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ORIGINAL CONTRIBUTION

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Carboxylation of linear low density polyethylene through gamma irradiation in presence of supercritical carbon dioxide. Grafted groups analysis via derivatization procedures

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Abstract A linear low-density polyethylene was gamma irradiated in presence of carbon dioxide under supercritical conditions. As already reported, this process can be an interesting way to graft carboxylated functions to the polyethylene chains. In this work a detailed analytical investigation of the carboxylation products grafted on LLDPE are presented. Derivatization procedures with sulfur tetrafluoride and nitrogen monoxide, in order to selectively convert the carboxylated functions into groups more easily identified and quantified by FTIR, were performed. The chemical nature of the grafted groups is very similar to that obtained through gamma irradiation in air; furthermore, a significant degree of crosslinking is observed.

Key words Gamma radiation – grafting – supercritical carbon dioxide – polyethylene carboxylation

Introduction

Gamma-radiation of polymeric materials can be an useful tool to modify their molecular structure and properties. It is well known that the interactions of gamma rays with polymers essentially cause the formation of free radicals which further stabilize in several ways [1]. The main molecular effects of free radicals reactions are degradation, chain branching and crosslinking, which extension depends on the molecular structure of the irradiated material and the irradiation conditions (irradiation temperature, irradiation dose rate, total absorbed dose, etc.) [2, 3].

In particular, when gamma-radiation of polymers is carried out in the presence of gases or liquids the follow up reactions generated by the free radicals formed in the system can be oriented to grafting of functional groups into the macromolecular chains [4, 5]. In the previous years, this experimental procedure has received increased attention due to the possible applications; for example, great efforts have been devoted to radiochemical-induced biocompatibilization of polymers and for the synthesis of ionic exchange membranes [6, 7]. Recently, radiation modified polyethylenes have been also proposed as compatibilizing components in polyethylene–polyamide blends [8].

Many gases or liquids can be considered as potential sources of functional grafted groups, in relation to their capability to act as radical and/or radical scavengers; among these one of the most interesting is carbon dioxide, which can be proposed for grafting of carboxylated functions in polymer chains.

Carbon dioxide is used as a building block in a large number of chemical processes and its permanent fixation through biological, catalytic and electrochemical methodologies is under investigation currently [9, 10]. Other source of interest is its use as a supercritical fluid in order to extract from various polymeric matrices monomers or oligomers, or to deliver into them guest molecules [11, 12].

In a previous work [13] we reported the first results about the irradiation of linear low-density polyethylene in the presence of carbon dioxide in both subcritical and supercritical conditions. We showed that, together with a significant increase of molecular weight, grafting of

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carboxylated functions in the polyethylene chains also occurs. In fact, IR analysis revealed the presence of absorption peaks at wave numbers of about 3400 and 1720 cm^{-1}. It is well known that these peaks can be generically attributed to several oxidized groups, i.e., carbonyl, carboxyl, ester, hydroxyl, hydroperoxide, etc. Here we present a more detailed analytical investigation performed by derivatization procedures with reacting gases, in order to selectively convert the specific carboxylation products grafted on LLDPE into groups more easily identified and quantified by FTIR.

Experimental

Materials

Carbon dioxide 99.997% was used in all the experiments.

Linear low-density polyethylene (LLDPE) RIBLENE LX ($M_w = 128\,000$, $M_w/M_n = 4.4$) was manufactured by ENICHEM and supplied in the form of pellets.

Samples preparation

Films about 50 μm thick were prepared by a twin screw laboratory extruder Brabender at 50 rpm. The temperature profile was: 157 °C, 190 °C, 205 °C, 218 °C.

The samples were kept in stainless steel reactors, carefully washed with a pure nitrogen flow before hand.

The irradiation was conducted by the IGS-3, a panoramic 3000 Ci ^{60}Co irradiator [14]. The irradiation conditions were: $T = 38$ °C; P(CO_2) = 15 MPa (corresponding to 0.8 g/cm^3 CO_2 density), dose rate 0.57 KGy/h, absorbed doses 250, 350 and 650 KGy.

Irradiated polyolefins are unstable at room temperature and can continue to slowly oxidize during storage, therefore after irradiation all the samples were stored at -30 °C until analysis was possible.

Materials characterization

Gas analysis was done on pure irradiated dense gas through a Perkin Elmer gas-chromatograph mod. Sigma 2000, equipped with a Carboxen 1000 column supplied by Supelco ($T = 160$ °C, carrier gas He, flow rate 30 ml/min, det. HWD). Moreover, for all the experiments the gaseous phase was analyzed before the irradiation, in order to control the absence of oxygen inside the reactor.

FTIR analysis was done by a Perkin–Elmer FTIR spectrophotometer mod. 1720; spectra on the same samples were recorded before and after derivatization with SF_4 or NO. Carboxylic acids were estimated as acyl fluorides after reaction with SF_4. Alcohols and hydroperoxides were converted to nitrites and nitrates, respectively, by reaction with gaseous NO in the absence of O_2. Both derivatizations were conducted in PTFE reactors under gas flow conditions and the completeness of the reaction was assured in both cases by the invariance of the absorptions in correspondence to the peaks of the derivatized functions. Unirradiated samples were subjected to the same derivatization procedure and analysis as control. The concentration of the grafted groups was evaluated by molar extinction coefficients reported elsewhere [15].

Gel extraction was carried out by a soxhlet extractor using xylene. Samples were exposed to gently refluxing solvent until constant weight was attained. In any case the extraction time was at least 72 h.

Results and discussion

Preliminary blank experiments in which supercritical CO_2 alone was gamma irradiated showed that, independently from dose and dose rate, stoichiometric correlated amounts of carbon monoxide and oxygen were chromatographically detected. Gas-analysis after the irradiation revealed the presence of small amounts of carbon monoxide and traces of oxygen which are formed through radiolitic decomposition of supercritical carbon dioxide [1].

In Fig. 1, the FTIR spectrum of an irradiated sample at 350 KGy is compared with that of the unirradiated one as reference.

As previously reported [13], the irradiation in presence of CO_2 leads to the grafting of carboxylated groups which are revealed by absorption peaks at about 1720 cm^{-1}. Furthermore, the spectral analysis indicates the presence of a weak and broad peak at about 3400 cm^{-1} due to alcoholic and/or hydroperoxide functions. It is relevant to note that the chemical nature of all these grafted groups is very similar to that observed in polyethylenes degradated through thermal, mechanical, photochemical and gamma-radiation processing in air [15–17].

The exact analytical resolution of groups present in the oxidized polyethylenes is usually complicated by their broad and overlapped absorptions. The derivatization procedures employ reacting gases such as sulfur dioxide, ammonia, sulfur tetrafluoride and nitrogen monoxide in order to selectively convert the specific oxidation products into groups more clearly identified by FTIR analysis [16, 17]. Among these, the most reliable results have been obtained by SF_4 and NO. Derivatization with sulfur tetrafluoride allows to distinguish carboxylic acid groups from ester, lactone, ketone or aldehyde groups. This reaction converts the broad absorptions of carboxylic groups

Fig. 1 FTIR spectra. (a) Unirradiated LLDPE; (b) LLDPE irradiated at 350 KGy

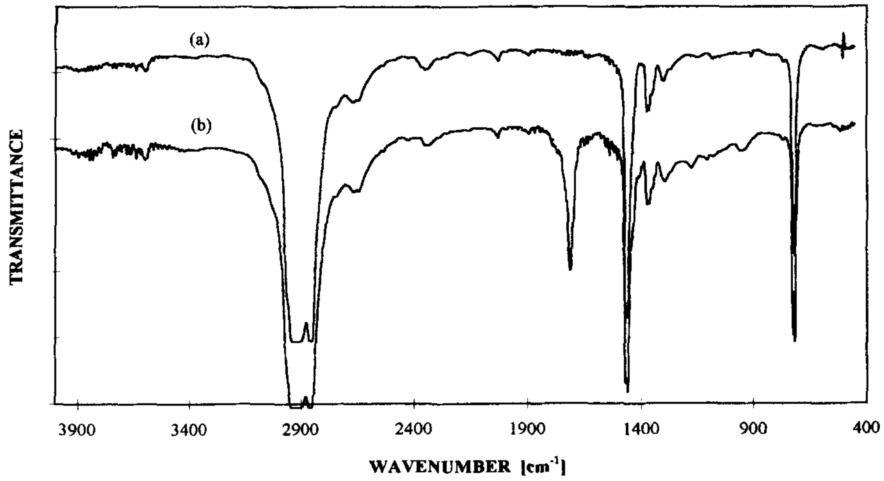
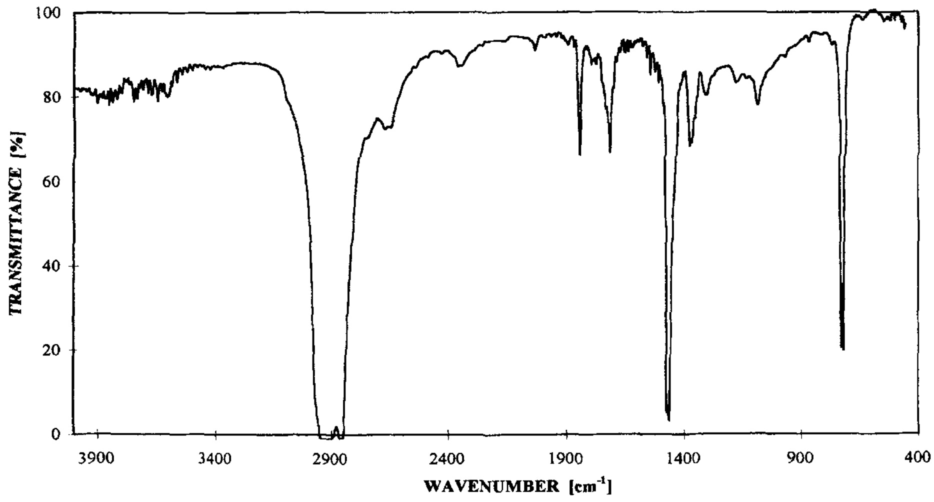


Fig. 2 FTIR spectrum of LLDPE irradiated at 350 KGy after derivatization with SF_4



into the sharp acyl fluoride bands, clearly detectable in the 1860–1820 cm^{-1} region of the spectrum, whereas the other species do not react, thus giving a simplified carbonyl envelope [15]. Nitrogen oxide reacts with alcoholic and hydroperoxide groups leading to the formation of nitrite and nitrate which absorb at different and easier detectable bands of the FTIR spectrum [16].

We used SF_4 and NO derivatization procedures to analytically resolve the chemical nature of the major groups grafted on the polyethylene irradiated in presence of supercritical carbon dioxide.

In Fig. 2, the spectrum of a sulfur tetrafluoride derivatized sample which has been irradiated at 350 KGy is shown.

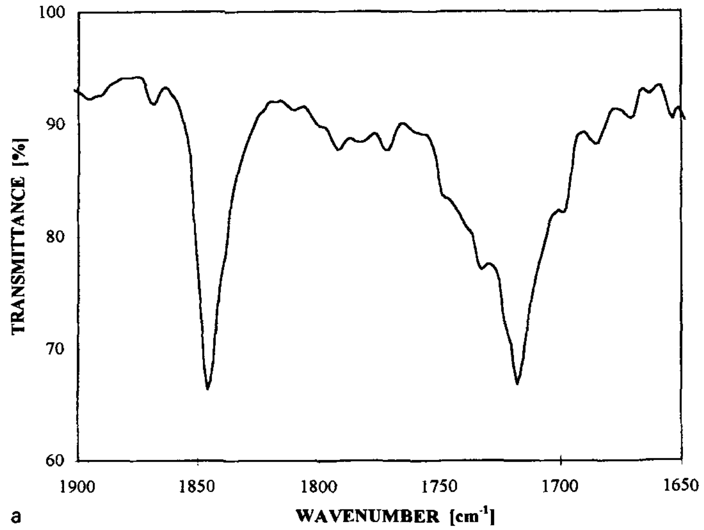


Fig. 2A Products identification of gamma irradiated and derivatizated with SF_4 LLDPE: magnification of the carboxylated groups absorptions peaks on the FTIR spectrum

a

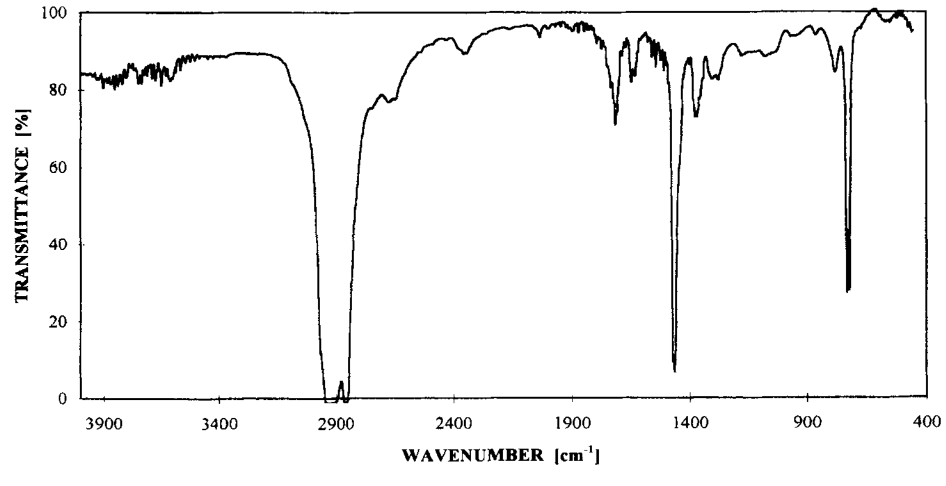
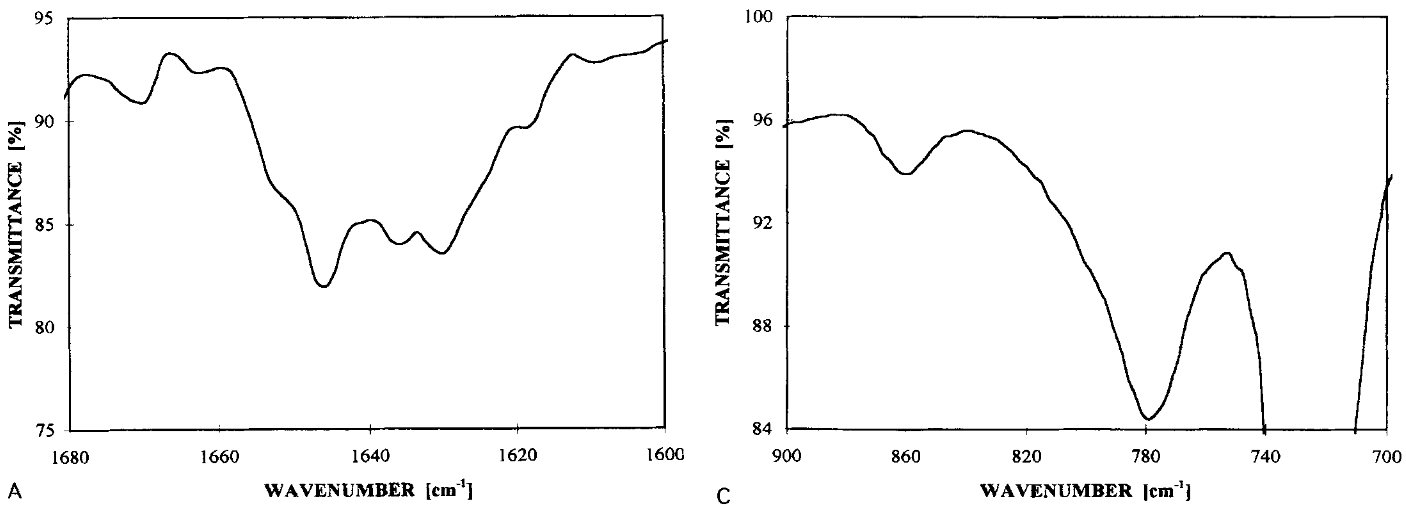


Fig. 3 FTIR spectrum of LLDPE irradiated at 350 KGy after derivatization with NO



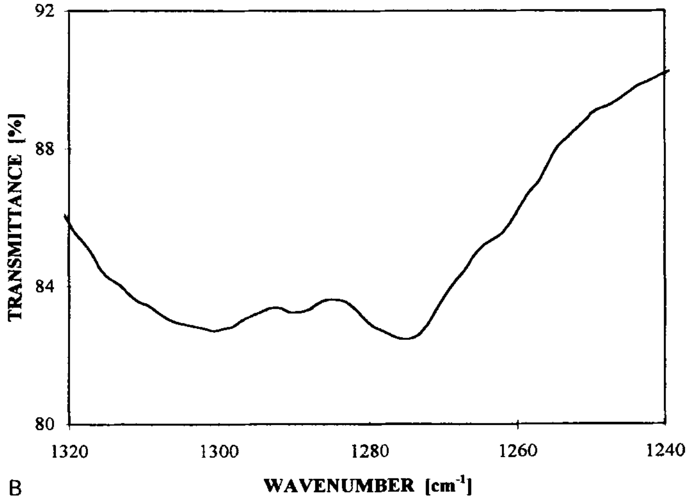


Fig. 3A, B, C Products identification of gamma irradiated and derivatizated with NO LLDPE: magnifications of the hydroxylic groups absorptions peaks on the FTIR spectrum

The underivatized sample absorption peak in the 1720 cm^{-1} region splits into two peaks lying in 1780–1700 and 1848–1839 cm^{-1} parts of the spectrum. So the presence of primary (1846 cm^{-1}) and secondary (1839 cm^{-1}) carboxylic groups and of γ-lactones (1784 cm^{-1}), esters (1748 cm^{-1}) and terminal (1725 cm^{-1}) and chain (1718 cm^{-1}) ketones has been detected, as clearly shown in Fig. 2A. Finally, the absorption peak at 1080 cm^{-1} is due to the formation of alkyl fluorides by reaction of SF_4 with alcoholic and hydroperoxide groups. In addition, SF_4 removes all OH species eliminating the problem of hydrogen-bonding-induced shifts in carbonyl absorptions, allowing valid assignments based on model compounds.

Fig. 4 Carboxylated groups concentration and gel fractions for a gamma irradiated LLDPE as function of the irradiation dose: (◆) RCH$_2$–COOH; (+) RR′CH–COOH; (▲) R–(C=O)–CH$_3$; (×) R–(C=O)–R′; (*) R–(C=O)–O–R′; (○) γ-lactone; (■) Gel, [%]

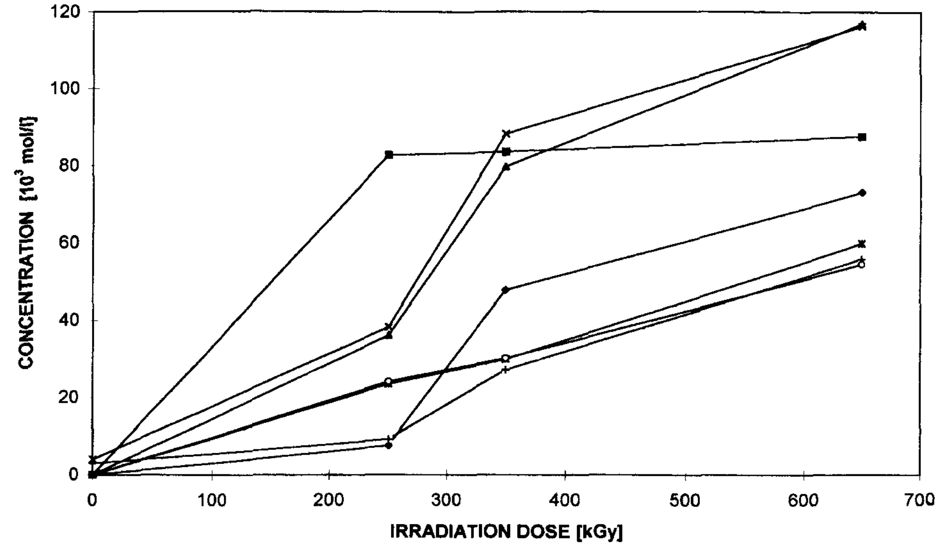
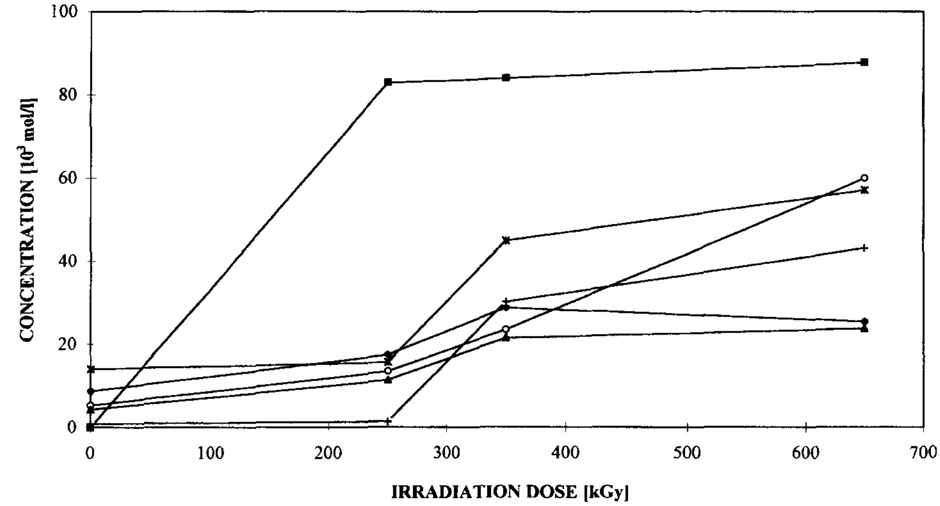


Fig. 5 Hydroxylic groups concentration and gel fractions for a gamma irradiated LLDPE as function of the irradiation dose: (◆) primary R–OH; (○) secondary R–OH; (▲) tertiary R–OH; (*) secondary R–OOH; (+) tertiary R–OOH; (■) Gel, [%]



In Fig. 3 the spectrum of the NO derivatized sample irradiated in the same conditions is shown.

The irradiation grafting of alcoholic and hydroperoxide functions in polyethylene chains is revealed by the presence of nitrite and nitrate groups. In particular, peaks at 1633, 1277, 867 cm^{-1} and 1630, 1300, 840 cm^{-1} correspond to nitrates formed from secondary and tertiary hydroperoxides respectively, while primary, secondary and tertiary alcohols are detected in correspondence to 1657, 780 cm^{-1}, 1648, 778 cm^{-1} ad 1638, 760 cm^{-1}, respectively (see Fig. 3A–C).

In Figs. 4 and 5 the concentrations of the different grafted groups for samples irradiated at various doses are reported. In both figures the gel fractions are also indicated.

As expected, the irradiation dose causes a general increase of both the concentration of the grafted groups and the insoluble fractions. It is worth noting that the gel fractions are surprisingly high considering the amount of functional grafted groups and compared to the effects on polyethylenes gamma irradiated in air, nevertheless the chemical nature of the grafted groups is the same [15–17].

All these experimental results suggest the presence of several reaction patterns, involving free radicals not only with carbon dioxide but also with other gaseous species formed in the irradiated supercritical dense gas. In fact, the formation of carboxylated species can be related to reactions of polymeric macroradicals and carbon dioxide, whereas the formation of alcoholic and hydroperoxide groups can be ascribed to reactions directly involving other oxygenated species, presumably formed by radiolytic scission of CO_2. This is in agreement with the results of the chromatographic analysis of the gas-phase after irradiation, which showed the presence of slight amounts of carbon monoxide. We can suppose that the oxygen reacts very quickly with the free radicals, leading to alcoholic and hydroperoxide groups grafted into the polymer chains. The presence of oxidative degradation reactions, due to oxygen, is also confirmed by gel fractions data which reach a plateau level lower than 100%. Of course, we cannot exclude the possibility that carbon monoxide could react with radicals and contribute to the formation of carbonyl and perhaps carboxyl groups.

Conclusions

Gamma radiation of LLDPE in presence of supercritical CO_2 causes grafting of carboxylated functions in polymer chains together with the formation of alcoholic and hydroperoxide groups. Derivatization procedures with SF_4 and NO allowed to analytically resolve these groups and to do their quantitative determination. The absorbed dose causes an increase of the concentrations of the grafted groups and of insoluble fractions. A comparison with the effects of polyethylene gamma radiation in air indicates that the chemical nature of the grafted groups is almost the same, but greater amounts of gel fractions are formed.

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