

Residual Metal Content in Ethylene-Propylene-Diene Monomers Synthesized Using Vanadium- and Zirconocene-Based Catalysts

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ABSTRACT: Ethylene-propylene-diene monomer (EPDM) terpolymers were prepared using either vanadium ($\text{VOCl}_3/\text{Al}_2\text{Et}_3\text{Cl}_3$) or zirconocene ($\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$) catalyst systems. Residual metal contents in EPDM films were determined by Rutherford backscattering spectrometry. Metallocene catalyst systems exhibited a higher activity, producing EPDM with lower molecular weight and narrower molecular weight distribution. The highest activity guaranteed lower residual metal content ($\text{Zr/C} = 10^{-5}$) than in the case of EPDM produced by $\text{VOCl}_3/\text{Al}_2\text{Et}_3\text{Cl}_3$ ($\text{V/C} = 10^{-4}$). Subsequent steps of dissolution of the polymer and its reprecipitation were seen to reduce the metal contents in both metal systems. Concerning the cocatalyst retention, despite initial use of a very high amount of methylaluminoxane/metallocene ($\text{Al/Zr} = 3000$) in the reactor, only about 4% of this initial concentration remained in the polymer. On the other hand, in the case of vanadium-based catalyst, almost all Al present in the initial conditions (≈ 8.3) remained in the polymer. In both cases, the residual Al/M ratio was close to the value generally proposed for the generation/stabilization of the active species. In the case of vanadium systems, a test in the synthesis of ethylene propylene rubbers indicated that the absence of diene in the polymer structure leads to a reduction in the residual vanadium content, indicating that the diene double bond might be responsible for partially vanadium coordination. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1997–2003, 1999

Key words: EPDM; vanadium; zirconocene; Rutherford Backscattering Spectrometry

INTRODUCTION

Copolymers of ethylene and propylene are of great industrial interest. These so-called EP polymers have elastic properties and, together with 0.1–5.0 wt % of dienes as third monomers, they constitute a family of terpolymers, ethylene-propylene-diene monomers (EPDM), which are elastomers of commercial importance, especially in

the automotive industry (e.g., hoses, gaskets, wipers, bumpers, belts) and in the housing industry (roofing).¹ Because there are no double bonds in the backbone of the polymer chain, EPDM is not very sensitive to oxygen and ozone, as well as to acids and alkalis.² Some very recent applications comprehend its use in composites and in blends with polyolefins,³ with carboxylated nitrile rubbers,⁴ and in microcellular rubbers.⁵ Besides it has been proposed as support for Ziegler-Natta catalysts in the production of polyethylene with narrow molecular weight distribution.⁶

The production of EPDM grades can be modulated, among other parameters, by the proper

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choice of the diene, as well as by its relative concentration. EPDM available from industry are mostly based on 2-ethylidenebi-cyclo [2.2.1]hept-5-ene (ENB),⁷ the preferred cyclic termonomer, or 1,4 hexadiene.⁸ For both technical and economical reasons, these termonomers are incorporated in ethylene/propylene chains only in very low concentrations (<2 mol %).

In most technical processes for the production of EPDM rubbers, soluble or highly dispersed vanadium compounds, such as VCl_4 , $V(acac)_3$ [$acac = acetylacetonate$], $VOCl_3$, $VO(OR)_3$, cocatalyzed by alkylaluminum chloride in the presence of organic halogen promoters, have been used. One inconvenience of this metal is that the residual vanadium content in the polymer must not exceed 10 ppm to avoid coloring, aging, and toxicity.⁹ Moreover, these vanadium-based systems present a drastic catalyst productivity loss in the presence of dienes, besides chain branching and crosslinking in the course of the terpolymerization.¹⁰ In addition to these facts, even an organoaluminum cocatalyst is capable of reducing the active V(III) species to an inactive V(II) one. Concerning this aspect, the immobilization of such vanadium catalyst on magnesium complex was recently shown to increase the resistance to reduction by aluminum cocatalysts.¹¹

Similar elastomers, which are less colored, have been obtained recently with metallocene/methylaluminoxane (MAO) catalysts at a much higher activity. Some examples are already mentioned in the literature. Kaminsky and Miri¹² had reported the terpolymerization of ENB with ethylene and propylene using the Cp_2ZrMe_2/MAO system. $Et(Ind)_2ZrCl_2/MAO$, either in solution or supported on MAO-modified silica was shown to be an excellent catalyst for terpolymerization.¹³ According to Malmberg and Löfgren¹⁴ terpolymers obtained using $Et(Ind)_2MCl_2$ ($M = Zr, Hf$) activated by MAO and ENB as termonomer were less crystalline and had lower glass transition temperatures (T_g). ENB polymerizes via vinyl group of the cyclic bond and the tendency of branching is low, leading to a narrow molecular weight distribution of about 2.¹⁴ $Et(Ind)_2ZrCl_2$ activated by tetrakis(pentafluorophenyl) borate and triethylaluminum afforded up to 44 wt % of ENB in the terpolymers,¹⁵ an incorporated content which hardly would be achieved with classical Ziegler-Natta catalysts. Linear dienes such as hexa-1,4-diene¹⁶ and hexa-1,5-diene¹⁷ also have been tested as termonomers in the presence of the *rac*- $Et(Ind)_2ZrCl_2/MAO$ system. In those cases, a

drastic fall of activity, as well as formation of side products were observed. In fact, very low diene concentration are enough to enable the incorporation of suitable amounts of termonomer in the chains in the case of metallocene catalysts, whereas much larger diene concentrations are required with vanadium systems. Metallocene catalysts show stability concerning the diene-induced deactivation reaction, contrary to what takes place, as already mentioned, in the case of classical vanadium-based catalyst.¹⁸

The EPDM worldwide production based on vanadium catalyst systems is presently higher than 6.5×10^5 tons/year. Projections for metallocene-catalyzed EPDM demand is about 5.0×10^5 tons/year within 10 years.¹⁹ This value, although small, is significant for this product and illustrates that metallocenes are facilitating the penetration of hydrocarbon polymers into areas currently served by high-cost engineering thermoplastics.¹⁹

The high activity of the metallocene catalyst might lead to lower residual metal content. The determination of elemental concentrations in polymers as well as their composition was reported in some recent publications, using different techniques. Fluorinated species at fluorocarbon film surface were measured by X-ray photoelectron spectroscopy, whereas hydrogen amounts in the fluorocarbon polymer films were determined by forward recoil spectrometry.²⁰ The permeation of Li^+ through thermosensitive membranes was evaluated by flame emission spectrophotometry.²¹ Mössbauer spectroscopy was reported as a method for studying the metal content and the structure of grafted-carboxyl-containing Fe^{3+} acrylates.²² Neutron reflectivity was also used to monitor the diffusion of linear polystyrene into crosslinked polystyrene.²³ Dye diffusion in polymer films was studied by Rutherford backscattering spectrometry (RBS).²⁴ We have reported recently on the use of RBS to determine the V/C and Al/V ratios incorporated in EPDM films, prepared using vanadium-based catalyst, under different initial Al/V molar ratios and initial diene concentrations.²⁵

In the present study, besides characterizing EPDM films produced by a vanadium-based catalyst ($VOCl_3$) cocatalyzed by $Al_2Et_3Cl_3$ and by a metallocene catalyst ($Et(Ind)_2ZrCl_2$), activated by MAO with respect to their molar masses, molecular weight distributions, crystallinities, and relative monomer incorporations, we determined the residual metal concentration by RBS. For com-

parative reasons, the metal residues were also analyzed in EPDM commercial samples and standard EP rubbers, all produced by vanadium-based catalysts. The effect of polymer washing on the residual metal content was also investigated.

EXPERIMENTAL

Materials

Polymerization grade ethylene and propylene were purchased from White-Martins (Porto Alegre, Brazil), deoxygenated, and dried through columns of activated molecular sieve (13 Å) before use. Pura grade toluene (Nuclear, Porto Alegre, Brazil) and hexane (Copesul S. A., Triunfo, Brazil) were deoxygenated and dried by standard techniques before use. The catalysts VOCl_3 (0.23M in hexane), $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ (Witco, Hamburg, Germany); the cocatalysts $\text{Al}_2\text{Et}_3\text{Cl}_3$ (1.00M in hexane) and MAO (generously supplied by Witco, 10.0 wt % toluene solution, 1.7 Al as trimethylaluminum (TMA), average molar mass $900 \text{ g} \cdot \text{mol}^{-1}$); and the ethylidenebicyclo [2.2.1] hept-5-ene (ENB by Aldrich, Milwaukee, WI) were used without further purification. All experiments were performed under Ar atmosphere using the Schlenk technique.

Polymerization

The polymerizations were performed in a 2-L glass reactor (Büchi) using *n*-hexane or toluene as solvent. The diene ($1.8 \times 10^{-3} \text{ M}$), the catalyst and the required amount of cocatalyst were introduced in this order into the reactor containing solvent (1 L) under positive pressure of a mixture of ethylene and propylene (25/75 in mass). Reactions with VOCl_3 ($2.3 \times 10^{-4} \text{ M}$ of V) were performed in hexane at 273 K. The temperature was allowed to increase up to 288 K and maintained at this temperature, under continuous flow of ethylene and propylene, for 30 min. The $\text{Al}_2\text{Et}_3\text{Cl}_3$ cocatalyst was used in an $\text{Al/V} = 8.3$. Reaction with $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ ($1.0 \times 10^{-5} \text{ M}$ of Zr) was performed in toluene at 313 K, using MAO as cocatalyst in an $\text{Al/Zr} = 3000$, for 30 min. The reactions were quenched by the addition of acidic ethanol. The polymers were collected, washed with acidic ethanol (1 L), and vacuum dried at 333 K for 48 h. Each polymerization reaction was repeated at least three times under identical conditions, leading to similar products.

For metal extraction, an initial mass (2.0 g) of EPDM was dissolved in 200 mL of hexane at 328 K, under stirring for 2 h, and precipitated in 200 mL of acidic ethanol. This procedure was repeated three times. Each complete cycle will be referred as a washing step in the following text. The metal content in the sample was analyzed after each step of washing.

Polymers Characterization

The polymer films were characterized by infrared spectroscopy (Mattson 3020 Fourier transform infrared spectrophotometer) measuring the ratio of the intensities of the 1155 cm^{-1} methyl band and the 720 cm^{-1} methylene band according to the ASTM D3900. The diene incorporation was monitored by the intensity of the 817 cm^{-1} band and compared with those obtained from commercial polymer samples with known iodine numbers.

Melting points (T_m) and crystallinities were determined on a DSC-PL (Polymer Laboratories Ltd., Surrey, U.K.) differential scanning calorimeter calibrated with Indium, using a heating rate of $20 \text{ K} \cdot \text{min}^{-1}$ in the temperature range 173–373 K. The heating cycle was performed twice, but only the results of the second scan are reported, because the former is influenced by the mechanical and thermal history of the samples. Molar masses and molar mass distributions were investigated with a Waters high-temperature GPC instrument, CV plus system, Model 150C, equipped with an optic differential refractometer and three Styragel HT type columns (HT3, HT4, and HT6) with exclusion limit 1×10^7 for polystyrene. 1,2,4-trichlorobenzene was used as solvent at a flow rate of $1 \text{ cm}^3 \cdot \text{min}^{-1}$. The analyses were performed at 413 K. The columns were calibrated with standard narrow molar mass distribution polystyrenes and then universally with linear low density polyethylenes and polypropylenes.

Metal contents were determined by RBS using EPDM polymer films (70-mm wide and 0.15-mm thick) produced by pressing the dried polymers under 12 MPa at 423 K. For an introduction to the method and applications of this technique the reader is referred elsewhere.^{25–27} The V/C, Zr/C, and Al/C atomic ratios were determined from the ratio of the heights of the signals correspondent to each of the elements in the RBS spectrum and converted to ppm.

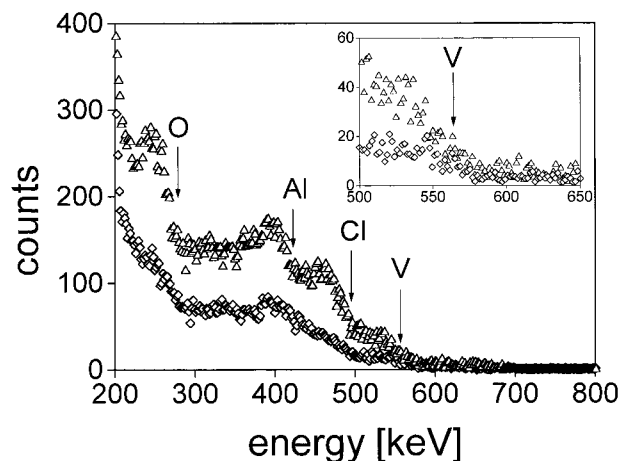


Figure 1 Rutherford backscattering spectra obtained under similar conditions of (Δ) a commercial EPDM film synthesized using vanadium-based catalyst system, and (\diamond) a standard EP film (ASTM2). The arrows indicate the outermost (surface) position of the corresponding elements in the samples. In the inset the V signals are magnified.

RESULTS AND DISCUSSION

Vanadium-Based Catalysts

Most of the commercial processes produce EPDM with technology based on vanadium catalyst systems. Such catalysts are extremely sensible to poisons. Moreover, as already mentioned, even the diene is capable of reducing the active V (III) species to the inactive V(II) one, leading to a decrease in catalyst activity.

Figure 1 shows the RBS spectra of a commercial EPDM film and a standard EP rubber (ASTM2) produced by vanadium catalyst systems. The absence of diene in the case of EP rubber might afford a smaller catalyst deactivation and thus a higher catalyst activity, which in turn will lead to a lower vanadium residual metal content. We have observed previously that the V content increases with the diene concentration and this might be an effect of activity loss by the increasing amount of diene.²⁵ Together with this fact, V atoms might interact somehow with unsaturations present in those terpolymers. We attributed this behavior to the coordination capability of the remaining double bond of the diene to the metallic center. Therefore, if we take into account that in the case of EP rubbers, the diene is absent in the copolymer structure, the absence of potential metallic coordination sites might also contribute to the lower observed residual vanadium content.

To investigate this interaction, we chose a high residual vanadium terpolymer prepared under our experimental conditions to study the influence of the washing steps on the residual metal content. Figure 2 shows the RBS spectra of EPDM films prepared using $\text{VOCl}_3/\text{Al}_2\text{Et}_3\text{Cl}_3$ catalyst system after quenching and washing procedures. As we repeated the process of dissolving the polymer in hexane followed by precipitation, we observed a complete elimination of V and Cl, while Al and some O remained bonded to the polymer chain.

Zirconocene-Based Catalysts

As already mentioned, zirconocene catalysts activated by MAO usually have high activity in the polymerization of α -olefins. Table I presents the catalyst activity and polymer properties of EPDMs obtained by vanadium and zirconocene-based catalysts. For comparative reasons, we present in Table I data corresponding to terpolymers having similar incorporated ethylene content.

According to Table I, the catalyst activity of the zirconocene system is about 40 times higher than that of the vanadium-based catalyst under the same ethylene/propylene ratio in the gas feed and ENB concentration in the reaction medium. Nevertheless, the weight average molecular weight of EPDM produced by metallocene is much lower than in the case of VOCl_3 , which in part can

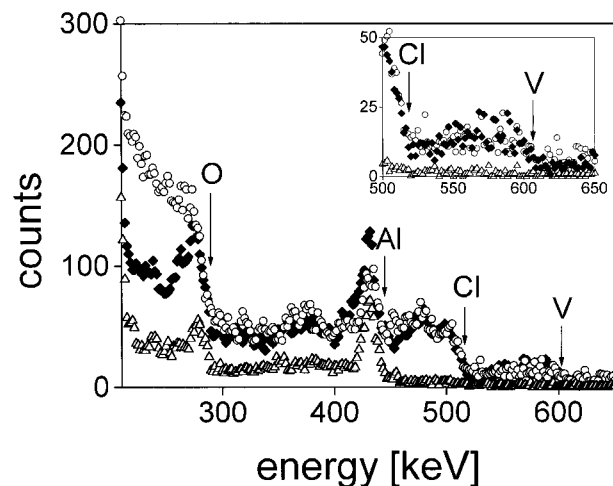


Figure 2 Rutherford backscattering spectra obtained under similar conditions of EPDM films synthesized using the $\text{VOCl}_3/\text{Al}_2\text{Et}_3\text{Cl}_3$ catalyst system. (\circ) after quenching, (\blacklozenge) after two, and (\triangle) three washing steps. In the inset the Cl and V signals are magnified.

Table I Catalyst Activity and Polymer Properties of EPDMs Synthesized Using Vanadium- and Zirconocene-Based Catalysts

Catalyst System	Activity (10^3 kg EPDM/mol M)	% Et	$10^{-5} M_w$ ($g \cdot mol^{-1}$)	$10^{-5} M_n$ ($g \cdot mol^{-1}$)	M_w/M_n	T_g (K)
$VOCl_3/Al_2Et_3Cl_3$	0.1	41	5.0	1.3	3.8	234
$Et(Ind)_2ZrCl_2/MAO$	4.4	44	0.3	0.1	2.5	246

M = V or Zr; % Et, weight percentage of ethylene incorporated in the polymer; M_w , weight average molecular weight; M_n , number average molecular weight; M_w/M_n , molecular weight distribution; T_g , glass transition temperature.

restrict the use of such terpolymer for technological applications, when mechanical properties are required. On the other hand, the molecular weight distribution (MWD) is lower in the case of EPDM produced by metallocene, which in fact is a characteristic of such single site catalysts. It is noteworthy that molecular weight distribution is a very important factor in determining mechanical and rheological properties of polymers for a given M_w . Polymers with narrow MWD have greater dimensional stability, higher impact resistance, greater toughness at low temperatures, and higher resistance to environmental stress cracking. Thus, for technological applications, EPDMs produced by metallocene still need to present higher molecular weight keeping the low MWD. This can be in part achieved by a higher ethylene/propylene ratio in the gas feed, which in turn guarantees a higher ethylene incorporation in the polymer, leading to higher molecular weights.

Ansa-metallocene like $Et(Ind)_2ZrCl_2$ are known to lead to a higher co- and termonomer incorporation than Ziegler-Natta catalysts. A higher diene incorporation causes an increase in the free volume among the polymer chains, which in turn leads to an increase in the T_g value. The higher T_g values observed for the metallocene catalyst as compared with the vanadium one is in agreement with the other EPDM properties presented in Table I.

Figure 3 presents the RBS spectra of EPDM films produced by $Et(Ind)_2ZrCl_2/MAO$ system. As expected, the residual metal content is smaller than in the previous case, because metallocene systems are more active than the vanadium-based ones. Cl and O were incorporated during the quenching step coming from the decomposition products of the catalyst/cocatalyst system. Their signals, observed in the nonwashed polymer, are reduced after subsequent washings. The Zr content, although small, remained practically unchanged after three washing steps.

It is noteworthy that, contrary to vanadium catalysts, metallocene systems demand a greater amount of Al-based cocatalyst, MAO in this case, to be stable and active. The role of MAO as cocatalyst still is not clearly elucidated²⁸ and many roles have been attributed to this compound, such as being responsible for the alkylation of the catalyst,^{29,30} stabilization of the cationic metallocene alkyl by acting as a counter-ion,³¹ and the prevention of bimolecular reduction of the catalyst.^{29,31–33} All these facts would account for the large amount of MAO required for high polymerization activity and chain transfer capabilities.³⁰ Aluminoxanes also scavenge impurities such as water and oxygen from the reaction milieu.²⁹ According to Figure 3, the Al residual content is initially higher, as compared with the EPDM obtained with the vanadium-based system (see also Fig. 2). However, the Al residual content is reduced after washing. Table II presents comparative data concerning residual metal contents in EPDM films. Comparing the initial Al/M (M = V

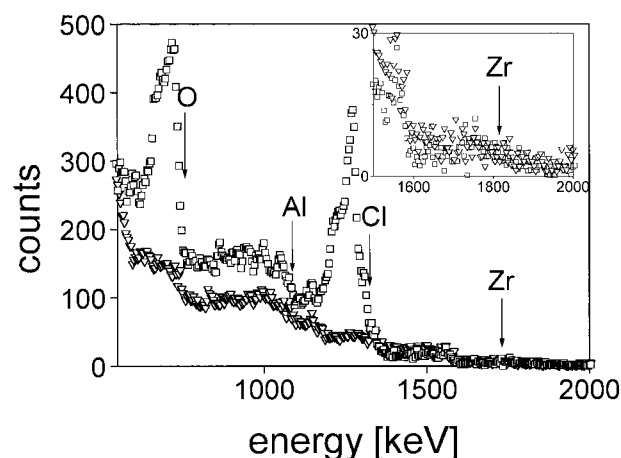


Figure 3 Rutherford backscattering spectra of (□) EPDM film made using the $Et(Ind)_2ZrCl_2/MAO$ catalyst system after reaction quenching, and (▽) after three washing steps. In the inset the Zr signals are magnified.

Table II Residual Metal Contents in EPDM Films

Catalyst System	Al/M (Initial)	M/C	Al/C	Al/M
V _q	8.3	4.7×10^{-4}	4.9×10^{-3}	10.4
V _w		1.7×10^{-4}	1.4×10^{-3}	8.5
Zr _q	3000	4.7×10^{-5}	6.3×10^{-3}	135
Zr _w		4.6×10^{-5}	5.2×10^{-3}	120

V = VOCl₃/Al₂Et₃Cl₃; Zr = Et(Ind)₂ZrCl₂/MAO; q, after reaction quenching; w, after three washing steps; M, metal (V or Zr); C, carbon; Al, aluminum.

or Zr) ratio for both systems we can observe that in the case of vanadium catalyst, practically all the initial Al/V ratio present in the reactor remained in the washed polymer. On the other hand, for the zirconocene systems, only about 4 % of the initial Al/Zr ratio remained in the EPDM.

According to those results, it seems that even after three successive washing steps, we cannot remove totally the metal content proceeding either from the catalyst or from the cocatalyst. It is noteworthy that those residual metal contents might be responsible for toxicity, color, or aging of such materials. Indeed, a higher catalyst activity guarantees a lower metal content in the case of metallocene systems. Related to this fact, the highest oxidation stability shown by polymers produced by metallocene in comparison with those synthesized using Ziegler-Natta or Cr catalysts was recently discussed in terms of competing degradation reactions; this behavior was attributed to the lower metal content, although it was not determined experimentally.³⁴

Besides, it was already shown that only 18% of the V in the reaction milieu is present as active species.³⁵ In a previous study,²⁵ we observed that the Al/V molar ratio incorporated in polymers remains roughly constant (between 6.0 and 7.5) independent of the initial Al/V molar ratio in the solution, which was attributed to the percentage of active V(III) species. Then it seems that the amount of Al/V, which remains in the polymer, corresponds to the metal ratio necessary to generate the active species.

Concerning the zirconocene, although the initial Al/Zr ratio used was large, the majority of it does not seem to remain chemically bound to the polymer. Recently, it has been demonstrated by UV-vis spectroscopy that it is necessary to have an Al/Zr ratio between 140 and 150 to complete the formation of the active metallocene species.³⁶ In Table II we can see that the residual Al/Zr ratio

remained in this range. As in the case of vanadium-based system, the Al/Zr residual content is very close to that attributed to be the necessary ratio for the formation of the active species. Moreover, the fact that the greatest part of the Al present in the reaction milieu is eliminated from the polymer confirms that its role can be in part to act as an impurity scavenger, besides being a stabilizer of the catalyst active species.

CONCLUSION

Metallocene catalysts showed higher activity in the production of EPDM terpolymers with narrower molecular weight distribution but the M_w of such polymers is lower, as compared with those produced by vanadium-based catalysts.

In the case of EPDM produced by VOCl₃/Al₂Et₃Cl₃, the residual vanadium content seems to be associated in part to the presence of the diene remaining double bond, because EP rubber practically did not show residual metal content.

On the other hand, EPDM made by zirconocene catalyst exhibited lower residual metal content (10^{-5} Zr/C), as compared with that of vanadium-based catalyst (10^{-4} V/C). After polymer washing, the Al/M residual ratio is about 8.5 (for vanadium-based catalyst) and 120 (for zirconocene catalyst), which correspond to values close to those proposed in the literature for the active species.

The RBS technique was shown to provide efficient elemental analysis of the resulting polymers without the necessity of sample digestion.

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