the surrounding solvent molecules in their treatment of SAXS data of PMLG. The aforementioned discrepancy between D NMR and SAXS values can be improved somewhat by adopting similar corrections. Teramoto et al.[32] have estimated the diameter of α-helical PBLG from the viscosity–molecular weight relation. The value of 15.6 Å thus derived is reasonably consistent with the present results.

The other conformation-dependent properties such as the average orientation of the terminal phenyl group, which is important in determining the surface chirality of the PBLG rod, or dielectric properties of the side chain can be easily elucidated. The results relating to these topics will be reported in a forthcoming paper.[33]

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Registry No. PBLG (SRU), 25038-53-3; PBLG (homopolymer), 25014-27-1; NCA, 3190-71-4.

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Orientational Order of α-Helical Poly(γ-benzyl glutamate) in the Lyotropic Liquid-Crystalline State. Comparison of Theory with Experiments

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ABSTRACT: The orientational order parameter S was determined for α-helical PBG in the lyotropic liquid-crystalline state by using the deuterium NMR technique. PBG-*N*-*d* samples having axial ratios of x = 185, 121, and 32 were compared. The measurements were extensively carried out in dimethylformamide, in which intermolecular association of the solute is known to be very weak. The value of S decreases gradually on dilution until the upper equilibrium concentration (B point) is reached where the locus of data points eventually discontinues. The concentration dependence of S was compared with those derived from theories proposed by Onsager, by Flory and Ronca, and by Khokhlov and Semenov. None of these theories can predict satisfactorily both the observed critical concentration and the order parameter at the transition. The orientational distribution functions derived from these theories are also reported.

Introduction

In the preceding paper in this issue[1] (hereafter referred to as paper 1), the deuterium NMR technique has been extensively employed in studying the oritentational ordering of PBLG molecules in the lyotropic liquid-crystalline state. The deuterium atoms incorporated in the

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amide and α-methine groups are tightly fixed on the α-helical PBLG rod and thus provide the orientational order parameter S of the backbone:

$$S = (2/3)\Delta\nu/q_h \quad (1)$$

where q_h is the component of the quadrupolar interaction tensor along the molecular axis and $\Delta\nu$ represents $\Delta\nu_N$ for the N–D or $\Delta\nu_\alpha$ for the C^α–D bond. The results of the analysis indicate that the D NMR data derived from these two sources are quite consistent. The details of the experimental procedure have been given in paper 1, where emphasis has been focused on the elucidation of side-chain conformations of PBLG molecules.

In this work, variation of the orientational order parameter S was studied as a function of concentration v_x, the volume fraction of the rodlike component with axial ratio x. Some of the results have been reported in a preliminary communication.[2] The D NMR technique is very useful in detecting the value of S in the anisotropic–isotropic biphasic equilibrium region, where a sharp single peak appears in the center of the spectrum in addition to the doublet characteristic of the anisotropic phase. As shown in Figure 5 of paper 1, the ratio $\Delta\nu_i/S$ for group i of the side chain remains nearly invariant with v_x, indicating that the lateral dimension of the molecule is unaffected by the neighbors up to a moderate concentration. In our previous studies,[1] the average separation of the terminal phenyl group from the α-helical axis, as expressed by the center-to-center distance, was found to be 8–9 Å. The lateral dimension defined in terms of the radius of gyration was estimated to be in a range 6.4–6.6 Å. These results are consistent with values of the diameter (d = 15–16 Å) conventionally used.[3,4] In the following analysis, we shall adopt a value[3] of d = 15.6 Å for the elucidation of axial ratios.

Experimental Section

Details of the sample preparation and the D NMR measurements have been described in paper 1. Two samples of PBLG-*N*-*d* were prepared. The axial ratios of the PBLG samples were estimated from the molecular weight determined by the viscosity measurements:[5] x = 121 and 32. In this work, similar measurements were also performed on a polymer sample prepared from the D isomer, i.e., PBDG-*N*-*d*. Since the observed value of S should not be affected by whether the sense of the α-helix is right- or left-handed, we shall include the data derived from PBDG of x = 185. The D NMR spectra were recorded at 76.65 MHz on a JEOL JNM-GX-500 spectrometer. The measurements were extensively carried out in dimethylformamide (DMF), in which intermolecular association of the solute is known to be very weak.[5]

Results and Discussion

Experimental Determination of the S–v_x Relation. The orientational order parameters were estimated from the observed deuterium quadrupolar splittings of the amide N–D bond. The constant q_h (=178.3 kHz) required in eq 1 has been determined in paper 1. The results obtained in DMF at 30 °C are listed in Table I. For comparison, the results in dichloromethane and 1,4-dioxane are also included. The values of $\Delta\nu_N$ for x = 121 in these solvents are the same as those reported in a previous paper.[2] Since here we adopted a revised value of q_h, instead of Chapman et al.'s value (q_h = 192.9 kHz),[6] the order parameters are higher by 8.2% than those previously reported. As shown in the table, the effect of solvent is small but definite: the values of S tend to be lower, in the order dichloromethane, 1,4-dioxane, and DMF.

The order parameter decreases gradually by dilution until the upper equilibrium concentration (B point) is reached. The locus of data points is eventually discontinued beyond this point. The data obtained in the anisotropic–isotropic biphasic equilibrium region are also included in Table I. Since the biphasic concentration gap is narrow, an accurate determination of the B point was difficult. The observed critical concentrations, v_x = 0.11 for x = 185, 0.12 for x = 121, and 0.20 for x = 32, are consistent with those determined by the microscopic observations.[4,7-10]

Table I
Observed Values of the Quadrupolar Splitting $\Delta\nu_N$ and the Orientational Order Parameters S Estimated Therefrom

solvent	x	v_x	$\Delta\nu_N$, kHz	S
DMF[a]	185	0.30	252.8	0.945
		0.25	250.4	0.936
		0.20	248.0	0.927
		0.16	242.9	0.908
		0.13	233.0	0.871
		0.11[c]	215.1	0.804
	121	0.30	248.5	0.929
		0.25	245.6	0.918
		0.20	241.6	0.903
		0.15	229.8	0.859
		0.12[c]	212.7	0.795
	32	0.35	245.6	0.918
		0.30	238.7	0.892
		0.25	233.2	0.872
		0.20[c]	211.8	0.792
dichloromethane[b]	121	0.30	258.5	0.967
		0.28	256.1	0.958
		0.21	249.2	0.932
		0.15	240.0	0.897
1,4-dioxane[a]	121	0.30	254.3	0.951
		0.25	249.3	0.932
		0.20	247.1	0.924

[a] Observed at 30 °C. [b] Observed at 21 °C. [c] The concentration corresponds to the biphasic equilibrium regime.

Theoretical Expressions for the Nematic Order Parameter. The thermodynamic properties of binary mixtures consisting of a low molecular weight solvent and a rodlike solute have been treated according to theory described by Onsager,[11] Flory,[12-14] and others.[15-17] The Onsager theory essentially depends on the derivation of the excluded volume for a pair of such rodlike molecules as a function of their relative orientation. Second virial coefficients were obtained by averaging the excluded volume over their equilibrium distribution of orientations. Higher terms in the virial expansion were ignored. Flory presented a more simplified treatment of such systems by an adaptation of the lattice model. The treatment depends on estimation of the number of configurations for solute molecule $j + 1$ when j molecules have previously been assigned to the solution.

According to Flory and Ronca,[14] the order parameter S can be expressed explicitly as

$$S = 1 - (3/2)(f_3/f_1) \quad (2)$$

where

$$f_p = \int_0^{\pi/2} \sin^p \psi \exp(-\alpha \sin \psi)\, d\psi \quad (3)$$

represents the $(p-1)$th moment of the distribution. The angle ψ designates the inclination of the molecular axis to the director of the domain, and α is the parameter related to the orientational part of the free energy by

$$\alpha = -(4/\pi)x \ln [1 - v_x(1 - \bar{y}/x)] \quad (4)$$

For a given concentration v_x, the equilibrium disorder index

$$\bar{y} = (4/\pi)x(f_2/f_1) \quad (5)$$

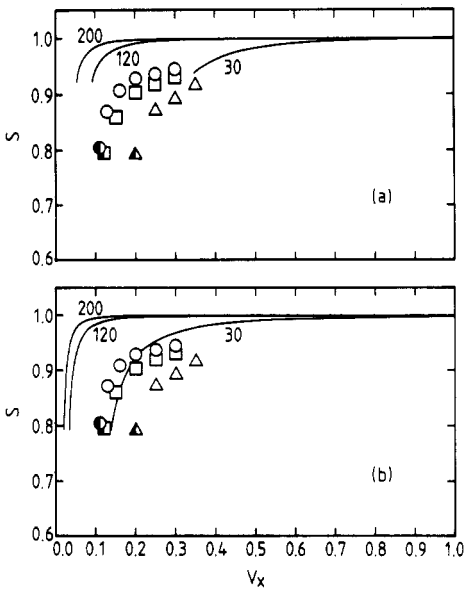

Figure 1. Variation of S with v_x. Theoretical results (solid curves) derived from (a) the Flory–Ronca and (b) the Onsager model are illustrated in separate diagrams. The axial ratios used in the calculations are indicated on each curve. The experimental values of S determined in DMF are shown by ○, □, and △, respectively, for x = 185, 121, and 32. Half-filled symbols designate the order in the biphasic equilibrium region.

can be calculated by an iterative process using eq 3–5. Some examples of the S vs v_x plot have been shown in a previous report.[2]

Lee and Meyer[17] provided a rigorous solution to the Onsager integral equation for the orientational distribution corresponding to the condition of minimum free energy. Calculations were carried out by assuming sufficiently long spherocylinders. The distribution function $f(\psi)$ has been obtained by solving the equation by numerical iterations. The orientational order parameter S follows immediately as

$$S = \int_0^{\pi/2} f(\psi)[1 - (3/2)\sin^2\psi]\, d\psi \qquad (6)$$

The authors have reported calculated values of S as a function of concentration.

Khokhlov and Semenov[15] have proposed a revision to the Onsager theory by taking account of semiflexibility characteristic of real polymers. In their treatment, the semiflexibility was interpreted as the directional fluctuation of the tangential vector along the contour of a wormlike chain. The configurational entropy arising from this source was estimated. The upper and lower equilibrium concentrations as well as the order parameter at the phase transition were expressed as a function of N ($=L/2a$), where L is the contour length and a the persistence length of the polymer chain. Odijk[16] performed more elaborate calculations and derived a set of refined coefficients for the Khokhlov–Semenov expressions. The theory has been applied to solutions comprising rodlike polymers such as PBLG, schizophyllan, DNA, and poly(hexyl isocyanate) by Odijk[16] and by Teramoto et al.[8] They found a reasonable agreement with experimental observations for the critical concentrations at the anisotropic–isotropic equilibrium. From the relation given by Odijk,[16] we may obtain an expression for the order parameter S_{crit} at the transition (B point):

$$S_{crit} = \exp\left(-\frac{0.166 + 3.51N + 22.34N^2}{1 + 45.19N^2}\right) \qquad (7)$$

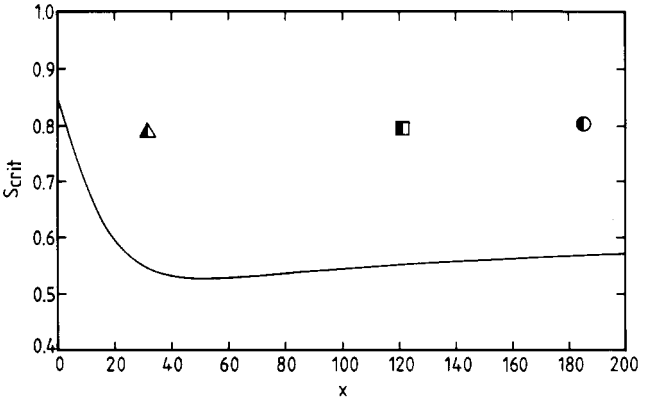

Figure 2. Variation of S_{crit} with x. The solid curve illustrates the relation derived from the Khokhlov–Semenov theory (eq 7). Half-filled symbols ◐, ◧, and ▲ represent the observed data for PBG samples having x = 185, 121, and 32, respectively.

where N can be related to the axial ratio x by $N = x/(2a/d)$. The persistence length of PBLG has been reported to be in a range from 700 to 1800 Å in the literature.[8,18] The most reliable estimate seems to be around a = 1500 Å.[8]

Comparison of Experimental Results with Theories. Values of the order parameter determined in DMF at 30 °C are compared with the theoretical S–v_x curves derived from the Flory–Ronca (Figure 1a) and Onsager theory (Figure 1b). The experimental results obtained in the anisotropic phase are indicated by the open circles, squares, and triangles for samples with x = 185, 121, and 32, respectively. Half-filled symbols are used for the data obtained in the anisotropic–isotropic biphasic equilibrium region. It should be noted in the figure that the transitions were observed at $S_{crit} \simeq 0.8$ for all samples. Calculations were carried out for round numbers of x as indicated on each theoretical curve. The order parameter decreases gradually by dilution and is eventually discontinued as the upper equilibrium concentration (B point) is reached. As shown by the curves for x = 200, 120, and 30, the agreement with experiment is only qualitative for both theories.

The Flory–Ronca theory predicts $S_{crit} \simeq 0.92$, being inconsistent with experimental observations (Figure 1a). The discrepancy between the calculated and observed critical concentrations tends to be larger as x becomes smaller. Various attempts have been reported to improve the agreement between the theory and experiment for the critical concentrations. While Teramoto et al.[7] introduced an orientation-dependent interaction energy term, Ballauff[19] examined the effect of flexible side chains, resulting in a revised expression for the polymer concentration. The S–v_x plots derived from these revised theories have been presented in a previous paper.[2] The revisions adopted above do not yield improvement in the agreement between calculations and experimental observations. The differences are also noted in the asymptotic behavior of the S–v_x plot. The calculated curves increase more rapidly than those observed.

As shown in Figure 1b, Lee et al.'s solution to the Onsager formula yields reasonable values of S_{crit} (0.8), but the corresponding critical concentrations are much too low. The asymptotic behaviors again are not in accord with those observed in this figure. As pointed out by Odijk[16] and by Teramoto et al.,[8] the agreement in the critical concentration can be improved by adopting the Khokhlov-Semenov theory,[15] which takes account of the semiflexibility of the polymeric chain. The relation given in eq 7 has been derived by using Onsager's trial function for the orientational distribution. According to this expres-

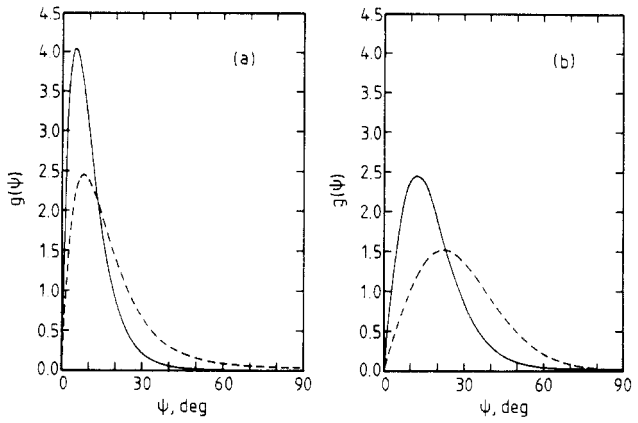

Figure 3. Normalized orientational distribution functions $g(\psi)$ as defined in eq 8: (a) the Flory–Ronca theory with parameters corresponding to $S_{crit} = 0.924$ (solid curve) and 0.80 (broken curve); (b) the Onsager theory for $S_{crit} = 0.793$ (solid curve) and the Khokhlov–Semenov theory for $S_{crit} = 0.610$ at lim $x \rightarrow \infty$ (broken curve).

sion, the value of S_{crit} reaches that of Onsager at the limit $x/a \rightarrow 0$. In Figure 2, the value of S_{crit} calculated by assuming $a = 1500$ Å for the α-helical PBG is plotted as a function of x. The curve passes through a minimum (0.53) around $x = 50$ and then increases gradually with x toward its asymptotic value (0.61). The experimental data are indicated by half-filled symbols in the same figure. The disparity between the calculated and observed results is significant.

As shown in Figure 1a, the values of S_{crit} calculated by the Flory–Ronca theory remain nearly invariant over a wide range of x. According to the relation given in eq 2–5, $S_{crit} \simeq 0.92$ requires $\alpha = 11.8$, and $\bar{y}/x = \langle \sin \psi \rangle = 0.23$. The normalized orientational distribution function

$$g(\psi) = (1/2\pi)f(\psi)/\int_0^{\pi/2} f(\psi)\, d\psi \qquad (8)$$

is shown by the solid curve in Figure 3a. In the Flory–Ronca theory, the effect of the distribution may be examined simply by treating α as an adjustable parameter. The observed value $S_{crit} \simeq 0.8$ can be reproduced by a somewhat lower value of α (7.2), which in turn, from eq 5, yields $\bar{y}/x = 0.38$. When this value of α is used, the distribution is broadened, as indicated by the broken curve in the same figure. Such a decrease in α, and an accompanied increase in $\bar{y}/x$, lowers the critical concentration at the B point, the agreement with observations being improved considerably in the lower range of x. These tentative calculations indicate that an experimental elucidation of the orientational distribution should provide a critical test of the theory.

The distribution function $f(\psi)$ for the Onsager theory has been reported by Lee et al.[17] The solid curve given in Figure 3b was derived on the basis of their calculations. This distribution yields $S = 0.793$. Khokhlov and Semenov[15] have formulated the distribution by using Onsager's trial function. At the Onsager limit ($x/a \rightarrow 0$), the shape of the distribution is similar to that shown by the solid curve in Figure 3b. Odijk[16] has estimated the variational parameter of the trial function at the limit $x/a \rightarrow \infty$. The corresponding distribution is indicated by the broken curve. As a result of the semiflexibility of the chain, the distribution is broadened and shifted toward higher angles, the corresponding S value being 0.610.

Finally, comparison presented in this section may be summarized as follows: (1) Values of S_{crit} estimated from the Flory–Ronca theory are about 0.92, being somewhat higher than those (0.8) observed. Tentative calculations indicate that such an enhancement in S may arise in part from an overestimate of the orientational free energy in the theory. (2) The Onsager theory yields reasonable values of S_{crit}. The theory, however, disagrees with experiment about the critical concentration. (3) In the Khokhlov–Semenov theory, the semiflexibility of polymeric chains is considered in the orientational entropy term within the framework of the Onsager scheme. The Khokhlov–Semenov theory significantly underestimates the degree of orientational ordering.

Conclusion

In this work, the order parameters of PBLG-*N*-*d* and PBDG-*N*-*d* in the lyotropic liquid-crystalline state have been studied by the D NMR technique. While these samples exhibit a cholesteric texture under the polarizing microscope, an equimolar mixture of PBLG and PBDG is known to form a liquid crystal with the nematic texture. The D NMR analysis was also performed for a mixture of PBLG-*N*-*d* and PBDG-*N*-*d* having an equivalent molecular weight. The quadrupolar splittings $\Delta\nu$ were found to be nearly identical with those observed for the parent PBLG, indicating that the orientational ordering of molecules is unaffected by the mixing of two optical antipodes.

Values of the order parameter determined in this work are somewhat higher than those (0.75) reported by Murthy et al.[20] from the broadening of the X-ray diffraction streaks of PBLG in dioxane. Sartirana et al.[21] estimated the order parameter of PBLG samples with $x = 92$ and 53 in the same solvent by using IR. They reported values of S varying from 0.84 to 1.0 by adopting a set of angles 23° and 69.5°, respectively, for the transition moment of the amide A and amide II bond.[22] The rate of increase of S with v_x was found to be much higher than those observed by the D NMR method.

As stated in the text, PBG is stereochemically very suited for the D NMR analysis. It may be controversial, however, whether or not PBG is also adequate for a critical test of the liquid-crystal theories. Attempts are being made to elucidate the orientational characteristics of some other polymer liquid crystals in our laboratory.

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Registry No. PBLG (SRU), 25038-53-3; PBLG (homopolymer), 25014-27-1.

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The Effect of Substituents on the Conformational Features of Polycarbonates

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ABSTRACT: A comparison of the conformational freedom of rotation of the contiguous phenyl groups in polycarbonates, with various substituents at the C_α atom, is presented. Conformational maps were calculated for the following substituents: (i) CH_3,CH_3; (ii) H,H; (iii) H,CH_3; (iv) H,C_6H_5; (v) CH_3,C_6H_5; (vi) C_6H_5,C_6H_5; (vii) cyclohexyl; and (viii) CCl_2. Synchronous rotation of the phenyls with a low-energy barrier is possible for (i), (iv), (v), and (vii). Although the extent of freedom of rotation depends on the nature of the substituent, there is very little difference in the characteristic ratio of the unperturbed end-to-end distance for these polycarbonates, and the temperature coefficient of the characteristic ratio is extremely small. In spite of the limited conformational freedom, it is shown that the steric symmetry and the geometric asymmetry of the chain segments enable the treatment of these chains in the framework of the freely rotating chain.

Introduction

Since the theoretical work of Williams and Flory[1] on the average chain dimension of bisphenol A polycarbonate (BPAPC), several papers have been published on the conformational aspects of this polymer. Some of these efforts[2-7] were aimed at calculating the average properties and crystalline conformational features. On the other hand, the molecular motion in polycarbonate and its interpretation in terms of the π flips of the phenyl groups and the rotation of the carbonate group have been the focus of several studies[8] using NMR and dynamical mechanical spectroscopy (DMS). To this end, the purpose of a number of conformational calculations[9-13] was to estimate the barrier to the rotations of the phenyls, in order to rationalize and interpret the experimental observations. A theoretical model[14] for the local motion in BPAPC and computer simulation[15] of the ring flip have also been described.

Yee and Smith[16] studied several polycarbonates by DMS, to estimate the relative influence of the substituents at the C_α atom, at the carbonate segment as well as on the phenyl. An in-depth discussion on the phenyl motion and a comparison of the NMR and DMS results have been presented. Jones et al.,[17] from NMR studies, concluded that the phenyl motion in chloral polycarbonate is more restricted, compared to the motion in BPAPC.

In a recent paper,[6] we reported the energy calculations on BPAPC in terms of the rotations ϕ and ψ (see Figure 1) of contiguous phenyl groups. The shapes of the segments, which would result from the perpetuation of a certain (ϕ,ψ) value, were analyzed in terms of the calculation of helix parameters. The results showed that both flat-helical and extended helical shapes are of equal energy in the accessible domains of the conformational map. The small value of the characteristic ratio $\langle r^2\rangle_0/nl^2$ and its temperature coefficient were rationalized as due to the equal energy of the above conformers. Cyclic polycarbonates were also found to be stereochemically possible. In addition, the conformational map showed features which could account for the phenyl motion which has been detected by NMR and DMS studies.

In this paper, a comparison of the conformational features of polycarbonates with different substituents at the C_α atom is presented. The analysis is restricted to the relative conformation of the contiguous phenyl groups. The interaction between these substituents and the carbonate group is expected to be negligible due to the large distance of separation between them. Conformational maps were calculated for the cases of the following substituents: (i) CH_3,CH_3 (2,2-diphenylpropane); (ii) H,H (diphenylmethane); (iii) H,CH_3 (1,1-diphenylethane); (iv) H,C_6H_5 (triphenylmethane); (v) CH_3,C_6H_5 (1,1,1-triphenylethane); (vi) C_6H_5,C_6H_5 (tetraphenylethane); (vii) cyclohexyl (1,1-diphenylcyclohexane); and (viii) CCl_2 (1,1-dichloro-2,2-diphenylethylene). The relative extent of freedom of rotation of the contiguous phenyls and its bearing on the average chain dimension are examined. Analysis of the chain shapes in terms of helix parameters is also given. In addition, the concept of describing the polycarbonates as freely rotating chains is discussed.

Details of Calculations

The bond lengths and bond angles for the skeletal geometry were chosen to be the same as before[6] and were derived from the crystal structure of diphenylcarbonate.[3] A value of 109.5° was assigned for the bond angle C_4–C_α–C_4'. Bond lengths of 1.36 and 1.1 Å were used for the C–C and C–H bonds in the case of aromatic substi-

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