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Synthesis and Properties of Block Polymers. 5. Phase Separation Thermodynamics for Star-Branched Systems

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ABSTRACT: The thermodynamics of phase separation for star-branched block polymers were analyzed and the results compared to those of the unlinked "parent" diblock arms. This topic was approached by considering systems of diblock molecules either in a phase-separated domain or in a completely mixed system. The free energy was calculated in each of these cases when f (the degree of branching) of the free ends of the B blocks are joined to form the star-branched material. Calculations were performed considering the nonuniformity of the distribution of chain ends for the phase-separated diblocks in the lamellar domain system. For star-shaped block polymers containing f diblock arms, the difference in free energy of phase separation between stars and diblocks can be given as $\Delta G = N_d kT[(f - 1)/f]$ (ln V_B - 0.14), where N_d is the number of diblocks and V_B is the volume fraction of the lamellar B domains.

The termination-free system of homogeneous polymerization involving alkyllithium initiators is known to lead to the preparation of linear[2,3] and star-branched block polymers.[4-8] It has been observed[6] that the tensile strengths (both the engineering stress and true stress) of these star-branched block polymers were greater than those of linear block polymers having identical segment molecular weights and compositions. Furthermore, morphological studies[6,9] via electron microscopy on star-branched block polymers containing relatively low molecular weight ($<10^4$) polystyrene segments have shown well-defined polystyrene domains whereas the linear di- and triblock counterparts show some evidence of partial phase blending.[9,10] Hence, it was deemed of interest to examine the thermodynamics of block polymer phase separation with reference to the star-branched architecture where the diblock arms radiate from a central junction point. This junction point can be, for example, poly(divinylbenzene) microgel[6,11] or the residue from a polyfunctional chlorosilane.[5,7,8,12,13] Various aspects of phase separation thermodynamics for linear di- and triblock polymers have been examined.[14-44] In this paper we consider some of the effects of the star-branched architecture on phase separation relative to that of the linear block polymers of equivalent compositions and segment molecular weights.

Discussion

The thermodynamics of block polymer phase separation involve a number of entropy and enthalpy changes. Krause[17-19,27,40,41] has described block polymer systems in macroscopic terms whereas Meier[14,15,20,33,44] and Helfand[29,34-39,42,43] give more detailed descriptions of the thermodynamic and morphological characteristics associated with the domain formation. The combined theories of Meier and Helfand yield results which are in general agreement with the experimental parameters concerning the morphological features of linear di- and trisegment block polymers.

It is of interest to determine what the influence of star-type branching is on the likelihood of phase separation. It is possible with the star-shaped block polymer system to produce an excellent first approximation for the difference between the free energy of phase separation of linear diblocks and that of star-shaped materials made up of f of these diblock arms.

Krause's macroscopic theory is a convenient analytical description of block polymer systems even though it omits terms involving domain microstructure. The possible placements of the junction point of the A and B blocks is described by a single term that does not change when the microscopic variables of the system change, e.g., the thickness of the interfacial region between domains.

Our calculations of the thermodynamics of phase separation for star block polymers starts with an approach similar to that of Krause. We do not, however, attempt to calculate the free energy change upon phase separation for star systems. Rather we find the difference in the free energy between that of star materials and the diblock arms from which they are made.

We can consider a system of AB segment linear block polymers. Star-branched species can be formed by linking together the free ends of the B blocks, f at a time. In the completely phase-blended system there is an entropy penalty paid by restricting the placements of the chains as a result of the common junction point at the star center. For the case of the phase-separated system, there is a similar change in the placement entropy. The approxi-

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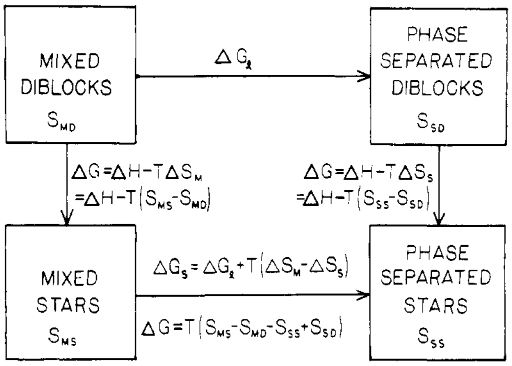

Figure 1. Energy diagram for the mixed and phase-separated block polymer systems.

mation made in our presentation is that the nature of the domains remains constant; i.e., the domain size, type, and interfacial zone remain the same. This seems reasonable as a first approximation since the random flight nature of the chains controls domain size. The thermodynamic effects of restricting the placement of the free ends of the B blocks should be much greater than the small changes in the domains.

Figure 1 is a free energy diagram that shows the four states of interest. They are for diblocks, and for stars made from f of those diblocks, each in the mixed state and the phase-separated state. There is a free energy change in going from one state to another. In going from a mixed diblock system to a phase-separated system, the change is ΔG_l, containing enthalpy and entropy terms, the details of which are not of importance to the calculations.

In going from a diblock to a star in each of the two morphologies, the enthalpy change is a consequence of the bond energy released in the linking process and is the same for each morphology. The entropy change is different in the two cases and can be calculated from the absolute placement entropy in the four states. These entropies can be calculated statistically (Appendix A). Other changes in entropy and enthalpy are zero in this first approximation since the nature of the domains remains constant after the linking of diblocks is accomplished.

Since the energy must be the same regardless of the path taken, the free energy change of phase separation for stars, ΔG_s, is equal to the sum of the other three steps:

$$\Delta G_s = \Delta G_l + T(S_{ms} - S_{md} - S_{ss} + S_{sd}) \qquad (1)$$

The star system can then be compared to the diblock system by finding the difference between ΔG_s and ΔG_l

$$\Delta G = \Delta G_s - \Delta G_l = T(S_{ms} - S_{md} - S_{ss} + S_{sd}) \qquad (1a)$$

This is useful in checking the effect of star branching itself. As defined by Figure 1, if ΔG is negative, stars will phase separate more readily than the diblock arms they are made from. If ΔG is positive, the opposite is true.

We can then consider a system where the probability of finding a chain end is constant throughout the domain it inhabits. The total number of placement sites in the mixed system is given by $N_d(n_A + n_B)$, where N_d represents the total number of diblock molecules, n_A the number of A units per chain, and n_B the number of B units per chain. The volume of an A site is assumed to be equal to that of a B site. In the phase-separated system, the total number of placement sites is $N_d n_B$ since the B blocks now inhabit only B domains.

In Appendix A the entropies for the mixed and separated states for the linear diblock and star-branched block polymers are calculated. These calculations involve only the placement entropy of the molecules. The first unit of a chain (either the free B unit or the link point) is placed in any available site while the remaining units of that chain occupy sites in its immediate vicinity. The free energy change favoring phase separation for the star-branched system can then be given by

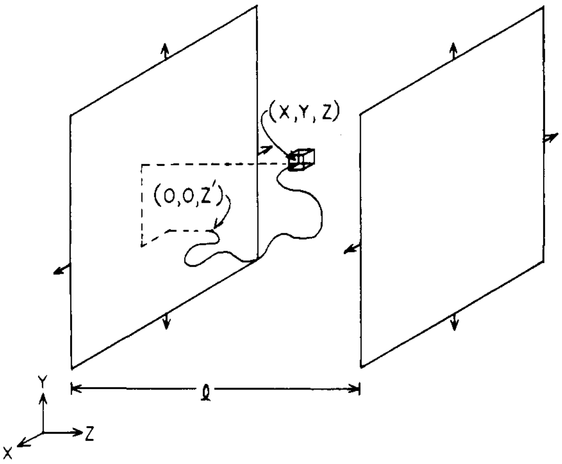

Figure 2. Polymer chain coordinate system.

$$\Delta G = N_d kT[(f - 1)/f] \ln V_B \qquad (2)$$

where f is the number of star diblock arms and V_B is the volume fraction of B domains.

Hence, there is a greater free energy push toward phase separation for stars than for its diblock arms. The entropy penalty paid in the linking process for phase-separated diblocks is less since the chain ends started with less placement entropy. When discrete B domains are present, the chain ends are in closer proximity to each other than in the mixed system. It is this proximity that causes the star-branched polymers to phase separate more readily than the parent diblocks.

The preceding analysis is based on a macroscopic analysis of a block polymer system similar to that developed by Krause.[17-19,27] Two assumptions have been made in the foregoing treatment: (1) The changes in configurational entropy of the chains upon linking is the same in each system; i.e., the domain size and type are the same for both the parent diblock and the star-branched system. (2) The concentration of the B segment chain ends is constant throughout the B domains. In regard to point 2, the junction of the A and B blocks must be at the surface of the domain with the B chain extending inward. Thus, the region with the highest concentration of chain ends would logically be the center of the B domain rather than, for example, the interface of the A and B domains.

The B-chain end distribution within the B domains can be calculated for simple systems. In the lamellar domain system the chain end distribution can be calculated by use of the diffusion equation. The probability of a chain originating at a point $(0, 0, z')$ and ending at a point with an x coordinate between x and $x + dx$, a y coordinate between y and $y + dy$, and a z coordinate between z and $z + dz$ with the restriction that no unit in the chain has a z coordinate of 0 or l is $P(x, y, z/0, 0, z'; l)\,dx\,dy\,dz$. Figure 2 shows this coordinate system and the chain restrictions. If n is the number of links and b the link length, the probability can be written as[45]

$$P(x, y, z/0, 0, z'; l) = \frac{3}{\pi n b^2 l} \exp\left[-\frac{3(x^2 + y^2)}{2nb^2}\right] \sum_{p=1}^{\infty} \exp\left(-\frac{p^2\pi^2 n b^2}{6l^2}\right) \times \sin\left(\frac{p\pi z}{l}\right) \sin\left(\frac{p\pi z'}{l}\right) \qquad (3)$$

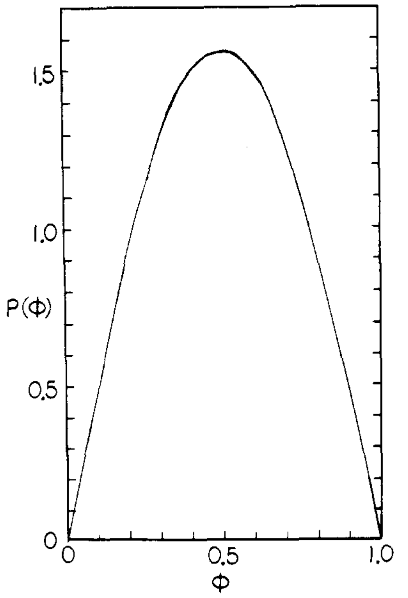

Figure 3. Plot of the probability density function.

Meier[20] has shown that the optimum ratio of lamella thickness, l, to end-to-end distance of the chain, $n^{1/2}b$, is $l/n^{1/2}b = 1.4$. Under these conditions, the segment density is nearly constant throughout the domain. If constraints were to be placed on the system requiring a constant segment density, the chain end distribution would be expected to change only slightly.

This function can be integrated over all values of x and y to give a probability density function for a chain starting at z' and ending at z while remaining inside the lamella. A limit can be taken as $z' \rightarrow 0$; i.e., the limit as the starting point approaches the domain interface. The probability density function thus generated considers all possible chain configurations. A different probability distribution function can be calculated which considers only the subset of chains that reside entirely within the lamella. Figure 3 shows the probability density function as calculated in Appendix B.

Figure 3 shows that there is a much higher concentration of chain ends near the domain center than near the interface. This means that there is less of an entropy penalty in joining these ends than in a system where the B-chain ends are equally distributed throughout B domains.

The entropies of the four states shown in Figure 1 are recalculated by this probability distribution function (Appendix C). Thus, the free energy gain for the star-branched system over that of the diblock system is

$$\Delta G = N_d kT\left(\frac{f-1}{f}\right)\left[\ln V_B - \int_0^1 P(\phi)\ln P(\phi)\, d\phi\right] \quad (4)$$

The integral was evaluated numerically and is equal to 0.14 for the lamellar domain system. Hence

$$\Delta G = N_d kT\left(\frac{f-1}{f}\right)(\ln V_B - 0.14) \quad (5)$$

The driving force in phase separation is the incompatibility existing between the A and B blocks. Balancing this is the fact that phase separation greatly decreases the entropy of the system. If the entropy loss can be lowered, there then is a greater force for domain formation; a lowering of the loss in entropy would be the expected outcome of the act of joining diblock chains into the star-shaped architecture.

This additional refinement leading to the factor of −0.14 applies only to the lamellar domain system. There is no easy analytical solution for the interesting cases where the star junction points are in the continuous matrix between rods or spheres. However, a negative term will result in any system where the chain end density is nonuniform.

The results of a totally macroscopic approach as in eq 2 can be viewed as a molecular weight effect since the linking process increases the molecular weight. However, a consideration of the fluctuations in chain end densities, as in eq 5, shows the results are based on more subtle entropic effects.

The apparent gain in free energy for the star-branched architecture has several implications. First, for systems near or at the critical point, star-branched materials would be expected to phase separate while their diblock or triblock counterparts would not. The critical interaction parameter (χ_{AB}) between the A and B blocks is lower for the star-branched system than in the diblock system. Thus, block types that will not phase separate as di- or triblocks may phase separate in the star-branched system.

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Appendix A

$$\Omega_{md} = \frac{1}{N_d!}\prod_{i=1}^{N_d}(N_d - i + 1)(n_A + n_B) = (n_A + n_B)^{N_d}$$

$$\Omega_{sd} = \frac{1}{N_d!}\prod_{i=1}^{N_d}(N_d - i + 1)n_B = n_B^{N_d}$$

$$\Omega_{ms} = \frac{1}{N_s!}\prod_{i=1}^{N_s}(N_s - i + 1)f(n_A + n_B) = [f(n_A + n_B)]^{N_s}$$

$$\Omega_{ss} = \frac{1}{N_s!}\prod_{i=1}^{N_s}(N_s - i + 1)fn_B = (fn_B)^{N_s}$$

Ω denotes the number of distinctive placement possibilities available to a chain end while n_A and n_B are the number of A and B units per diblock (or units per arm). f is the number of arms and N_d is the number of diblock molecules. $N_s = N_d/f$ is the number of star molecules.

$$S_{md}/k = N_d \ln (n_A + n_B)$$

$$S_{sd}/k = N_d \ln n_B$$

$$S_{ms}/k = (N_d/f) \ln [f(n_A + n_B)]$$

$$S_{ss}/k = (N_d/f) \ln (fn_B)$$

$$\Delta G = T(\Delta S_m - \Delta S_s) = T(S_{ms} - S_{md} - S_{ss} + S_{sd})$$

$$\Delta G = N_d kT\left(\frac{f-1}{f}\right)\ln\left(\frac{n_B}{n_A + n_B}\right)$$

But $n_B/(n_A + n_B) = V_B$, the volume fraction of B units, since the volume of an A unit is assumed equal to the volume of a B unit.

$$\Delta G = N_d kT\left(\frac{f-1}{f}\right)\ln V_B$$

Appendix B

Assume the lamellar thickness $l = 1.4n^{1/2}b$; hence eq 3 becomes

$$P(x, y, z/0, 0, z'; l) = \left[\frac{3(1.4)}{\pi l^3}\right]^2 \exp\left[-\frac{3(1.4)^2(x^2+y^2)}{2l^2}\right] \times \sum_{p=1}^{\infty} \exp\left(-\frac{p^2\pi^2}{6(1.4)^2}\right) \sin\left(\frac{p\pi z}{l}\right) \sin\left(\frac{p\pi z'}{l}\right)$$

Integration over all x and y yields $p(z, z')$, i.e., the probability that a chain starting at z' and ending at z stays in a lamella of thickness l

$$P(z, z') = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} P(x, y, z/0, 0, z'; l)\ \mathrm{d}y\ \mathrm{d}x$$

$$P(z, z') = \frac{2}{l}\sum_{p=1}^{\infty} \exp\left(-\frac{p^2\pi^2}{6(1.4)^2}\right) \sin\left(\frac{p\pi z}{l}\right) \sin\left(\frac{p\pi z'}{l}\right)$$

As $z' \rightarrow 0$, $\sin(p\pi z'/l) \rightarrow p\pi z'/l$ so that in this limit

$$P(z, z') = \frac{2\pi z'}{l^2}\sum_{p=1}^{\infty} p \exp\left(-\frac{p^2\pi^2}{6(1.4)^2}\right) \sin\left(\frac{p\pi z}{l}\right)$$

This is the probability that a chain starting at z', which is near the AB interface at $z = 0$, ends at z and no unit in the chain is at a z coordinate of 0 or l.

Normalize considering only chains that remain within the lamella. Let $P'(z, z')$ be the probability that an A chain starts at z' and ends at z. Considering only these chains that remain within the domain, $K(z')$ is the constant of proportionality

$$K(z')P(z, z') = P'(z, z')$$

Now

$$\int_0^l P'(z, z')\ \mathrm{d}z = 1$$

so

$$K(z')\int_0^l P(z, z') = 1$$

Therefore

$$K(z') = \left[\frac{4z'}{l}\sum_{p=\mathrm{odd}}^{\infty} \exp\left(-\frac{p^2\pi^2}{6(1.4)^2}\right)\right]^{-1}$$

so

$$P'(z, z') = \left(\frac{\pi}{2l}\right)\sum_{p=1}^{\infty} p \exp\left(-\frac{p^2\pi^2}{6(1.4)^2}\right) \sin\left(\frac{p\pi z}{l}\right) \times \sum_{p=\mathrm{odd}}^{\infty} \exp\left(-\frac{p^2\pi^2}{6(1.4)^2}\right)$$

which is now independent of z'. Using fractional distance $\phi = z/l$

$$P'(\phi) = 3.6314\sum_{p=1}^{\infty} p \exp\left(-\frac{p^2\pi^2}{6(1.4)^2}\right) \sin(p\pi\phi)$$

Hence, for chains that start at both lamellar surfaces

$$P(\phi) = \tfrac{1}{2}[P'\phi + P'(1-\phi)] = 1.8157 \times \sum_{p=1}^{\infty} p \exp\left(-\frac{p^2\pi^2}{6(1.4)^2}\right)[\sin(p\pi\phi) + \sin(p\pi(1-\phi))]$$

Appendix C

Assume that the ith grouping of chain ends has N_i chain ends in g_i sites

$$\Omega_i = \frac{1}{N_i!}\prod_{j=1}^{N_i}(N_i - j + 1)\frac{g_i}{N_i} = \left(\frac{g_i}{N_i}\right)^{N_i}$$

$$\Omega_{\mathrm{total}} = \prod^{\mathrm{all}\ i}\Omega_i$$

$$S/k = \ln \Omega_{\mathrm{total}} = \sum^{\mathrm{all}\ i} N_i \ln\left(\frac{g_i}{N_i}\right)$$

The number of sites is equal to the volume occupied by the chain ends divided by the volume of a site, V_s or $g_i = V_i/V_s$ so

$$S/k = \sum^{\mathrm{all}\ i} N_i \ln\left(\frac{V_i}{N_i V_s}\right)$$

Now as the i units become of differential size

$$S/k = -\int_0^{N_\mathrm{T}} \ln\left(\frac{\mathrm{d}N}{\mathrm{d}V}V_s\right)\mathrm{d}N$$

In the mixed system $\mathrm{d}N/\mathrm{d}V = N_\mathrm{T}/V_\mathrm{T}$, where N_T and V_T are the total number of chains and total volume

$$S/k = -N_\mathrm{T} \ln\left(\frac{N_\mathrm{T}V_s}{V_\mathrm{T}}\right)$$

so

$$S_{\mathrm{md}}/k = -N_\mathrm{d} \ln\left(\frac{N_\mathrm{d}V_s}{V_\mathrm{T}}\right)$$

$$S_{\mathrm{ms}}/k = -(N_\mathrm{d}/f) \ln\left(\frac{N_\mathrm{d}V_s}{V_\mathrm{T}f}\right)$$

In the phase-separated system $\mathrm{d}N/\mathrm{d}V = N_\mathrm{T}P(\phi)/V_\mathrm{T}V_\mathrm{B}$. $P(\phi)$ is the probability function found in Appendix B. $V_\mathrm{T}V_\mathrm{B}$ is the total volume of B domains.

$$S/k = -\int_0^{N_\mathrm{T}} \ln\left(\frac{N_\mathrm{T}P(\phi)V_s}{V_\mathrm{T}V_\mathrm{B}}\right)\mathrm{d}\phi$$

$$S/k = -\int_0^1 \frac{\mathrm{d}N}{\mathrm{d}\phi} \ln\left(\frac{N_\mathrm{T}P(\phi)V_s}{V_\mathrm{T}V_\mathrm{B}}\right)\mathrm{d}\phi$$

$$\mathrm{d}N = N_\mathrm{T}P(\phi)\ \mathrm{d}\phi$$

so

$$S/k = -\int_0^1 N_\mathrm{T}P(\phi) \ln\left(\frac{N_\mathrm{T}P(\phi)V_s}{V_\mathrm{T}V_\mathrm{B}}\right)\mathrm{d}\phi$$

$$S_{\mathrm{sd}}/k = -N_\mathrm{d}\left[\int_0^1 P(\phi) \ln P(\phi)\ \mathrm{d}\phi\right] + \ln\left(\frac{N_\mathrm{d}V_s}{V_\mathrm{T}V_\mathrm{B}}\right)$$

$$S_{\mathrm{ss}}/k = -\frac{N_\mathrm{d}}{f}\left[\int_0^1 P(\phi) \ln P(\phi)\ \mathrm{d}\phi\right] + \ln\left(\frac{N_\mathrm{d}V_s}{V_\mathrm{T}V_\mathrm{B}}\right)f$$

$$\Delta G = T(S_{\mathrm{ms}} - S_{\mathrm{md}} - S_{\mathrm{ss}} + S_{\mathrm{sd}})$$

$$\Delta G = N_\mathrm{d}kT\left(\frac{f-1}{f}\right)\left(\ln V_\mathrm{B} - \int_0^1 P(\phi) \ln P(\phi)\ \mathrm{d}\phi\right)$$

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but since

$$\int_0^1 P(\phi) \ln P(\phi)\, \mathrm{d}\phi = 0.14$$

so

$$\Delta G = N_{\mathrm{d}}kT\left(\frac{f-1}{f}\right)(\ln V_{\mathrm{B}} - 0.14)$$

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Synthesis and Polymerization of Methyl α-Fluoroacrylate

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ABSTRACT: Methyl α-fluoroacrylate (MFA) has been synthesized and both homopolymerized and copolymerized by bulk, solution, and emulsion methods. The reaction of methyl α-chloroacetate with KF gave methyl α-fluoroacetate, which was treated successively with dimethyl oxalate, NaH, paraformaldehyde, and sodium methoxide to yield MFA. The kinetics of MFA homopolymerization and copolymerization has been investigated in acetonitrile, using azobis(isobutyronitrile) (AIBN) as an initiator. The rate of polymerization (R_{p}) could be expressed by $R_{\mathrm{p}} = k[\mathrm{AIBN}]^{0.6}[\mathrm{MFA}]^{1.1}$. The overall activation energy was calculated to be 73.6 kJ/mol. Thermogravimetric analysis of poly(methyl α-fluoroacrylate) showed a 10% weight loss at 350 °C in N_2. The glass transition temperature (T_{g}) of poly(methyl α-fluoroacrylate) was observed to be 128 °C by thermomechanical analysis. The relative reactivity ratios of MFA (M_1) copolymerizations with styrene ($r_1 = 0.15$, $r_2 = 0.62$) and methyl methacrylate ($r_1 = 0.36$, $r_2 = 1.17$) were obtained. Applying the Q, e scheme (in styrene copolymerizations) led to $Q = 0.47$ and $e = 0.73$ for MFA. This value of Q is less than the values of Q for the chlorine and bromine analogues.

The necessity for manufacturing very fine patterns of submicron size on integrated circuit devices has increased.[1] Electron-beam[2,3] and X-ray[4,5] lithography offer higher resolution than the conventional UV method. Such fabrications require resists which are sensitive to an electron beam or X-rays. Resist polymers which degrade by chain scission to give lower molecular weight materials are called positive resists. Those that cross-link upon irradiation are

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