Ethylene Copolymers with Fischer-Tropsch Olefins

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SUMMARY: The properties of ethylene copolymers, terpolymers and multipolymers prepared with even and uneven carbon number linear and branched α-olefins were compared. The most likely microstructures of ethylene / linear α-olefin copolymers was assigned by considering co-unit bulkiness, average crystallizable sequence lengths and thermal properties. The higher α-olefins were found to be more effective at decreasing density, but peak melting temperatures were higher. In terpolymers where lower α-olefins such as 1-butene and 1-pentene were used as comonomers, density was decreased more than the mathematical average expected from the ratio of comonomers in the terpolymers. Peak melting temperatures were also lower. Based on NMR evidence and the microstructures of the different copolymers the rationale for this occurrence could be ascribed to decreased clustering for these terpolymers. Branched α-olefins produced ethylene co- and terpolymers with significantly decreased densities as compared to the linear α-olefins. Impact strength of these polymers was also substantially higher, even at low comonomer content. Thermal evidence indicates that the microstructure of the co- and terpolymers containing branched α-olefins are very similar to that of the copolymers prepared with linear α-olefins of the same carbon number.

Introduction

Historically, industrial development of the various polyethylenes was the result of new catalysts and processes, followed by the use of different comonomers. These comonomers were the even carbon number α-olefins such as 1-butene, 1-hexene and 1-octene obtained from ethylene oligomerization processes. While this remains a stable source of even carbon number α-olefins, uneven and branched olefins are now available from the Fischer-Tropsch process. Apart from the new ethylene copolymers produced with these odd carbon number linear and branched α-olefins, ter- and multiple polymerization using combinations of these comonomers offer an even larger number of possibilities for the industry and the polymer scientist. As previously shown[1], for copolymers having similar molar comonomer contents, densities decrease with increased branch length. WAXD measurements on ethylene / α-olefin copolymers show an increase in the a and b dimensions with increasing comonomer content which could be interpreted as incorporation of co-units into the crystalline lattice. However, with increased comonomer content, the crystallizable ethylene sequence lengths decrease, leading to decreased lamellar thickness. As already predicted in 1947 by Vand and de Boer[2], the thinner the lamellae, the smaller the lateral attraction between adjacent

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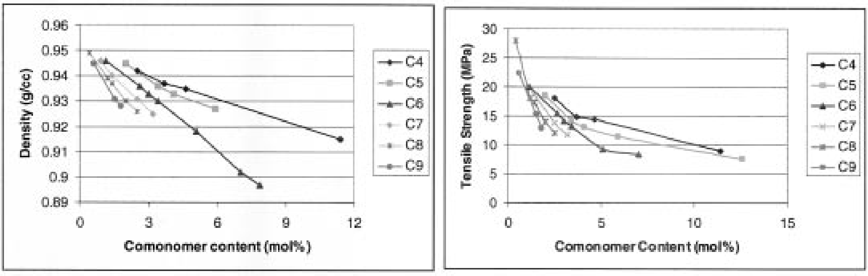
methylene groups in neighboring chains the crystal, leading to expansion of the a and b dimensions. Vonk and Reynaers concluded from SAXS measurements that the observed variations in lattice could be wholly accounted for by variations in lamellar thickness[3]. Further, the density of the amorphous layers can not be higher than that of the crystalline phases and a substantial amount of chain stems in the crystals must be connected by folds in the phase boundary. As the comonomer content and thus the concentration of the uncrystallizable sequences in the interlamellar regions rise[4], so do the fold lengths, but these longer folds do not relieve the overcrowding effect[5]. Overcrowding of the chains exiting the crystals limits lateral growth and thus restricts the crystallite thickness[6]. A heterogeneous catalyst will form heterogeneous copolymers because of differences in copolymerization characteristics of the different active sites[7] resulting in intermolecular and intramolecular heterogeneity. The heterogeneous distribution of comonomer units which result is very long and very short crystallizable sequences is therefore responsible for a range of lamellar thicknesses, the thick ones having higher melting temperatures than the thinner ones[8].

Various effects resulting from the use of different comonomers and comonomer combinations were observed and these findings are presented below.

Ethylene / α-Olefin Copolymers

Fundamental properties of some of the copolymers prepared for this study are presented in Table 1. A plot of density against comonomer content (Figure 1a) shows the influence of comonomer type and content on density. Clearly, the longer branches are more effective at reducing density than the shorter ones.



(a) (b)

Fig. 1. Comparison of comonomer type and content on copolymer density (a) and tensile strength (b)

Table 1. Properties of ethylene / α-olefin copolymers

1-Butene (%)	**Density (g/cm^3)**	**MFI (dg/min.)**	**Yield Strength (MPa)**	**Modulus (MPa)**	**Hardness**	**Impact Strength (kJ/m^2)**
2.5	0.942	1.2	18.1	650	56	14.5
3.7	0.937	2.4	14.9	499	51	16.8
4.64	0.935	2.7	14.4	450	49	21.1
11.4	0.915	1.3	8.9	243	40	35.1
1-Pentene (%)						
2.0	0.954	1.9	18.5	700	56	17.1
3.4	0.936	1.8	14.3	487	51	28.3
4.1	0.933	2.0	13.1	426	49	35.4
5.94	0.927	4.5	11.4	360	45	34.7
1-Hexene (%)						
1.15	0.946	1.1	20	760	58	12.9
2.63	0.936	4.8	15.5	514	51	27.2
5.1	0.918	3.6	9.2	342	42	35.7
7.01	0.902	0.7	8.4	336	37	33.3
1-Heptene (%)						
0.9	0.946	2.86				11.3
1.4	0.940	1.77	18.64	690		19.3
2.5	0.931	1.86	13.8	490		30.8
3.2	0.925	1.58	11.73	395		35.8
1-Octene (%)						
0.4	0.949	0.2	28.0	913	62	15.1
1.2	0.939	0.97	18.1	700	56	30.1
1.4	0.937	0.84	17.4	663	55	34
2.0	0.930	1.2	13.9	530	51	32.1
1-Nonene (%)						
0.6	0.945	1.5	22.4	826	60	16.5
1.5	0.931	0.3	15.3	607	53	40.0
1.8	0.928	0.4	13.0	532	51	51.1

As can be seen from Table 2, the calculated effect of each comonomer prepared with the particular catalyst used for this study is directly related to the length of the side chain it introduces in the copolymer.

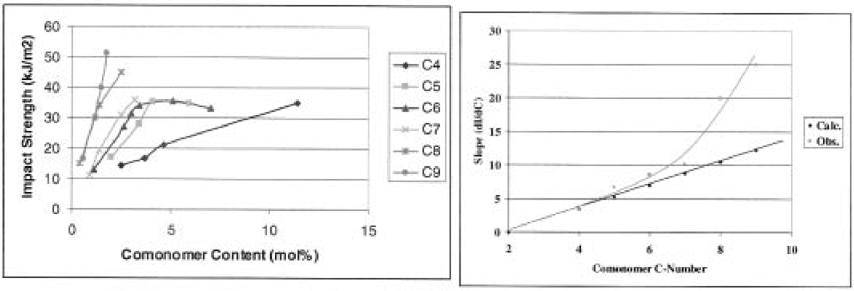
Table 2. Observed *vs.* calculated comonomer content at a fixed density of $\rho = 0.930\ g/cm^3$

Comonomer	**Branch Length**	**Relative Effect**	**Observed Content (%)**	**Calculated Content (%)**	**Difference**
1-Butene	2	1	6.5	-	-
1-Pentene	3	1.5	4.8	4.3	0.50
1-Hexene	4	2	3.3	3.25	0.05
1-Heptene	5	2.5	2.6	2.6	0.00
1-Octene	6	3	2.1	2.17	-0.07
1-Nonene	7	3.5	1.6	1.86	-0.26

The same trend as that observed for density can be seen for tensile strength (Figure 1b) and a very close correlation was observed between branch length and observed tensile strength.

However, modulus shows a significant deviation from this trend, resulting in modulus values being higher than expected from calculations based on branch length.

The slopes of the impact strength curves increase with increasing carbon number of the comonomer (Figure 2a). For impact strength a very large deviation from the expected values was observed and is shown in Figure 2b. Although not really significantly large for C_5 to C_7, values for C_8 and C_9 increased much more rapidly than what was expected.



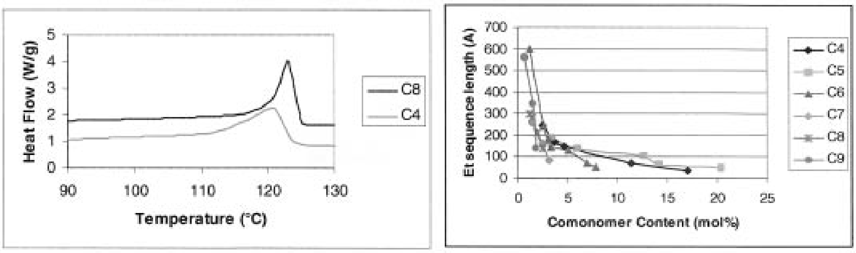
(a) (b)

Fig. 2. Effect of comonomer type and content on notched Izod impact strength (a) and deviation from the expected increase in impact strength (b)

From DSC it was observed that at the same comonomer content, even though the density is lower, the peak melting temperature of a 1-octene copolymer for example, is *higher* than that of a 1-butene copolymer (Figure 3a). This can only be the case if a significantly higher proportion of the crystallites of the 1-octene copolymer is thicker than that of the 1-butene copolymer. Because the distance between branches in a polyethylene chain limit the crystal thickness, it is believed that more chains in the 1-octene copolymer are linear or less branched. By calculating the average ethylene sequence lengths from ^{13}C NMR spectra by using Equation 1:

$$\tilde{n}_{\mathrm{E}} = (N_{\mathrm{EE}} + 0.5N_{\mathrm{EC}})/0.5\,N_{\mathrm{EC}} \qquad (1)$$

where N_{EE} is the ^{13}C NMR intensities of the CH_2 carbons of $\mathrm{E\underline{EE}E}$, $\mathrm{E\underline{EE}C}$ and $\mathrm{C\underline{EE}C}$ dyads and N_{EC} is the ^{13}C NMR intensity of the CH_2 carbons of the $\mathrm{E\underline{EC}E}$, $\mathrm{E\underline{EC}C}$, $\mathrm{C\underline{EC}E}$, $\mathrm{C\underline{EC}C}$ dyads[9], in line with the DSC results, it was found that in general, the ethylene sequences in the copolymers containing the higher α-olefins were longer than those of e.g. the 1-butene copolymers (Figure 3b). However, at the same comonomer content, branch type is not expected to have an effect on the *average* ethylene sequence lengths. For both 1-butene and 1-octene copolymers, $\tilde{n}_{\mathrm{E}}$ should be the same. A simple model considering active sites having different accessibilities that reject co-units based on size was constructed and ethylene sequence lengths of different suggested microstructures were calculated. It was found that by introducing clustered co-units into the model, the average ethylene sequence lengths can be adjusted to correspond with the experimental finding. Clustering of the lower olefins is well-known[10] and these clustered co-units for 1-butene copolymers were also clearly observed when comparing the NMR spectra of the different copolymers.



(a) (b)

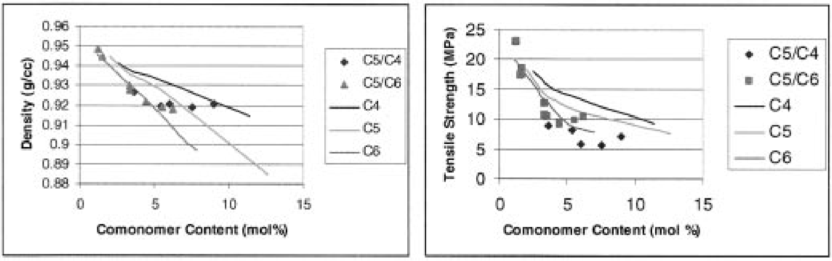
Fig. 3. Melting peak temperatures of C_4 and C_8 copolymers having similar comonomer contents (a) and ethylene sequence lengths of C_4 C_8 and C_9 copolymers (b)

Based on the DSC and NMR results, it is suggested that the microstructures of the different copolymers possibly result from the different accessibilities of the catalytic centers. If different active sites have different accessibilities and thus reject monomer units according to size, it would be expected (and may be shown by the model) that during copolymerization, large co-units would be incorporated into the polyethylene chain by fewer active sites than 1-butene for example. This results in crowding of the larger co-units in a smaller number of chains and a higher number of linear polyethylene chains or chains having very low branch content which can easily form thicker crystals having higher peak melting temperatures. The smaller co-units will be distributed between a larger number of chains, thereby decreasing the number of linear chains or chains having low comonomer contents that form thicker, higher melting crystallites.

Ethylene/1-Pentene/α-Olefin Terpolymers

It was expected that the densities of the terpolymers should be situated between those of the corresponding copolymers. Accordingly, an ethylene/1-butene/1-pentene terpolymer containing a certain total amount of comonomer was expected to have for instance a density between those of ethylene/1-butene and ethylene/1-pentene copolymer densities at the same comonomer content. This was not observed with all the comonomers. At very low (high) 1-

butene : 1-pentene ratios, the terpolymer densities tended towards those of the ethylene/1-pentene (ethylene/1-butene) copolymer densities, but at intermediate 1-butene/1-pentene ratios, densities were even lower than those of the ethylene/1-pentene copolymers. For the ethylene/1-pentene/1-hexene copolymers, the effect was smaller although densities of terpolymers having intermediate 1-pentene : 1-hexene ratios were very similar to those of the ethylene/1-hexene copolymers. In Figure 4a the densities and in Figure 4b the tensile strength of ethylene/1-pentene/1-butene and ethylene/1-pentene/hexene terpolymers are compared to those of ethylene/1-butene, ethylene, 1-pentene and ethylene/1-hexene copolymers.

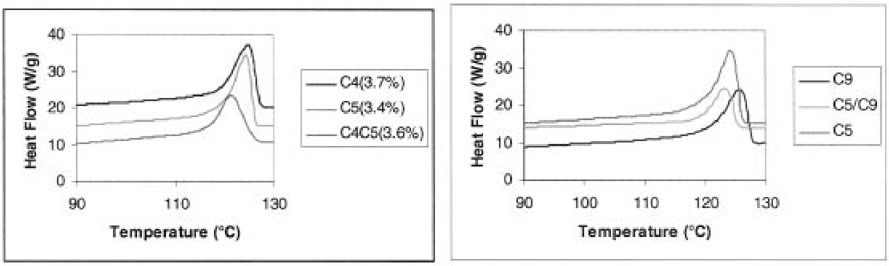


(a) **(b)**

Fig. 4. Density (a) and tensile strength (b) of 1-butene- and 1-hexene containing terpolymers as compared to the corresponding copolymers

For the α-olefins larger than 1-hexene, this effect was not observed and the densities and mechanical properties of the ethylene/1-pentene/higher α-olefin terpolymers were found to lie between those of the ethylene/1-pentene and corresponding ethylene/higher α-olefin copolymers.

The terpolymer containing 1-butene was expected to have a melting peak lower than that of the ethylene/1-pentene , but very similar to that of the ethylene/1-butene copolymer. From Figure 5a it can be seen that the peak melting temperature of the 1-butene containing terpolymer is, in fact, lower than both of the corresponding copolymers, the latter two having very similar peak melting temperatures. This similarity in peak melting temperatures of the copolymers is understood as the result of two opposing influences; a) smaller olefins are rejected by less active sites which lead to a better distribution of these units among the polyethylene chains. This leads to a decrease in the number of linear chains and thus a decrease in peak melting temperature and b) in contrast, these smaller olefins also tend to cluster more which increase the ethylene sequence lengths and thus the peak melting temperature. Overall, the effect leads to a higher peak melting temperature for the ethylene/1-butene copolymer. It therefore seems that clustering, which increases the peak melting temperature of a copolymer, occurs significantly less in the ethylene/1-pentene/1-butene terpolymers, resulting in the observed decreased peak melting temperature. Calculations of the average ethylene sequence lengths from ^{13}C NMR confirm that $\tilde{n}_E$ for ethylene/1-butene copolymers are longer than those of the ethylene/1-pentene/1-butene terpolymers[11].



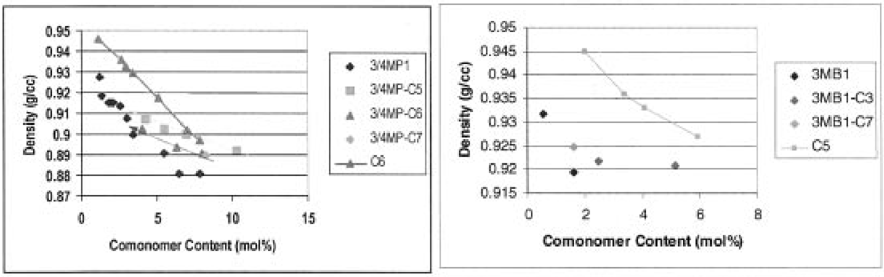
(a) (b)

Fig. 5. Melting peaks of $C_2/C_5/C_4$ (a) and $C_2/C_5/C_9$ (b) terpolymers compared to those of the corresponding copolymers

The terpolymers containing an α-olefin higher than 1-pentene such as the 1-nonene containing terpolymer of which the peak melting temperature is compared to the corresponding copolymers in Figure 5b behave as expected. Similar as described before, the higher olefins produce copolymers having larger numbers of linear polyethylene chains with high peak melting temperatures. Further, according to our interpretation, is 1-nonene not incorporated by sites that reject 1-pentene. Consequently, this does not have any significant effect on the number of linear polyethylene chains present in the terpolymer as compared to the copolymer. Accordingly, the peak melting temperatures of the etyhlene/1-pentene copolymer and the ethylene/1-pentene/1-nonene terpolymer were expected to be very similar. The peak melting temperature of the ethylene/1-pentene copolymer is slightly higher than that of the terpolymer, but since clustering of the lower olefins is known to occur, the peak melting temperature of the copolymer would be expected to be higher than that of the terpolymer.

Ethylene/Branched α-Olefin Co-, Ter- and Multipolymers

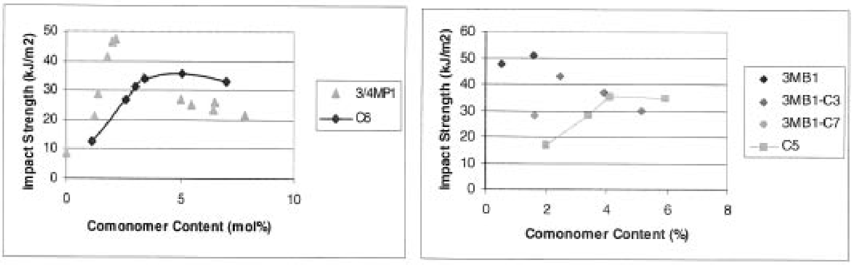
When branched α-olefins were used as comonomer, a significantly larger decrease in density was observed than that achieved using linear α-olefins. The densities of copolymers of ethylene with a C5 branched α-olefin (3-methyl-1-butene) and mixtures of C6 branched α-olefins (3-methyl-1-pentene : 4-methyl-1-pentene) were compared to those of ethylene copolymers with linear C5 and C6 α-olefins (propylene, 1-pentene, 1-hexene and 1-heptene) as well as terpolymers containing both linear and branched α-olefins. For the preparation of the multipolymers the molar content of the total branched and linear olefin fed to the reactor was kept constant while the linear vs. branched ratio was changed. In Figure 6a the sizeable difference between the densities of the ethylene / branched C6 terpolymers and the ethylene/linear C6 copolymers is shown. By changing the molar comonomer feed composition from purely linear C6 to purely branched C6, the density can be seen to progress directly to that of the ethylene/branched C6 multipolymer, with the resulting densities very close to the mathematical average expected from the feed composition. At the same ethylene/comonomer feed composition the linear C6 content in the copolymer is higher and the copolymer density is lower than that of the corresponding reaction using branched C6, but that at the same comonomer content, the branched α-olefin is clearly more effective at reducing density.



(a) (b)

Fig. 6. Comparison of ethylene/3-methyl-1-pentene/4-methyl-1-pentene (a) and ethylene/3-methyl-1-butene (b) ter- and multipolymer densities with those of ethylene/1-hexene and ethylene/1-pentene copolymers

The reactivity of the γ-branched 3-methyl-1-pentene is, similar to 3-methyl-1-butene, very low compared to that of ethylene and the amount incorporated into the polymer was found to be below 10% that of the 4-methyl-1-pentene content. Only limited amounts of 3-methyl-1-butene (<1.5%) was incorporated, but its effect on density as compared to that of the ethylene/1-pentene copolymers is evident (Figure 6b). The influence of the branch type and content on polymer properties in terpolymers containing two branched α-olefins will be investigated as a continuation of this study. In Figure 7a,b the notched Izod impact strength as a function of comonomer type and content of ethylene/branched α-olefin co- and terpolymers are compared to those of the ethylene/linear α-olefins.

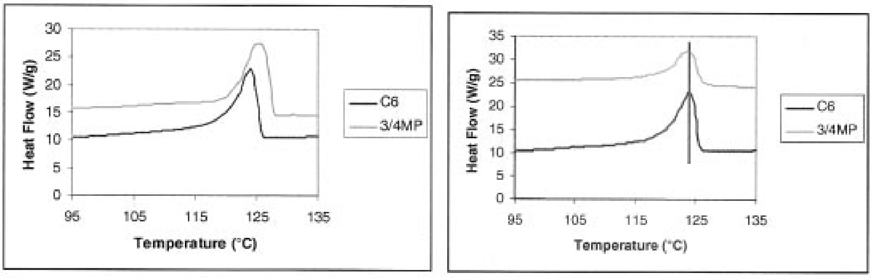


(a) (b)

Fig. 7. Comparison of ethylene/3-methyl-1-pentene/4-methyl-1-pentene (a) and ethylene/3-methyl-1-butene (b) co- and terpolymer impact strengths with those of ethylene/1-hexene and ethylene/1-pentene copolymers

It can be seen that for the copolymerisation with branched olefins the initial slope of the polymers containing branched α-olefins is steeper than that of the corresponding copolymers containing linear α-olefins. Maxima in the impact curves are thus obtained at lower comonomer contents. Therefore, despite the lower reactivities of the branched α-olefins, and the fact that not very high levels of especially the γ-branched olefins were incorporated with the catalyst used lower densities and higher impact strength copolymers were obtained.

The comonomer response of the catalyst towards the 3/4-methyl-1-pentene mixture was as sluggish as with the higher α-olefins such as 1-nonene. Moreover, the densities of the ethylene/3/4-methyl-1-pentene terpolymers were also similar to those of the ethylene/linear higher α-olefins. It was thus decided to examine the microstructure by DSC, similar to that done for the co- and terpolymers with linear α-olefins.



(a) (b)

Fig. 8. Peak melting temperatures comparing copolymers produced with linear and branched α-olefins having similar densities (a) and similar comonomer content (b)

At the same density, the branched C6 α-olefin content is lower than that of the linear C6. Therefore the average ethylene sequence lengths are longer for the branched comonomers and a higher peak melting temperature was expected and experimentally observed as shown in Figure 8a. Now, if the branched olefins are rejected by the same sites as those rejecting the higher olefins, again the average ethylene sequence length should not be influenced, but the distribution of very long and very short crystallizable sequences will. Comonomer units will be crowded into chains produced with sites capable of incorporating the co-units into the chains resulting in very short crystallizable sequences. Similarly, the sites rejecting the co-units produce very long crystallizable sequences. These chains will crystallize into thick, high melting lamellae with the overall effect of increasing the peak melting temperature of the polymers containing the branched α-olefins. As shown in Figure 8b, this was not the case. The melting temperatures are very similar which suggests that the distribution of crystallizable sequences are very similar in the copolymers produced with both linear and branched α-olefins.

Conclusions

The properties of ethylene polymers are strongly dependent on the type of comonomer used. The use of primarily linear, even carbon number α-olefins limited the application range of the ethylene copolymers produced. By introducing uneven numbered α-olefins, the change in density between different α-olefin based polyethylenes allow for smaller increments between different grades. By addition of a third α-olefin, the properties can be tailored to an even wider range of application properties. The combination of 1-butene with 1-pentene as well as 1-hexene with 1-pentene as comonomers showed better effectiveness at decreasing density that can improve the economics of such a process. Branched α-olefins has the ability to decrease density even more than what is possible with the corresponding linear α-olefins, even at low concentrations. In addition, impact strengths are also higher. The introduction of a diverse range of new comonomers offers a substantial increase in the number of application possibilities. This work may therefore be considered as a modest contribution to the studying of the important and still unexplored field of Fischer-Tropsch polymerization.

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