASAq/DMF have shown A_2 values that indicates better polymer–solvent interactions, when compared to the other systems (see Tables 3 and 4).

The $\bar{M}_w$ values determined by light scattering show discrepancies to $\bar{M}_w$ values determined by SEC. It is understandable since the SEC technique was performed in THF and needs calibration with polystyrene standards.

The higher M_w obtained for ASA6 in THF is probably due to the contributions of polyamino-isoprene blocks to the scattered light intensity since these blocks are isorefractive in toluene.

Looking at the ρ parameter results, they all indicate a cylindrical chain conformation in solution, according to the literature, even for the quaternized system (ASAq/DMF).

As mentioned early, for the ASA/DMF system it was not possible to calculate the above-mentioned parameters due to the strong angular dependence of the normalized light-scattering intensity, which indicates stronger polymer–polymer interactions when compared to the polymer–solvent interactions (i.e., there is evidence of aggregate formation in these solutions).

The quaternization of the amino block favors its solvation in polar solvents, as seen by the static light-scattering results. This is due to the ionic interactions between the cationic amino blocks and the solvent. Based on the results, we can extrapolate this effect to other polar solvents, that is, THF and 1,4-dioxane should be also a good solvent for ASAq.

Morphologies from quaternized ASA triblock copolymer

Morphologies of crew-cut aggregates from copolymers of styrene and quaternized 5-(*N,N*-diethyl-amino)isoprene were studied as a function of the organic solvent, initial concentration, and copolymer molecular weight and architecture in a previous paper [12].

Here, as a matter of illustration, we will present only some examples of the aggregates formed from DMF, THF, or dioxane as initial organic solvents, and subsequent water addition. The aggregates could be directly observed by TEM due to the high Tg of polystyrene, and their dimensions were measured readily from the digital micrograph files. It was previously found that the investigated triblock copolymer yielded multiple morphologies in various solvents. A more detailed description of the self-assembly process in given elsewhere [7].

In the early stages of aggregation, a thermodynamic equilibrium between unimers and aggregates can be assumed. As more water is added, the organic solvent is progressively extracted from the cores up to a point where the aggregates can be considered kinetically frozen. In the course of the micelliza-tion phenomena, many different morphologies can result. It has been reported that the nature of the or-ganic solvent is one of the most important morphogenic factors, since polymer–solvent interactions de-termines the coil dimensions of each block. The way that the copolymer is expected to assemble will be a direct consequence of the degree of swollenness of mainly the hydrophobic chain, since ca. 90 mol % of the copolymer is composed by PS (see Table 1).

In THF, for example, PS chains are more extended, since the PS–solvent interaction is stronger when compared to dioxane or DMF. Therefore, when the solvent is THF, it is expected that the dimen-sions of the aggregate would be bigger because the solvent content in the core will be higher [10]. One of the most interesting finding on the present copolymer systems was the formation of an unexpected morphology, resembling the shape of a bowl. The bowl-shaped aggregates consist of a new morphol-ogy encountered only in the triblock copolymers in dioxane and THF. This novel morphology was ex-tensively described, and a possible mechanism of formation was proposed in a recent paper [7].

Figure 4 shows TEM micrographs demonstrating the morphologies obtained from ASAq at ini-tial concentration of 0.01 wt % in various solvents. When the common solvent was THF (Fig. 4A), the triblock formed spheres and some rods coexisting with bowl shapes. When dioxane is employed as the
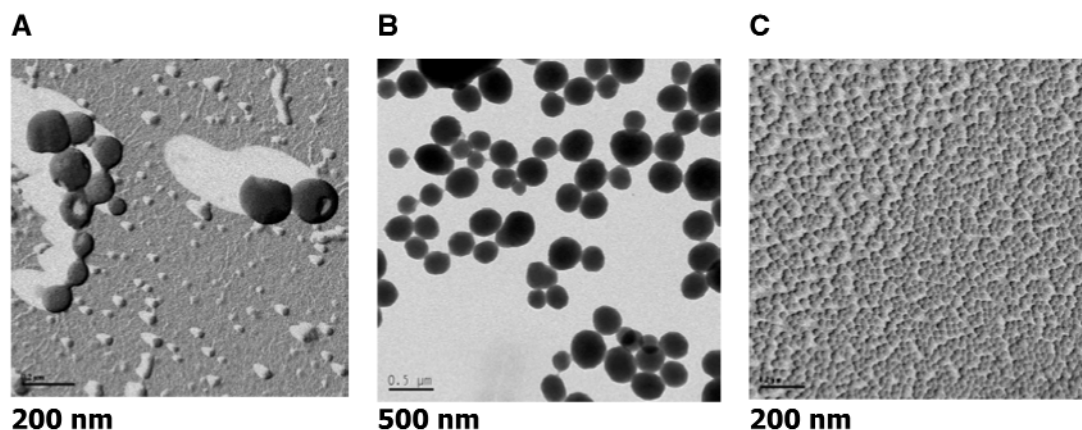
Fig. 4 TEM micrographs of the aggregates from ASAq at 0.01 wt % initial concentration in various solvents: THF (A); dioxane (B); and DMF (C). Scale bar lengths are indicated.

common solvent, the morphology changes to compound micelles, with an average diameter of 144 ± 39 nm (Fig. 4B). Compound micelles are believed to be composed of an assembly of reverse micelles [13]. On changing the common solvent to DMF, primary micelles can be seen (Fig. 4C) with an average diameter of 23 ± 3 nm. The formation of mainly spherical aggregates in DMF, can be attributed to the high dielectric constant ($\varepsilon = 38.2$) of this solvent, which decreases the PS–solvent interaction. In DMF, the repulsion among the corona chains is high, and consequently the degree of stretching of the PS chains is decreased, leading to the formation of this type of aggregates. These results are in agreement with what was observed in the LS experiments.

CONCLUSIONS

Some aspects relative to the dynamics and structure of an amphiphilic triblock copolymer of styrene and 5-(*N,N*-diethylamino)isoprene in various solvents was investigated. Toluene, THF, 1,4-dioxane, or DMF were used to prepare the solutions.

The introduction of few polar amino groups at both ends of an unpolar polystyrene chain is not sufficient to modify strongly its solution behavior, however, upon quaternization a quite different result was obtained.

It was found that the quaternized poly(aminoisoprene) copolymer (ASAq) is better solvated in DMF when compared to the nonquaternized one. This result can be extrapolated to other polar solvents, as, for example, THF and 1,4-dioxane.

The resulting aggregates from pure solvents were investigated by TEM, under direct observation of the aggregates. The morphologies were found to depend on the nature of the common solvent due to the different degree of swollenness of the PS core in each solvent (THF, 1,4-dioxane, or DMF). The stronger the interactions of PS–solvent, the bigger was the resulting aggregate. Therefore, the larger aggregate dimensions were found in THF, followed by dioxane, and then to DMF. Additionally, the favorable polymer–solvent interaction is evident in THF due to the occurrence of coexisting morphologies.

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