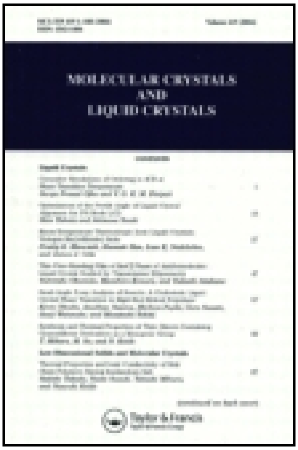

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Dielectric Behavior of Side Chain Liquid Crystal Polymers: A Study by the Thermally Stimulated Current (TSC) Method

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Version of record first published: 04 Oct 2006.

To cite this article: F. Faubert , J. M. Gilli , P. Sixou , J. Dandurand & C. Lacabanne (1990): Dielectric Behavior of Side Chain Liquid Crystal Polymers: A Study by the Thermally Stimulated Current (TSC) Method, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 178:1, 133-142

To link to this article: http://dx.doi.org/10.1080/00268949008042714

Mol. Cryst. Liq. Cryst., 1990, Vol. 178, pp. 133–142
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Printed in the United States of America

Dielectric Behavior of Side Chain Liquid Crystal Polymers: A Study by the Thermally Stimulated Current (TSC) Method

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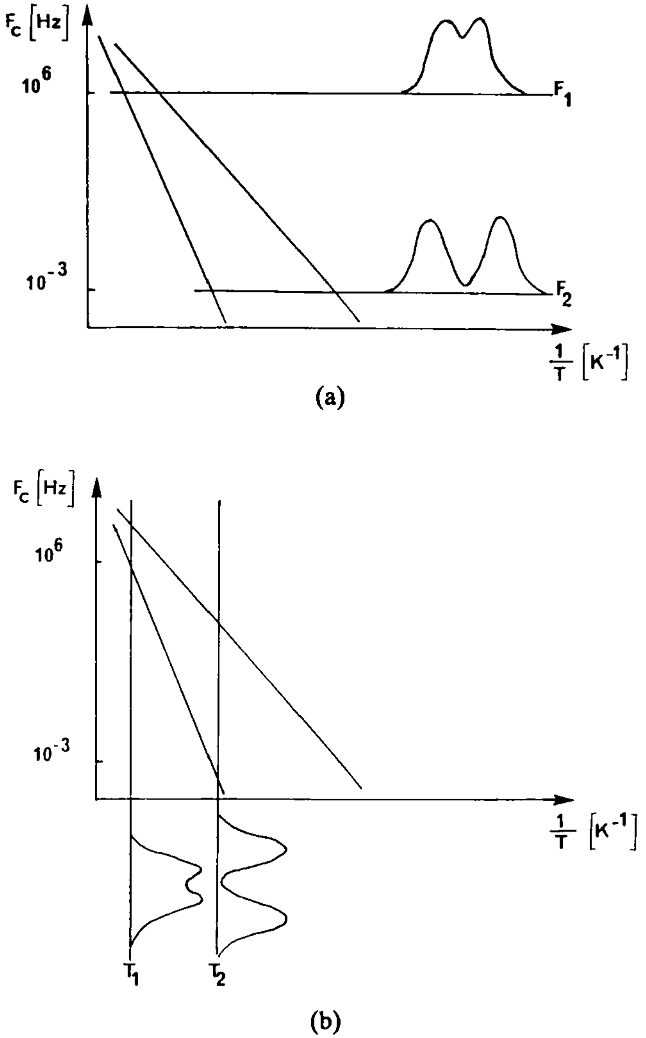
(Received October 1988; in final form August 1989)

A thermally stimulated current investigation has been carried out on a polybutadiene liquid crystal side chain polymer, in order to study the dielectric relaxation of both main and side chains. Two TSC peaks have been found showing the existence of motions of the backbone and reorientations of the mesogenic units.

I. INTRODUCTION

The thermostimulated current method (TSC) proposed by C. Bucci and R. Fieschi (1964)[1] is closely related to dielectric relaxation. The general principle consists in the application of a dc electric field to a polarizable material, in the freezing of the polarization thus created by quenching rapidly the sample, and finally in the measurement of the current induced by the molecular disorientation in this medium when it is warmed up at a controlled rate. It has been applicated to various materials like ice, ionic crystals and more recently of amorphous polymers,[2] but never, to our knowledge, to mesomorphic polymers. We present here a first study using this method. In particular we show that it can exhibit some advantages compared with the classical studies of dielectric relaxation spectrum.

Dielectric relaxation measurement[3–5] is a suitable method for the study of molecular dynamic motions and it allows the measurement, with impedance analyzers, of relaxation times roughly ranging from 10^{-10} s to a few seconds. The thermostimulated current allows reaching lower frequencies while working at lower temperatures. This is a useful tool for the study of amorphous polymers which have small dielectric relaxation amplitudes and often present overlapping peaks which are difficult to separate with the classical dielectric bridge investigation. Figure 1 illustrates a schematic representation of the separability of two relaxation phenomena at low frequencies with two weak activation energies.



(a)

(b)

FIGURE 1(a and b) Schematic representation of dielectric response for a medium with two independent relaxation times ($f_c = 1/2\pi\tau$, τ = relaxation time). The activation enthalpy of the processes are assumed different. (a) Constant frequencies ($F_1 > F_2$); (b) Constant temperature ($T_1 > T_2$).

II. DIELECTRIC RELAXATION OF LIQUID CRYSTALS, POLYMERS, AND LIQUID CRYSTAL POLYMERS

Dielectric method have been used for the study of liquid crystals[6] and in this case the Debye model has been extended to anisotropic systems. When the liquid crystal is oriented, an anisotropy of dielectric permittivity has been predicted and measured.[7,8] The relaxation in the nematic phase, exhibits a complex behavior if the mesogenic unit does not have its dipole moment normal or parallel to the great molecular axis.

Concerning amorphous polymers,[9-11] one often observes two prevailing relaxation phenomena, usually designated by α and β according to their order of appearance: towards higher frequencies, when the temperature is kept constant, and towards lower temperatures when the frequency is kept constant. The α process is attributed to a cooperative motion of the polymeric main-chain, while the β process is typically due to side-chain relaxations.

The main studies of liquid-crystalline side-chain polymers are due to Zentel,[12-14] Attard.[15-20] We can notice that in this case the nomenclature, due to Zentel, is different from the preceding one. Two different interpretations come out from these works.

A. Zentel has found two principal relaxations named α and δ. In the same way as in amorphous polymers, the α process is due to main-chain motion and becomes observable at the glass transition of the polymer, at the lowest frequencies. This motion induces the reorientation of adjacent ester dipoles (CO=O) attached to the main chain. The α relaxation plotted in an Arrhenius form is curved and converges to T_g at low frequencies.

On the other hand the relaxation designated by δ occurring at higher temperatures at a fixed frequency, is attributed to a 180° reorientation of the long axis of the mesogenic groups around the main-chain. Zentel notes that it is possible to find similar reorientation in nematic phases of low-molecular-weight liquid crystals. This motion always appears at temperature higher than T_g since it does need brownian motion.

B. Attard's interpretation is slightly different from the preceding. He recognizes the existence of the two relaxations α and δ but he gives another explanation. He studies a polysiloxane liquid crystalline side chain polymer in which the main-chain does not bear adjacent ester dipole groups. Furthermore the mesogenic part has two components of the dipole moment $\mu_{\parallel}$ and $\mu_{\perp}$ relatively to the main axis of the mesogen. Consequently the α relaxation could not be assigned to the motion of the main-chain, since it does not have any dipole moment. Moreover the determination of the temperature of appearance of the α relaxation, is not sufficiently defined to be related to T_g. When the mesogenic units are aligned under an electric field, he shows that the more the sample is aligned the more the intensity of the α relaxation is decreasing and the δ relaxation increasing. He associated the δ process with the motions of the longitudinal component $\mu_{\parallel}$ of the dipole moment and the α process with that of the tranverse moment $\mu_{\perp}$.

In order to test the validity of these different interpretations, we have chosen to study a polybutadiene mesomorphic polymer, whose mesogenic units have only a dipole moment in the direction of the molecular axis. In the same way we use a method[21–25] allowing us to separate the possible relaxation mechanisms.

III. PRINCIPLE OF THE METHOD

a. General method: single relaxation time.

Consider a dielectric containing only one type of dipole for which the relaxation phenomenon can be characterized by a relaxation time τ, obeying an Arrhenius equation:

$$\tau = \tau_0 \exp(\Delta H/kT) \tag{1}$$

where τ_0 is the preexponential factor and ΔH is the activation enthalpy.

The sample is first subjected to an electrical field E_p at a temperature T_p for a time Δt. Δt is chosen so as to induce a complete orientation of the dipolar units. This means that we must have $\Delta t >> \tau$ to obtain a saturation polarization P_0 such that:

$$P_1 = P_0(1 - \exp(-t/\tau)) \tag{2}$$

The sample is then quenched down to the temperature $T_f << T_p$, where any molecular motion is completely frozen and the field is then switched off. The sample is warmed at a controlled rate, and the depolarization current $j(T)$, due to the dipolar reorientation, and the temperature, are recorded versus time t.

The relaxation time $\tau(T)$ is given by:

$$\tau(T) = P(T)/j(T) \tag{3}$$

According to Equation 1, the plot of ln (P/j) as a function of $1/T$ gives a straight line, whose slope directly gives the activation enthalpy ΔH.

Thus a single experiment allows us to determine the parameters characterizing the relaxation phenomenon. Besides, in the lack of space charge, that could arise from the blocking of charge carriers at the electrodes, the relaxation peak may be observed without any conductivity contribution. Finally the amplitude of the phenomenon can be amplified by increasing the polarization voltage. Taking into account the dielectric rigidity of the samples and the sensitivity of the measuring device, the method is more sensitive than the conventional impedance measurement.

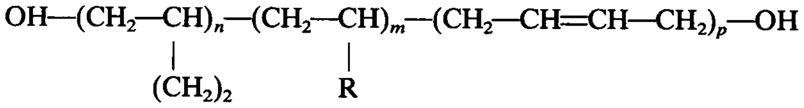
Polymeric materials are characterized by several relaxation times, as several peaks are observed which are, by far, much better resolved than in the case of a high frequency spectrum. If however relaxation times are extremely close, separation is always possible by a proper choice of the polarization temperature, or by a partial discharge. In that case, each elementary spectrum can be analyzed as presented above.

b. Fractional polarization method: distribution of relaxation times.

The fractional polarization method[26] has been used in order to resolve each complex TSC peak into elementary processes. This method consists in polarizing successively the different elementary processes whose spectra could also be analyzed with the Debye formalism. The sample is polarized at the temperature T_p during constant intervals of time (typically two minutes). Entities with relaxation time $\tau(T_p)$ lower than two minutes are thus being oriented. The temperature is lowered by a quantity ΔT in presence of the electric field and after switching off the field, the temperature remains constant during two minutes. So the entities whose relaxation times at $(T_p - \Delta T)$ are lower than $\tau(T_p - \Delta T)$, return to their equilibrium state. After quenching the sample the depolarization current is recorded. Finally the summation of elementary peaks gives practically the complex spectrum.

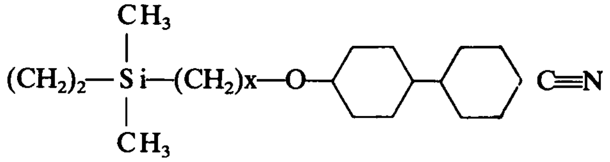
IV. EXPERIMENTAL RESULTS

These studies have been made with a liquid crystalline polybutadiene polymer whose synthesis and physico-chemical characterization have been previously described.[27,28] The molar mass is about 2000 g/mol corresponding to about 37 monomeric units. The number of (1—2) and (1—4) bonds is respectively n and p and the location of these units is random. The grafting leads to the polymer whose general formula is:

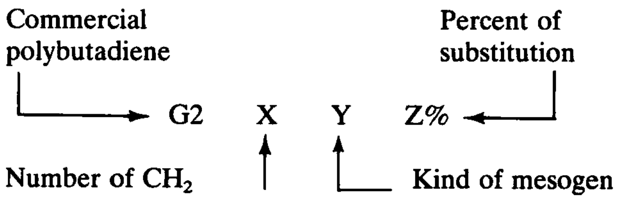


$$\mathrm{OH{-}(CH_2{-}\underset{\underset{\displaystyle (CH_2)_2}{|}}{CH})_n{-}(CH_2{-}\underset{\underset{\displaystyle R}{|}}{CH})_m{-}(CH_2{-}CH{=}CH{-}CH_2)_p{-}OH}$$

where R is:



In the latter we shall describe the polymers by G2XYZ where G2 is the polybutadiene polymer and Z the substitution percentage. The mesogenic part (R) is composed of a rigid molecular root, designated by (Y), which is in this study a cyanobiphenyl and of a flexible part constituted by a variable number X of CH_2. This can be schematically represented by:



a. Complex TSC spectra:

Figure 2 shows the thermocurrent peaks obtained for the sample G24A90% polarized at 42°C during 10 minutes. The rate of rise of the temperature is 0.1°C per second. One can isolate the different peaks by the following procedure. The low temperature peak is obtained by polarizing at the temperature (T_{M1}) where its amplitude is maximum. The high temperature peak is obtained by polarizing at temperature (T_{M2}) then discharging the low temperature peak (Figure 3a–3b). We can notice that both peaks have a linear behavior towards the polarization voltage. No variation in the amplitude of the peak was found when the polarization time was increased beyond ten, and even up to, thirty minutes, showing that maximum polarization has been obtained.

b. Fine structure of TSC spectra:

Each peak has been resolved into elementary processes. In these experiments, the temperature window was 10°C; the polarization temperatures were varying by steps of 10° below 0° and 5° above 0°C. Figure 4 shows the various elementary peaks that can be described in the hypothesis of single relaxation times obeying Equation 1. The temperature variations of the relaxation times were plotted on an Arrhenius diagram: Figure 5a corresponds to the lower temperature peak and Figure 5b to the higher temperature peak. In both cases, the majority of the processes have relaxation times that become equivalent ($\tau = \tau_c$) at a peculiar temperature ($T = T_c$). Such "compensation" mechanisms show that the elementary relaxation times are well described by a compensation law.

$$\tau = \tau_c \exp(\Delta H/k(T^{-1} - T_c^{-1})) \tag{4}$$

where the compensation time τ_c and temperature T_c are constants.

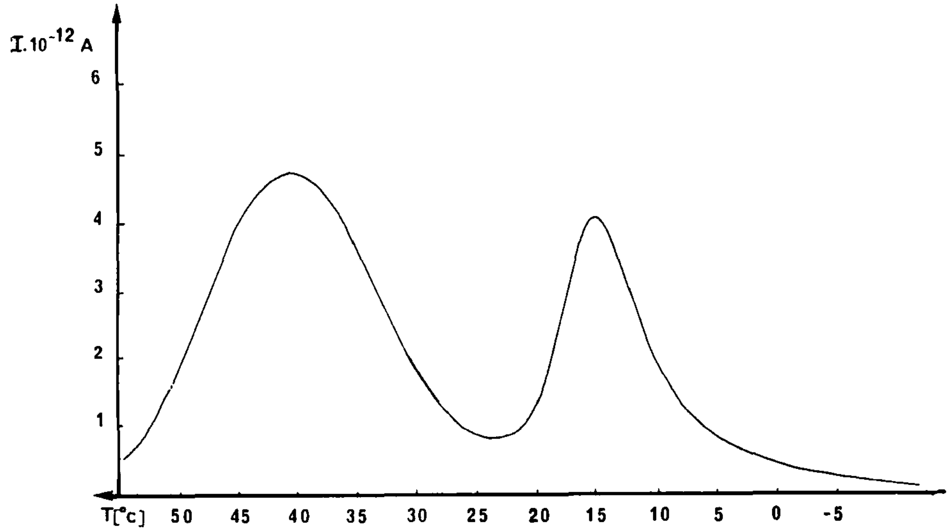
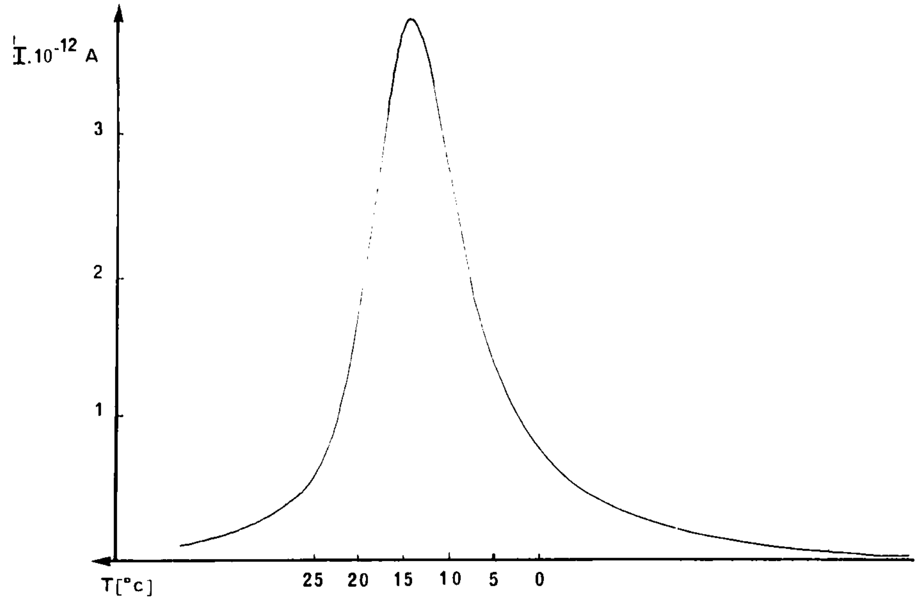
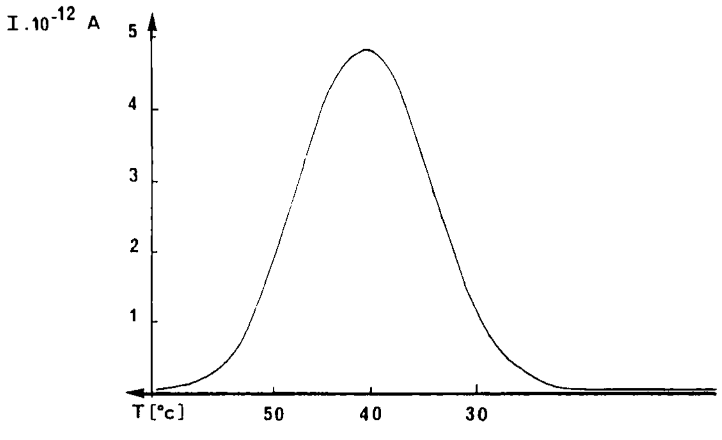


FIGURE 2 TSC curve for G24A90. Polarization temperature: 50°C, time of polarization: 10 min. Heating rate: b = 0.1°C/s between −100°C to 100°C.



(a)



(b)

FIGURE 3(a) TSC curve for G24A90. Polarization temperature: 15°C, time of polarization: 10 min. Heating rate: *b* = 0.1°C/s between −100°C to 50°C. The high temperature peak does not appear.

FIGURE 3(b) TSC curve for G24A90. Polarization temperature: 41°C, time of polarization: 10 min. Heating rate: *b* = 0.1°C/s between −100°C to 100°C. The low temperature peak has been discharged.

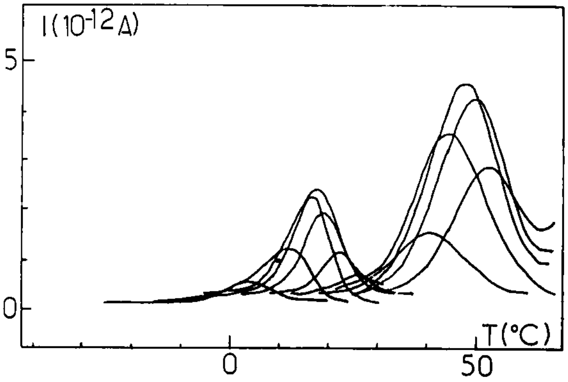
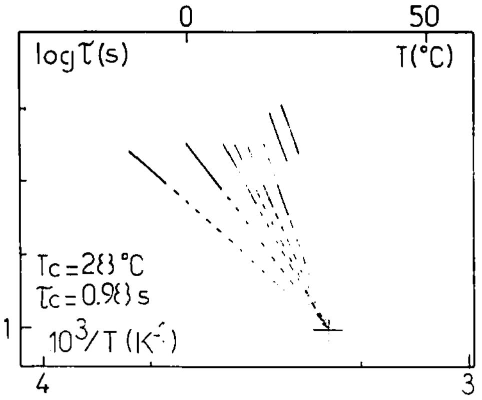
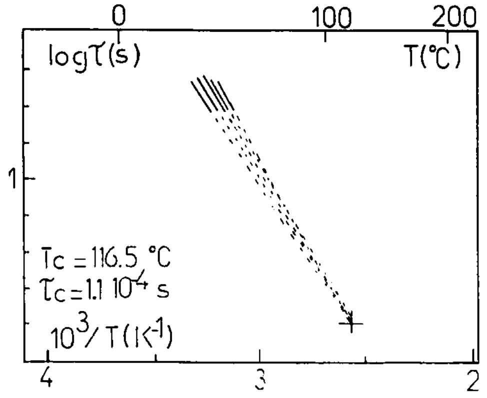


FIGURE 4 TSC curve for G24A90. Obtained with fractional polarization.



(a)



(b)

FIGURE 5(a) Arrhenius diagram: Lower temperature peak.
FIGURE 5(b) Arrhenius diagram: Higher temperature peak.

For the lower temperature mode:

$$\tau_c = 0.98 \text{ sec. and } T_c = 28°\text{C with } 0.9 \text{ eV} < \Delta H < 3.25 \text{ eV}$$

and for the higher temperature mode:

$$\tau_c = 1.1\ 10^{-4} \text{ sec. and } T_c = 116°\text{C with } 1.7 \text{ eV} < \Delta H < 2.0 \text{ eV}$$

V. DISCUSSION

Lower temperature mode

For the peak observed at low temperature, the maximum temperature T_m is very close to the glass transition T_g: (T_m = 18°C, T_g = 12°C). Beside, the compensation phenomena found for the corresponding distribution of relaxation times is characterized by parameters that are typical of processes associated with the glass transition: indeed, $T_c = T_m + 10°\text{C}$ and τ_c is of the order of 1 second. When such a behavior is identified in amorphous polymers,[29,30] the corresponding relaxation or retardation mode is attributed to cooperative motions of the main chains involving various sequence lengths. On the other hand, very high values of activation entropies S are defined by the Eyring equation:

$$\tau_0 = (h/kT)^* \exp(-\Delta S/k) \tag{5}$$

where h is the Planck constant. Taking into account the Boltzmann equation:

$$S = k \ln W \tag{6}$$

we can deduce a very high number of configurations W. This result is coherent with the well known flexibility of the polybutadiene backbone. An analogous behavior has been observed by TSC for polymers of the same family with various mesogen or spacer length. This relaxation due to cooperative motions of the main chains is the α so called mode. Although the main chain has not an important permanent dipole, the modification of the polarization observed could be attributed to the mesogen motion due itself to the motion of the main chain at the glass transition temperature.

Higher temperature mode

Despite lower activation enthalpies, this peak is situated at higher temperature because of the relatively high values of the preexponential factors. So, we can deduce from these observations that the mobile units are quite stiff and the potential barrier which is opposed to the reorientation is very high. In fact, the side chain is involved in this relaxation mode and it is not surprising to find important relaxation times regarding the large size of the mesogenic units.

VI. CONCLUSION

The thermally stimulated current method is an interesting tool never used before for the study of mesomorphic polymers. The separation of relaxation phenomena is essential if one looks for a coherent interpretation. The low temperature peak is associated with the modification of the polarization induced by the molecular motion at T_g. On the other hand, the high temperature peak characterizes the reorientation of the mesogenic part. Obviously a peak is observed even in the lack of perpendicular dipolar moment in the mesogen. Thus the real influence of this dipolar moment, normal to the great axis of the mesogen has still to be investigated. More results concerning the influence of different parameters like spacer length, grafting rate, or mesogen nature will be presented later.

Acknowledgment

We gratefully acknowledge Monsieur M. Fontanille for furnishing the polymeric samples.

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