A model for the onset of entanglements of transient hydrogen-bonded intermolecular structures in oligomeric poly(propylene glycol)

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This paper presents a model for the hypothesis that entanglement effects between transient intermolecular structures in poly(propylene glycol) (PPG) can lead to an additional (to segment modes) low-frequency relaxation above a quasi-critical molecular weight far below the critical molecular weight of the bulk. The model describes the formation of end-to-end hydrogen-bonded intermolecular structures and explains the fact that tube-like topological restrictions occur when the quasi-critical molecular weight of the primary chains M' is reached. By comparison with the experimental value $M' \approx 1300\,\mathrm{g\,mol^{-1}}$ for PPG at room temperature, it is concluded, from a kinetic point of view, that the timescale for the relevant hydrogen-bond kinetics is comparable with the timescale of chain-end mobility on the spatial scale of the molecular radius for the primary oligomer chain in the crossover regime.

(Keywords: entanglements; hydrogen-bond kinetics; poly(propylene glycol))

INTRODUCTION

Recently, some experimental evidence of entanglement effects between transient intermolecular structures formed by hydrogen bonds has been offered[1,2].

Ultrasonic and nuclear magnetic resonance (n.m.r.) measurements in poly(propylene glycol) (PPG) melts with molecular weights M ranging from 520 to $3200\,\mathrm{g\,mol^{-1}}$ showed an additional (to segment modes) low-frequency relaxation in samples with $M > M' \approx 1300\,\mathrm{g\,mol^{-1}}$. Measurements of the viscosity showed a crossover in the power dependence $\eta \sim M^p$ from $p \approx 0.6$ for $M < M'$ to $p \approx 1.4$ for $M > M'$. The effect vanishes by converting the OH end-groups into trimethylsilyl groups.

Although there are different explanations for different parts of the experimental findings[2], we think that, from a more general point of view, the various experimental facts as a whole can be put together in the best way by an entanglement hypothesis. The basic assumption of our model is the formation of transient end-to-end hydrogen bonds between PPG chains having molecular weights M below the critical molecular weight[3] of the bulk, $M_c \approx 7000\,\mathrm{g\,mol^{-1}}$, and therefore the formation of effective chains, $M_{\mathrm{eff}} > M_c^{(p)}$, above a quasi-critical molecular weight M' of the primary PPG chains. $M_c^{(p)}$ denotes the critical molecular weight of the polydisperse melt and will be discussed later.

The plan of this paper is as follows. First, we will briefly discuss the statistical treatment of forming a polydisperse melt (characterized by $\bar{M}_n$) of linear chains built up from a homodisperse melt of primary chains of molecular weight M. Secondly, we will explain that topological restrictions, caused by the uncrossability of the chain contours, suddenly occur when the molecular weight M of the primary chains exceeds a quasi-critical value $M = M'$. The results of the calculations will be compared with experimental values and discussed from a kinetic point of view.

THE FORMATION OF LONG CHAINS

We will use two kinetic concepts: the kinetics of hydrogen bonds, which is related to a small distance ε between OH end-groups (e.g. $\varepsilon \leqslant 0.5\,\mathrm{nm}$), and the polymer kinetics, covering all other mobilities of chains or chain segments. That is, we will distinguish between 'chemistry' and 'physics' in this way.

The mean lifetime of the 'supermolecules' formed is assumed to be long enough to form entanglements which may be discussed in the framework of the tube-like reptation model[4]. As a first approximation, we can consider the reactivity of the end-groups to be independent of the size of the molecules to which they are attached. That is, bond formation is assumed to be determined by equilibrium or rate constants that are given by the 'chemistry' involved. The statistical description of bond formation will be greatly simplified if a sufficiently 'strong' definition of the bond is used[5]. (On the other hand, if specific diffusion control were assumed to be operative, the apparent reactivity of the reacting group would be dependent on the size of the chain to which it is attached[6].)

The general case of non-linear non-reversible polymerization, including the effect of gelation, has been discussed by Stockmayer[7] and Flory[8]. But the formation of a polydisperse melt of linear chains caused by end-to-end hydrogen bonding of homodispersed primary chains of molecular weight M will simply be viewed as a reversible random chemical polymerization of bifunc-

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tional structural units. In the case of reversible cluster formation, a statistical thermodynamic counterpart was discussed by relating the 'extent of reaction' to the thermodynamic variables, temperature and density[9].

The assumption of forming hydrogen bonds between the ends of different chains presents us with the problem of calculating the number z_n of formed polymers composed of n primary molecules of molecular weight M. Ring closures will be ignored because their probability depends on $x^{-3/2}$ for Gaussian chains with step x. The most probable distribution can be deduced from the total number of ways (Ω) in which Z primary molecules may be transformed into z_1 original molecules, z_2 'dimers',..., z_n 'n-mers',... and so on:

$$\Omega = Z! \prod_n (2^{n-1})^{z_n}/z_n! \tag{1}$$

Equation (1) follows from the number of distinguishable ways ($w_n(2)$) in which a primary chain may form a linear n-mer. Neglecting ring formation, the theory of Stockmayer[7] yields $w_n(2) = 2^{n-1}n!$. The term n-mer, of course, designates a macromolecule built up of n primary molecules. Maximizing Ω subject to the condition that the number of primary molecules:

$$Z = \sum_{n=1}^{Z} n z_n \tag{2}$$

and the number of formed molecules:

$$Z' = \sum_{n=1}^{Z} z_n \qquad (Z' \leqslant Z) \tag{3}$$

are constant, leads to the most probable distribution:

$$z_n = AB^n 2^{n-1} \tag{4}$$

where A and B are introduced as Lagrangian multipliers. From (2) and (3) it follows that:

$$A = 2Z(1-\alpha)^2/\alpha \qquad \text{and} \qquad B = \alpha/2 \tag{5}$$

where $\alpha = (Z - Z')/Z$ is the 'extent of reaction', and α can vary between 0 and $(Z-1)/Z$ (≈ 1).

A relation between the extent α, the number density of primary chains ρ and a typical *capture length* l^* can be found by use of the connection between gelation and reversible cluster formation[9]. The capture length l^* characterizes the effectiveness of bonding (not to be confused with ε) and will be discussed in the last section. We will confine ourselves to the case of bifunctional reacting units. The statistical description of hydrogen-bonded macromolecules is greatly simplified (independently of the potentials, one assumes) if such a sufficiently 'strong' definition of the bond is used[5,10]. Corresponding to the ε concept above, l^* also absorbs the bonding energy, which may be assumed to contribute only when the conditions for hydrogen bonding are satisfied, namely the proper relative distance (and orientation) of the OH end-groups. In the following, the length l^* is considered as a free parameter in our approach.

The connection mentioned between gelation and cluster formation[9] yields:

$$A = 2V/l^{*3} \tag{6a}$$

where V is the volume of the system. By comparing with equation (5) it follows that:

$$\rho l^{*3} = \alpha/(1-\alpha)^2 \tag{6b}$$

with $\rho = Z/V = n_s'/Nl^3$. Here n_s' denotes the reduced segment number density (the number of segments per volume l^3), N the number of segments of a primary chain and l the statistical segment length. From (6b) and (2) we can see that the extent of reaction (α) increases, i.e. the number of molecules decreases, with increasing capture length l^*.

Remarks. The number-average molecular weight is $\bar{M}_n = M/(1-\alpha)$ and the weight-average molecular weight is $\bar{M}_w = M(1+\alpha)/(1-\alpha)$. By characterizing the polydispersity by $U = (\bar{M}_w/\bar{M}_n) - 1$, we obtain $U = \alpha$, i.e. in our model the polydispersity is equal to the conversion. Equation (6b) now reads

$$\rho l^{*3} = (\bar{M}_n^2/M^2)U \tag{7}$$

which tends to $\rho l^{*3} = \bar{M}_n^2/M^2$ for large α, that is for $\bar{M}_n \gg M$.

ONSET OF TUBE-LIKE TOPOLOGICAL CONSTRAINTS

In a separate paper[11], a criterion for the onset of 'non-Rouse behaviour' of a *polydisperse* polymer melt was derived. There, it was assumed that the large-scale motion of individual chains longer than the critical chain length is restricted by the presence of all neighbouring chain contours exceeding the critical length. These tube-like restrictions are topological in origin, because of the uncrossability of the chain contours. Further, the communal topological interactions (entanglements) between large ($n > n_c$) or small ($n < n_c$) macromolecules (in our case 'supermolecules') are assumed not to be equally effective as obstacles for the motion of the interacting pair: only those molecules with $n > n_c$ act as tube-forming units. Here $n_c \equiv M_c^{(p)}/M$ is the number of units (in our case primary molecules) necessary to build up a molecule of critical molecular weight $M_c^{(p)}$ of the polydisperse melt. Here we shall report only the main steps of the approach.

$M_c^{(p)}$ is assumed to follow a Graessley–Edwards scaling equation[12]:

$$M_c^{(p)} \sim (n_s'')^{-1} \tag{8}$$

In the monodisperse case of chains longer than the critical length, n_s'' is equal to the reduced segment number density n_s'. In the polydisperse case, n_s'' is the reduced (by l^3) number density of the segments of all topological constraining and tube-forming chains with $n > n_c$ primary chains:

$$n_s'' = \sum_{n=n_c}^{Z} n_s' n (1-\alpha)^2 \alpha^{n-1} \tag{9}$$

with the property $n_s'' = n_s'$ for $n_c = 1$. In a polymer melt n'_s is

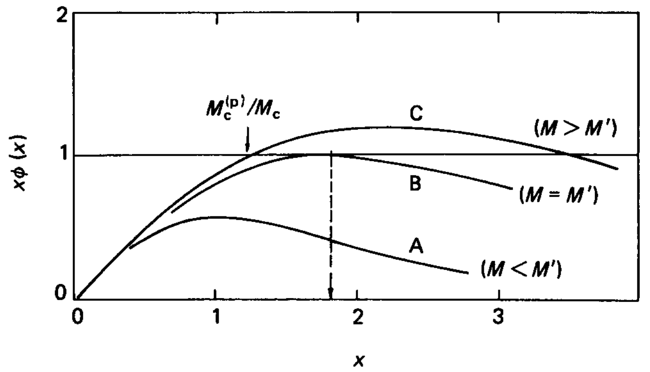

Figure 1 Bifurcation behaviour of equation (10) written as $x\phi(x)=1$. The variable x can only have meaning when $x\phi(x)=1$, then $x=m_c=M_c^{(p)}/M_c$. The molecular weight of the primary chain, M, enters equation (10) via the parameter $m=M_c/M$ ($M_c=7000$ for PPG). The arrow labels $m_c(\mathrm{B})=1.81$, that is $M_c^{(p)}=12\,700\,\mathrm{g\,mol^{-1}}$ for PPG. The curves A, B and C are discussed in the text

a constant. Typical values are $n_s'\approx 2.1$ for polydimethylsiloxane[13] and $n_s'\approx 5.0$ for PPG.

With $n_c=M_c^{(p)}/M$, the critical molecular weight is contained in both sides of the equation (8). Physically, the scaling equation (8) expresses the fact that the r.m.s. end-to-end distance of a critical chain is only slightly larger but of the order of the lateral topological tube dimensions (cf. also the mean-field theory[14]). From (8) and (9) the following 'self-consistent' equation results for the polydisperse melt:

$$m_c\phi(m_c)\equiv[(1-\alpha)m_c m+\alpha]\alpha^{mm_c-1}=1 \qquad (10)$$

where $m_c=M_c^{(p)}/M_c$ (>1) and $m=M_c/M$. Here ϕ results from the Flory distribution in (9), and the quantity m denotes the number of primary molecules necessary to form a molecule of critical length in the bulk.

Qualitatively, equation (10) shows the property of bifurcation. A (physical) solution $m_c>1$ exists only for $\bar{M}_n$ larger than an average $\bar{M}_n^*$, which characterizes the distribution where the onset of a solution m_c of (10) can be registered. Its value is larger than the critical weight M_c of the corresponding homodisperse melt[11].

This behaviour is illustrated in *Figure 1*, where the input data are chosen with reference to the PPG melt[2]. In the case $\bar{M}_n<\bar{M}_n^*$, the functions $f_1(x)=x\phi(x)$ (curve A) and $f_2=1$ do not cross and equation (10) has no real solution. Physically, this means that the number of 'supermolecules' with molecular weights $nM\geqslant M_c^{(p)}$ is too small to build up a configurational constraining tube according to ref. 14. All chains show 'Rouse-like' behaviour (better, chain segment modes). In the case of curve B, the polydisperse ensemble with a number average $\bar{M}_n=\bar{M}_n^*$ shows the onset of a solution $x=m_c$ of equation (10): 'critical' point B. According to (6), this number average $\bar{M}_n^*$ is related to a critical (onset) value of the capture length l_c^*. In the case $\bar{M}_n>\bar{M}_n^*$ (curve C), equation (10) exhibits two solutions, m_c, and only the smaller one has physical meaning. With increasing $\bar{M}_n$ (i.e. decreasing part of segment mode chains with $M_n<M_c^{(p)}$), m_c tends to unity whereas the second (unphysical) solution goes to infinity.

The dependence of the onset capture length l_c^* on the quasi-critical molecular weight M' of the primary chains can be calculated by solving equations (6b) and (10) together with $\partial f_1/\partial x=0$. *Figure 2* shows the results for the PPG data input[3,15] ($n_s'=5$, $M_c=7000\,\mathrm{g\,mol^{-1}}$, 1 segment $=2$ monomeric units). Additionally, *Figure 2* contains the dependence of $R=l(M/M_s)^{1/2}$ on M'. This 'radius' of the molecule is considered as a measure of the r.m.s. end-to-end distance of the primary (oligomer) chain. The curve $R(M')$ crosses the decreasing function $l_c^*(M')$ at $M'=1700\,\mathrm{g\,mol^{-1}}$, which is slightly larger than the experimental value of $M'\approx 1300\,\mathrm{g\,mol^{-1}}$, the onset of the additional low-frequency relaxation[2]. The corresponding solution of (10) is $m_c=1.81$; i.e. the critical molecular weight of the polydisperse melt, $M_c^{(p)}=12\,700\,\mathrm{g\,mol^{-1}}$, is nearly twice that ($M_c=7000\,\mathrm{g\,mol^{-1}}$) for the homodisperse melt.

DISCUSSION AND CONCLUSIONS

Essentially we compared two timescales: (i) chemical timescale τ_ε—mutual capture of tightly neighboured (spatial scale ε) OH end-groups by hydrogen-bond kinetics; and (ii) physical timescale τ—mobility of unbonded chain ends. More precisely, let r be a given length and assume that the other OH end-group is just (not in the mean) at this distance. Then $\tau=\tau(r)$ denotes the mean time interval in which the given OH end-group can touch (ε scale) the other OH end-group by scanning the volume r^3 due to their mobility. Clearly, $\tau(t)$ is an increasing function.

The capture (or saturation) length l^* is defined by the coincidence $\tau_\varepsilon=\tau(r)$ for $r=l^*$. Obviously, $\tau(l^*)$ is an increasing function, too.

The formulation 'the other' used above is made in order to call attention to the following. For the definition of $\tau(l^*)$, or for description of a relevant experiment with given frequency, we do not have a hierarchy of timescales, but rather their coincidence. In the stationary case, with respect to ergodicity, we can equally well say 'one of the neighbouring' or 'the next in time' OH end-group(s).

Consider a given molecular weight M of the primary chains and assume for the time being that τ_ε could hypothetically be varied (*Figure 3*). For small $\tau_\varepsilon\ll\tau(r=l)$, l being the segment length, nothing happens. If τ_ε reaches the timescale of the chain segment modes ($l^*\approx$mode length $\gtrsim l$), then the hydrogen bonds can modify the

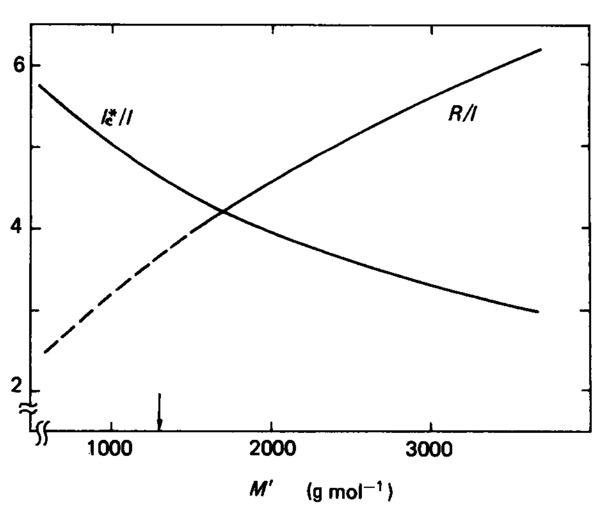

Figure 2 Reduced (by segment length l) onset capture length, l^*_c, and radius of primary chain, R, as functions of the quasi-critical molecular weight M' for PPG. The arrow marks the experimental value $M'=1300\,\mathrm{g\,mol^{-1}}$

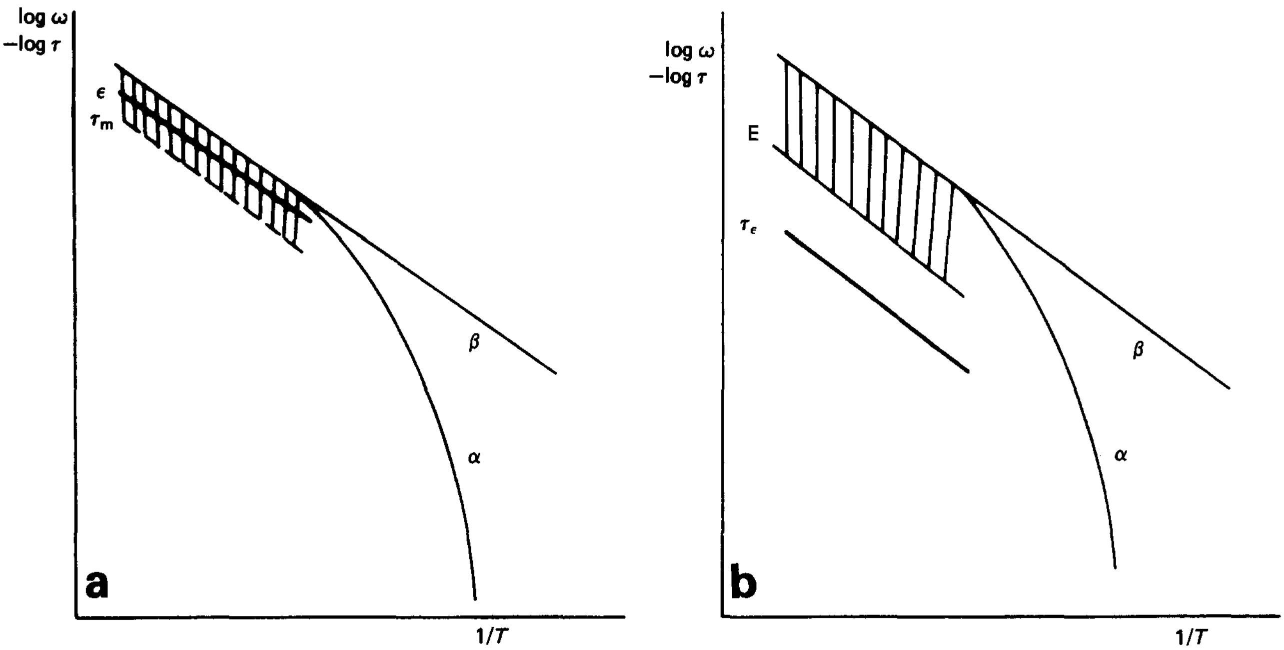

Figure 3 Arrhenius diagram. Crossover from (a) chain segment modes to (b) transient entanglement (E) caused hypothetically by increasing the timescale of hydrogen-bond kinetics τ_ε. The chain segment modes are hatched; τ_m is the time of the slowest segment mode. The real case, varying the molecular weight M of the primary chains, is discussed in the text; see also the Arrhenius diagrams in ref. 2

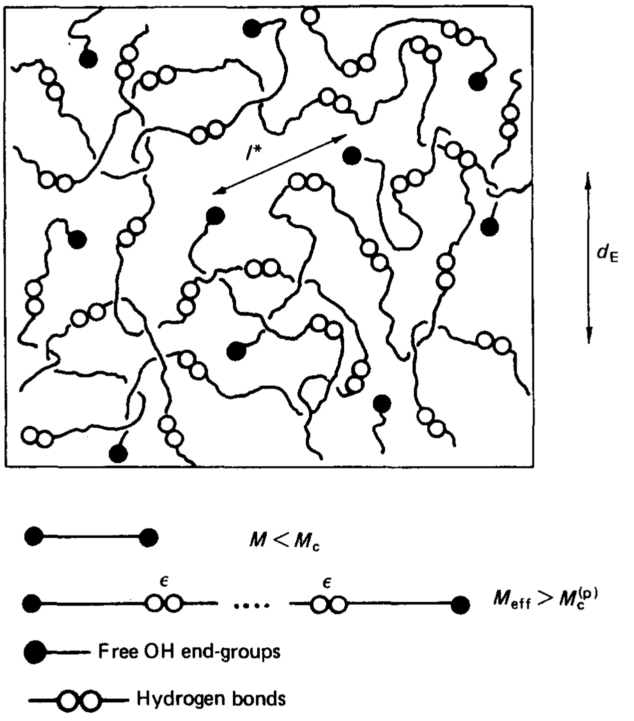

Figure 4 Geometric picture of the transient entanglement in the stationary state assuming end-to-end hydrogen bonds in PPG. Here ε is the effective 'chemical radius' (distance where a hydrogen bond becomes active), l^* is capture length (see text) and d_E is transient entanglement spacing

molecular mobility. Roughly speaking, l^* will now be a measure for enlarging the effective chain length. Increasing τ_ε (and therefore l^*) further, an effective critical molecular weight of the (polydisperse) polymer melt, $M_c^{(p)}$, will be reached where the onset of the entanglement dispersion can be observed (crossover regime, $l^* = l_c^*$). Beyond this ($l^* > l_c^*$), owing to reptation, the function $\tau(l^*)$ will change its specific behaviour (entanglement regime). The additional low-frequency relaxation[2] can only occur in this regime.

The real case treated in our statistical approach is obtained from a 'mapping' of the hypothetical case 'given M' on the case 'given τ_ε'. The regime can now be varied by the molecular weight of the primary chains, M (including, of course, a variation of OH group concentration and polymer mobility). For small $M < M'$ we have the non-entanglement (segment mode) regime, and for large $M > M'$ we have the entanglement regime. The whole timescale concept is hidden beyond the variable capture length l^*: in fact, the increasing variable l^* makes the change from segment mode to entanglement regime at $l = l_c^*$. It is the introduction of the length l^* that enables us to investigate the problem with statistical tools. In this 'ergodic' picture for the stationary case at a given moment of time, l^* is a mean distance between the free (not captured by hydrogen-bonds) OH end-groups (*Figure 4*).

Finally, the curve $l_c^*(M')$ in *Figure 2* obtained by statistical calculation shows how the crossover ($M = M'$) depends on the capture length l_c^* necessary for the onset of entanglement (which stands, as mentioned above, for a certain timescale coincidence). Thus, coming back to the kinetic point of view, the crossing with the $R(M')$ curve (*Figure 2*) near the experimental value M' means that, in PPG at room temperature, the hydrogen-bond timescale τ_ε is comparable with the timescale $\tau(r)$ of that molecular chain-end motion in the crossover regime which corresponds to a length scale r of the primary chain radius, $r = R$. If we know the spatial aspects of the polymer mobility in this regime, we can calculate the hydrogen-bond kinetics from experiments like those in refs. 1 and 2 (and, in a sense, vice versa).

If, again hypothetically, for a given set of molecular weights M, the timescale τ_ε can be varied (e.g. increased), then the crossover M' will be inversely changed (in the example, decreased). Therefore, the fact that a (relatively large) value of $M' = 1300\,\mathrm{g\,mol^{-1}}$, but well below the bulky $M_c = 7000\,\mathrm{g\,mol^{-1}}$, was experimentally observed in PPG implies that the experiment is a rather sensitive test for the hydrogen-bond kinetics in this polymer. Since both timescales, τ_ε and τ, can be varied with temperature, it would be interesting to study the precise temperature dependence of the crossover. The (as yet crude) experimental fact[2] that the onset of relaxation is confined to between $M' = 1000$ and $2700\,\mathrm{g\,mol^{-1}}$ in the frequency region between 10^4 and 10^8 Hz (and the corresponding temperature region) implies some temperature–time parallelism between hydrogen-bond and polymer kinetics in PPG (as sketched in *Figure 3*).

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