Measurement of the Variation of Crystal Lattice Structures of Ethylene Copolymers with High-Resolution Cryogenic FTIR Spectroscopy

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ABSTRACT: High-resolution cryogenic Fourier transform infrared spectroscopy (FTIR) was used to measure the variation of the unit cell volume of ethylene-octene copolymers (EG) in this study. It was found that both the comonomer content and thermal history have great influence on the crystal lattice structure of ethylene polymers. With the increase of the octene content, the unit cell volume of EG copolymers expand, and quenching treatment favors the increase of distance between two molecular chains in orthorhombic crystals and causes more crystal lattice deformation. Compared with traditional wide-angle X-ray diffraction method, high-resolution cryogenic FTIR spectroscopy, as a powerful technique for measuring the changes of crystal lattice structures of polyethylene and ethylene copolymers, can provide more accurate information on the characterization of the changes of crystal lattice structures of semicrystalline polymers. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2072–2077, 2011

Key words: high-resolution cryogenic FTIR; ethylene copolymer; unit cell parameter; crystal structure

INTRODUCTION

The crystallization behavior of semicrystalline copolymers has become an interesting and important area of study in the field of polymer research. The deformation of crystal lattices of polymers has great influence on their ultimate structures and properties, for the reason that without an essentially complete understanding of the crystallization behavior, it is impossible to obtain adequate and predictive structure–property correlations. Many factors, including temperature, comonomer units, processing methods, and tensile stress, and so on, can change the unit cell dimensions of polymers, hence induce the deformation of crystalline lattices. To characterize the variation of unit cell dimensions of typical crystalline polymers, such as polyolefins, quite a number of literatures have been accumulated over the years on this topic.[1–7]

Swan[1] investigated the variation of the orthorhombic unit cell dimension of linear polyethylene with increasing temperature by X-ray diffraction measurements, and he has proved that the orthorhombic unit cell dimensions of polyethylene expand with the increase of temperature, and that a set of parameters *a*, *b*, and *c* for the orthorhombic unit cell have different expansion coefficients with temperature variation: a large, nonlinear expansion for the *a* dimension of the unit cell, a considerably smaller expansion for the *b* dimension, and an apparently constant value for the *c* dimension along the polymer chains. This result is in good agreement with Müller's observations.[7] After treating X-ray data with the least-square procedure, Swan established a group of equations of the unit cell parameters as a function of temperature. Vonk,[8,9] Salyer and Kenyon[10] and Bunn[11] studied the variation of the unit cell dimensions of ethylene copolymers (EAc (ethyl acetate), EVA (ethylene vinyl acetate), LDPE (low-density polyethylene)) by WAXD and found that the unit cell dimensions expand and distort with the increase of side group concentrations. They attributed the above variation of unit cell structure mainly to the effect of the side groups either being incorporated in the crystalline

lattice or assembled near the surfaces of the lamellar crystals. After a comprehensive literature search, it was found that almost all the studies on this topic, as exemplified by the above-mentioned studies, were performed with WAXD technique, which is now believed to be insensitive to the small variation of the crystal lattice of semicrystalline polymers.

FTIR spectroscopy, which is considered as a powerful tool for the characterization of crystal lattice vibration of polyolefins, can provide abundant structural information at molecular level and has received wide attention.[12–28] Previous investigation showed that there are two molecular chains in each orthorhombic unit cell of polyethylene, and the methylene rocking bands split into doublet peaks at 720–730 cm^{-1}. The deformation of orthorhombic crystal lattice of polyethylene can be characterized quantitatively by the variation of peak positions, half-widths, as well as the ratio of integrated area at 720 and 730 cm^{-1} bands. It is generally accepted that the splitting of methylene rocking bands is attributed to the interaction between two molecular chains in the orthorhombic unit cell and the shifts of crystalline bands has intimate relation with the distance between two molecular chains.

Su et al.[20] investigated the variation of the unit cell parameters of high-density polyethylene (HDPE) with high-resolution FTIR spectroscopy, and finally established a quantitative correlation between the band shifts of the crystalline region and the variation of the unit cell parameters. It is well known that the crystalline phase of ethylene copolymers is mainly composed of ethylene segments, and their crystallization behavior is similar to that of polyethylene. Therefore, the deformation of the unit cell parameters of ethylene copolymers can also be measured by the similar method.

The purpose of this study is to investigate the variation of unit cell parameters of ethylene-octene copolymers with high-resolution cryogenic FTIR spectroscopy based on established quantitative relationships between the crystalline band shifts and the variation of the unit cell parameters, and to study the effects of comonomer content and thermal history on the deformation of the crystal lattice of ethylene-octene copolymers. As the measurement precision of high-resolution cryogenic FTIR spectroscopy method is much higher than that of WAXD method, it has many potential applications in the area of polymer physics.

EXPERIMENTAL SECTION

Materials and sample preparation

HDPE pellets with a trade name of 5200B were purchased from Beijing Yansan Petrochemical, China.

TABLE I
The Physical Parameters of HDPE and EG Copolymers

Samples	Density (g/cm^3)	Octene content (wt %)	MI (g/10 min)	Melting temperature (°C)
HDPE 5200B	0.964	–	0.35	135
EG8403	0.913	9.5	30	88
EG8401	0.885	19	30	76
EG8150	0.868	25	0.5	55
EG8180	0.863	28	0.5	49

Ethylene-octene copolymers were from Dupont-Dow Company. The physical parameters of aforementioned resins were listed in Table I. The melting temperatures of all the samples were measured using a Mettler DSC 822e differential scanning calorimeter at a heating rate of 10 K/min.

All the sample films used for FTIR measurements were obtained by two-step melt-pressing, i.e., the resin pellets were first melt-pressed to form a film with a thickness of $\sim$ 100 μm, then the film was pressed to reduce its thickness to about 20 μm. The films were sandwiched between two aluminum plates during the pressing process. The film-pressing temperature was 40°C higher than the melting point of the samples. HDPE films were obtained by annealing method, i.e., the molten films were slowly cooled down to 125°C and then isothermally crystallized at this temperature for about 1 week. To investigate the influence of thermal history on the lattice structures of EG, the molten EG films were either naturally cooled down in air or quenched in liquid nitrogen.

Measurements

IR spectra were recorded on a Nicolet Magna 750 FTIR spectrometer with a MCT detector, 0.125 cm^{-1} resolution, and 64 scans. The variable temperature experiments were carried out on a Perkin–Elmer's variable temperature device with NaCl windows. The IR spectra of the samples were recorded from −130°C to room temperature with 5°C intervals. To prevent the condensation of moisture on the surface of the samples at low temperature, the experiments were carried out in vacuum. The peak positions of crystalline bands were determined by an OMNIC E.S.P IR software provided by Nicolet Company. Baseline correction was made before determining peak positions.

It should be pointed out that, for the rocking bands of EG copolymers, the absorption band of amorphous fraction is wide and hidden under the two narrow bands of 720 and 730 cm^{-1}, respectively. The monoclinic phase also appears as a shoulder overlapped with other bands. So, curve-fitting procedures

were taken to separate different bands and to measure their integrated intensities in this study.[27]

RESULTS AND DISCUSSION

With the help of FTIR spectroscopy, it is generally accepted to use four absorption bands between 750 and 700 cm^{-1} to describe the rocking bands of methylene group, among which the doublets at 730 and 720 cm^{-1} are assigned to the orthorhombic crystalline structure, 723 cm^{-1} the amorphous state, and 717 cm^{-1} the monoclinic crystalline structure.[12,13,18,23,24] Compared with room temperature FTIR spectroscopy, the high-resolution cryogenic FTIR spectroscopy can provide more stable low-temperature condition and allow more sensitive detection of the structural variation of crystalline polymers (Fig. 1). As high-resolution (0.125 cm^{-1}) cryogenic technique was adopted for the IR spectra measurement in this experiment, there was no band-overlapping of 720 cm^{-1} with 730 cm^{-1}, thus the variation of the IR peak positions can be accurately characterized.

Figure 2 shows the variable temperature FTIR spectra of HDPE film prepared by annealing method. The temperature decreased from room temperature to $-130°C$ at $5°C$ intervals. It can be seen that, with temperature decreasing, the 720/730 cm^{-1} doublet become sharper and stronger, and a blue-shift can be observed. Because IR band shifts of crystalline region in HDPE imply the deformation of crystal lattice, the red-shifts of both 720 and 730 cm^{-1} indicate the variation of the unit cell volume of the orthorhombic crystal. The 730 cm^{-1} peak, due to its higher sensitivity to temperature variation, was selected hereafter to characterize the changes of the crystalline lattice.
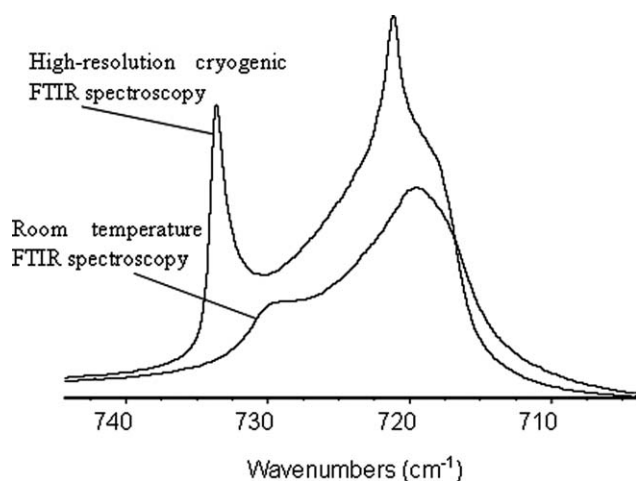

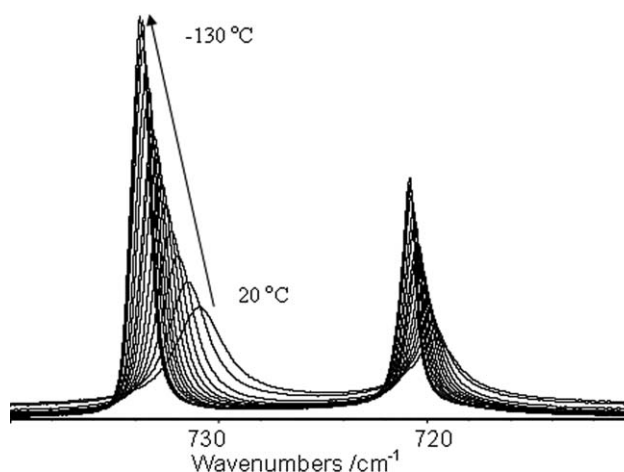**Figure 1** Room temperature and high-resolution cryogenic FTIR spectra of EG copolymer.

Figure 2 The high-resolution variable temperature FTIR spectra of HDPE: from room temperature down to $-130°C$ at $5°C$ intervals.

Combining Swan's equations[1] with the band shift data of the crystalline region measured in this study, a relationship between the IR band shifts of the crystalline region and the variation of unit cell parameters was established.[20] Moreover, we have proved the following linear equations, which can quantitatively measure the variation of the unit cell parameters and the specific unit cell volume of HDPE.

$$\Delta a = 0.01 - 0.068\Delta v_{730} \tag{1}$$

$$\Delta b = -5.62 \times 10^{-4} - 9.7 \times 10^{-3}\Delta v_{730} \tag{2}$$

$$\Delta V = 1.25 \times 10^{-3} - 1.11 \times 10^{-2}\Delta v_{730} \tag{3}$$

From the aforementioned equations, it can be seen that the specific unit cell volume decreases as the crystalline bands shifting to higher frequency, and the contraction ratio of the specific unit cell volume shows a good linear correlation with the band shift of the crystalline peak. Hence, the changes of the unit cell volume can be calculated according to the band shifts of crystalline region in the high-resolution cryogenic FTIR spectra.

It is well known that the crystalline phase of ethylene copolymers is mainly composed of ethylene segments and their crystallization behavior is similar to that of polyethylene.[19] Therefore, the deformation of the unit cell parameters of ethylene copolymers can also be measured by the above-mentioned equations. However, in ethylene copolymers with long side group and high comonomer content (such as EDAM (ethylene-dimethylaminoethyl methacrylate), EG and EVA), besides the normal orthorhombic crystalline phase, monoclinic crystalline phase can also be detected.[15,19] For example, the monoclinic band of EVA at 717 cm^{-1} appears as a shoulder on the right side of 720 cm^{-1} band, but it has no obvious effect on the peak position of 730 cm^{-1} band.[19]
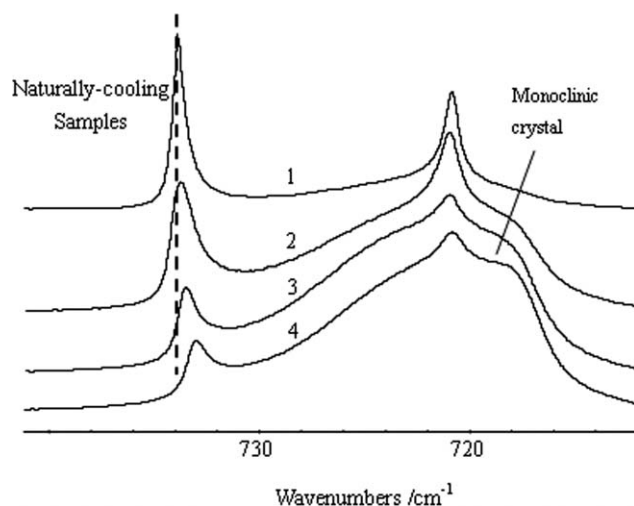
Figure 3 High-resolution cryogenic FTIR spectra of EG copolymers ($\gamma(CH_2)$) after naturally cooling treatment. (1) EG8403, (2) EG8401, (3) EG8150, and (4) EG8180.

Figures 3 and 4 show the high-resolution cryogenic FTIR spectra of EG films prepared with the methods of melt-pressing/naturally cooling in air and melt-pressing/quenching in liquid nitrogen, respectively. All the spectra were collected at $-130°C$. It is obviously that, at low temperature, the S/N ratios of IR spectra of all the EG samples are improved significantly and the peak positions are clearly detected.

Figure 5 shows the variation of the peak positions of 730 cm^{-1} bands of a series of EG copolymers as a function of octene content. With increasing the comonomer content, the 730 cm^{-1} peak for both naturally cooled and quenched samples shift gradually to lower frequencies. In addition, thermal history also has a remarkable effect on the band shift of 730 cm^{-1} peak, i.e., the band shifts of crystalline region of naturally cooled samples are more remarkable than that
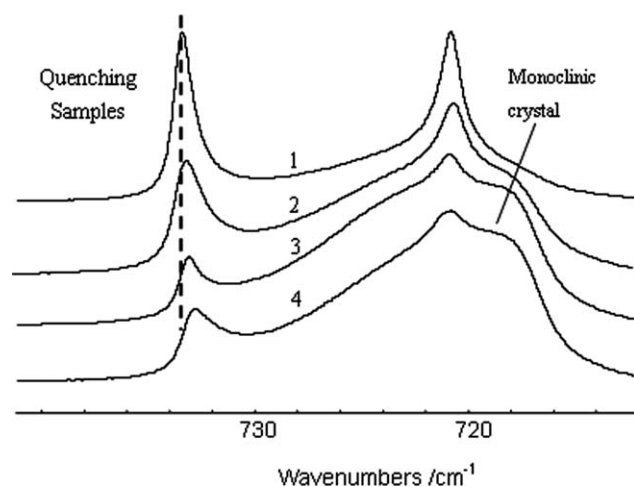

Figure 4 High-resolution cryogenic FTIR spectra of EG ($\gamma(CH_2)$) copolymers after quenching treatment. (1) EG8403, (2) EG8401, (3) EG8150, and (4) EG8180.

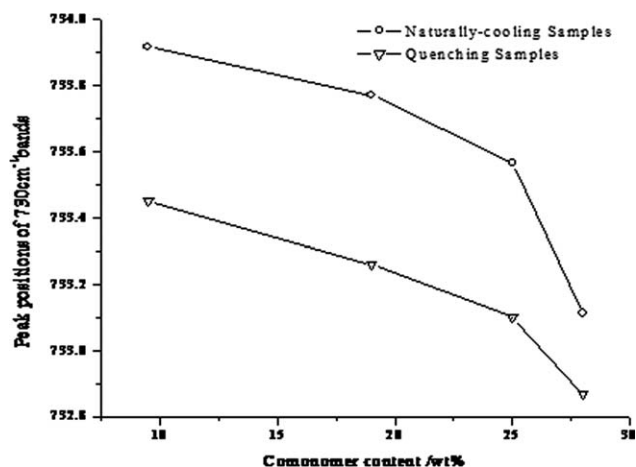**Figure 5** The relationship between peak positions of 730 cm^{-1} bands and comonomer content of EG copolymers.

of quenched samples. As the octene content rises from 9.5 to 28 wt %, the maximum peak shifts of 730 cm^{-1} band for naturally cooled and quenched samples are 0.904 and 0.583 cm^{-1}, respectively.

According to eq. (3), it can be calculated that, when the comonomer content increases from 9.5 to 28 wt %, the unit cell volume of the quenched EG samples expands 0.577% and that of the natrually cooled EG samples expands 0.895%. The expansion of unit cell volumes indicates that the distance between two molecular chains in the orthorhombic unit cell increases with the increasing of the comonomer content, and the interaction between two molecular chains simultaneously decreases. For both naturally cooled and quenched EG samples with the same octene content, the band shifts of 730 cm^{-1} peak of naturally cooled samples are larger than those of the quenched samples, implying that the unit cell volumes of the naturally cooled samples are smaller than those of the quenched samples, which leads to a conclusion that quenching treatment has enhancing effect on increasing the distance and decreasing the interaction between two molecular chains in the orthorhombic unit cell.

It was proved in the previous section that the deformation of the unit cell has intimate relationship with comonomer content and thermal history. As for the deformation mechanism, the idea that it is caused by the entering of octene group into the crystalline unit cell fails to give convincing evidences. Previous results[29–31] indicated that about 60% methyl groups entered the unit cell, but all these branches/comonomers only existed in the defects of the unit cell. If the dimension of the side groups or comonomer is larger than that of the methyl group, they can only exist in the amorphous region. In this study, the dimension of octene group of EG is much larger than that of methyl group, so it cannot enter the crystalline lattice at all. The deformation of the
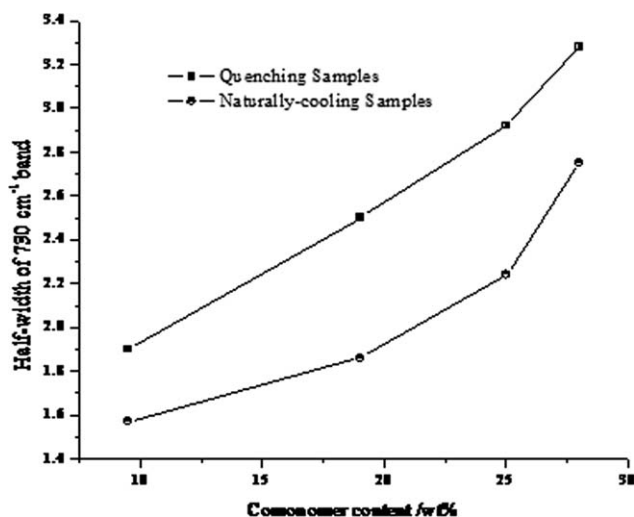
Figure 6 The relationship between half-width of $730 cm^{-1}$ band and comonomer content of EG copolymers.

unit cell may be caused by the interaction among the unit cells which had been proved in our previous work.[15] For ethylene copolymers, the interaction among the unit cells increases with the increase of the comonomer content, resulting in the deformation of unit cell and the band shifts of the crystalline region. At the same time, quenching treatment hinders the arrangement of unit cell and leads to further deformation of the crystalline lattice.

The half-width of the $730 cm^{-1}$ band, and the ratio of the integrated area of the two crystalline bands at 720, $730 cm^{-1}$ (A_{720}/A_{730}), are correlated with the crystallization perfection (including the packing of molecular chains and the deformation of unit cell) of ethylene copolymers,[19] which provides useful information about the unit cell structure of ethylene copolymers. Narrower half-width of $730 cm^{-1}$ band and smaller A_{720}/A_{730} value correspond to more ordered crystalline structure of ethylene copolymers. The crystallization perfection of ethylene copolymers can be characterized quantitatively by the variation of the half-width of crystalline bands and the value of A_{720}/A_{730}. Figure 6 shows the variation of the half-width of $730 cm^{-1}$ peak of EG copolymers as a function of octene content. It is observed that, either quenched or naturally-cooled samples, the half-widths of EG increase with the increase of octene content. The half-widths of quenched samples are much bigger than those of the naturally cooled samples. It can be explained that the octene groups of EG hinder the ethylene segments' movement in the crystallization process and thus affect the ordered packing of ethylene segments. At the same time, the average sequence length of the crystallized ethylene segments is shortened with the increase of the comonomer content, finally resulting in the decrease of the crystallization perfection and the increase of the deformation of the crystalline lattice. Quenching

treatment made the ethylene segments frozen in ultra short time, therefore many molecular chains could not be adjusted to lowest energy state and were confined to be thermodynamically metastable state. As a result, more crystal lattice deformation existed in the quenched EG samples than in naturally cooled ones, leading to the wider half-width of $730 cm^{-1}$ band.

It is commonly known that polymer crystals are built up by regularly arranged chain segments. The longitudinal (along the molecular axes) rigidity of covalent bonds in molecular skeletons is substantially higher than the rigidity of van der Waals or hydrogen bonds between two molecular chains. These factors are responsible for the different expansion coefficients of a set of unit cell parameters (a, b, and c) of orthorhombic crystal. Therefore, the deformation of unit cell may bring in the change of the dihedral angle of orthorhombic crystal; bigger dihedral angle corresponds to higher A_{720}/A_{730} ratio.[19,20] In the process of investigating the deformation of orthorhombic crystal, the changes of the dihedral angle of orthorhombic crystal can be expressed by the ratio of A_{720}/A_{730}. For EG copolymers with higher comonomer content, however, besides the occurrence of normal orthorhombic crystalline phase, monoclinic crystalline phase was also detected at $717 cm^{-1}$ in the cryogenic FTIR spectra (Figs. 3 and 4). With the help of curve-fitting, the integrated intensities of the orthorhombic crystal bands were obtained. Figure 7 shows the variation of the A_{720}/A_{730} values of EG copolymers as a function of the octene content. It is clear that the ratio of A_{720}/A_{730} increases with the increase of comonomer content, indicating the decrease of the crystallization perfection of EG copolymers. Moreover, the dihedral angles of the quenched samples are larger than those of the naturally-cooled samples, implying that
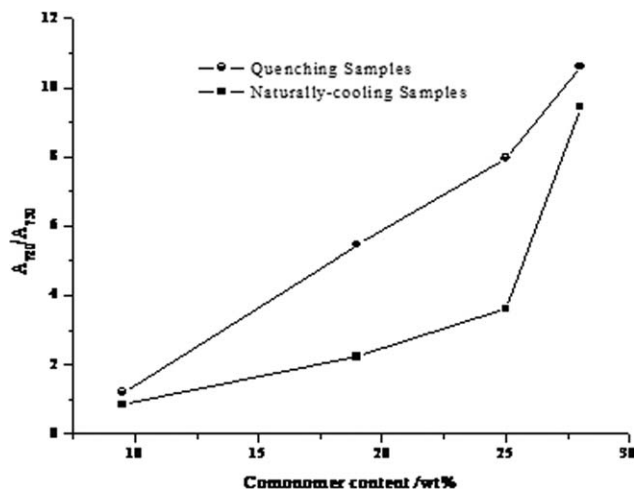

Figure 7 The relationship between A_{720}/A_{730} values and comonomer content of EG copolymers.

quenching favors the increase of the dihedral angles of orthorhombic crystal.

CONCLUSIONS

High-resolution cryogenic FTIR spectroscopy was used for the first time to characterize the variation of unit cell dimension of ethylene copolymers. The experimental results indicated that thermal histories and chain structures had great influences on the crystal lattice structure of ethylene copolymers. With the help of high-resolution cryogenic FTIR spectroscopy, it was found that the unit cell volumes of EG copolymers expand with the increase of the octene content, and quenching treatment favors the increase of distance between two molecular chains in orthorhombic crystals and causes more crystal lattice deformation.

The variations of the half-width of 730 cm^{-1} and the dihedral angle (A_{720}/A_{730}) of orthorhombic crystal have close relationship with the packing of molecular chains and the deformation of unit cell, which provides useful information about the unit cell structure of ethylene copolymers. By investigating the variation of the half-width of crystalline bands and the value of A_{720}/A_{730}, the crystallization perfection of EG copolymers was characterized quantitatively.

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