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Determination of Polyacetylene Molecular Weight by Radioquenching

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ABSTRACT: Polyacetylene, the precursor to a class of organometallic conductors, is insoluble and infusible. Its molecular weight cannot be determined by conventional methods. Radiotagging of the chain end with tritiated methanol has been used here to obtain the number-average molecular weight ($\bar{M}_n$). Depending upon the catalyst concentration, catalyst to activator ratio, monomer pressure, temperature, and other particular effects of crystallization–polymerization, the values of $\bar{M}_n$ were found to range from 500 to 120 000. The free-standing *cis*-polyacetylene film made by a procedure commonly employed by researchers of this field has a quite uniform $\bar{M}_n$ value of 10 500 ± 1500 for sections cut at various heights above the catalyst solution. These results make it possible to investigate the relationships between molecular weight and conductivity, crystallinity, structure, morphology, or other properties of polyacetylene.

Acetylene was first polymerized with a $Ti(OBu)_4/4AlEt_3$ catalyst, hereafter referred to as the catalyst, by Natta and co-workers.[1] Ito et al.[2] discovered a way to prepare free-standing polyacetylene film, which upon the injection of charge carriers by chemical[3] or electrochemical[4] means, resulted in more than 13 orders of magnitude increase in conductivity. These discoveries immediately attracted physicists and chemists into a joint effort of intensive investigations. Immobile and diffusive neutral defects have been shown to exist[5,6] in *cis*- and *trans*-$[CH]_x$, respectively. The neutral defects in *trans*-$[CH]_x$ have been likened to topological solitons.[7,8]

In Ziegler–Natta polymerization, the monomer undergoes cis opening of its π bond and is inserted into a Ti–σC bond of a propagating chain.[9] However, crystallization occurs simultaneously to form semicrystalline fibrils[10] which are neither fusible nor soluble. Attempts have been reported to convert polyacetylene into a soluble derivative in order to determine its molecular weight indirectly through that of the derivative. Shirakawa et al.[11] have used high temperature and H_2 pressure on n-doped polyacetylene to obtain partially hydrogenated products with $\bar{M}_n \sim 6200$. Enkelmann et al.[12] have reacted $[CH]_x$ with chlorine under mild conditions to give a product of $\bar{M}_n \sim 5900$; the $\bar{M}_n$ of the material changed upon standing for unknown reasons. These methods share certain drawbacks. Not all of the polymer was converted to the soluble derivatives, and the structures of the reaction products are ill-defined. Either the parent $[CH]_x$ or its derivatives can undergo side reactions before, during, or after the intended modifications.

The central purpose of this work was to develop a radioquenching technique for the determination of polyacetylene molecular weight and then apply the method to study the effects of catalyst concentration, $AlEt_3/Ti(OBu)_4$ ratio (Al/Ti ratio), monomer pressure, temperature, and other polymerization determinants on the polyacetylene molecular weight. This method has none of the disadvantages described above for the indirect methods.

Materials and Methods

Materials. Acetylene was purified by passage through concentrated H_2SO_4 and molecular sieves kept at 195 K. Argon was purified by passage through BTS-supported copper catalyst (BASF), molecular sieve, and KOH pellet columns. Toluene was purified by treatment with concentrated H_2SO_4, neutralized, washed, dried, distilled, and kept refluxing under an argon atmosphere in the presence of CaH_2. $Ti(OBu)_4$ was distilled under reduced pressure, $AlEt_3$ (Ethyl Corp.) was used as received.

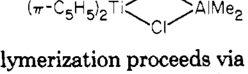
The catalyst mixture, usually in molar ratios of 4Al/1Ti unless otherwise stated, was aged at 298 K for 30 min. The monomer pressure was always less than 760 torr to avoid explosion. The monomer solubility in toluene at 1 atm of pressure has been determined[13] from 195 to 341 K; it is 0.31 M at 273 K with a heat of solution of -0.82 kcal·mol^{-1}.

Stock solution of tritiated methanol (CH_3OH^*) was prepared by adding a minute quantity of $H_2{}^*O$ of very high tritium specific activity to anhydrous methanol and stored under dry argon. The specific activity of this CH_3OH^* was determined to be 32.2 ± 2.3 mCi·mol^{-1} by liquid scintillation counting compared with known standards.

Polymerizations. All polymerizations were carried out in a 200-mL crown-capped glass pressure reactor equipped with side arms for it to function like a Schlenk-type apparatus. The reaction mixture was stirred magnetically and quenched with the injection of an amount of CH_3OH^* in excess of that required to react with the catalyst. After 1 h or more of radioquenching, the polymer was washed with 10% HCl in cold methanol and then with methanol, dried under vacuum, and assayed by combustion and subsequent liquid scintillation counting by New England Nuclear Laboratories.

Polyacetylene was formed in three distinct reaction zones with different macroscopic morphologies: film on the reactor wall (F), gel on the surface of the catalyst solution (G), and powder in the reaction medium (P). By varying polymerization conditions one type of product can be favored over the others. For instance, shaking to deposit a layer of high Ti concentration catalyst solution on the reactor wall followed immediately by the admission of monomer gave the largest yield of F. Low catalyst concentration and stirring with a magnetic bar can sometimes produce exclusively P. Medium catalyst concentration under quiescent conditions maximized the formation of G. Though they differ in gross physical appearances, all three types of polymer products share the same basic fibrous morphology as shown by transmission electron microscopy.

Determination of $\bar{M}_n$. The basis of $\bar{M}_n$ determination by radioisotope techniques had been established previously for Ziegler–Natta catalyst initiated olefin polymerizations. For instance, in the ethylene polymerization by $(\pi\text{-}C_5H_5)_2TiCl_2/AlMe^*{}_2Cl$, a ^{14}C-labeled methyltitanium species



was formed, and polymerization proceeds via insertion of ethylene into the Ti–Me* bond. Quenching of polymerization with $^{131}I_2{}^*$ labeled the polyethylene chain with $^{131}I^*$ and/or $^{14}C^*$.[14] This elaborate double radiolabeling was employed to differentiate and quantify various chain-transfer and termination processes. The values of $\bar{M}_n$ thus obtained were in agreement with values obtained by fractionation. Similarly, ^{14}C-labeled $Al(C^*{}_2H_5)_2Cl$ was synthesized and used to produce the active site $TiCl_2C^*{}_2H_5(s)$, where s represents the surface of $TiCl_3$ crystallites. The values of $\bar{M}_n$

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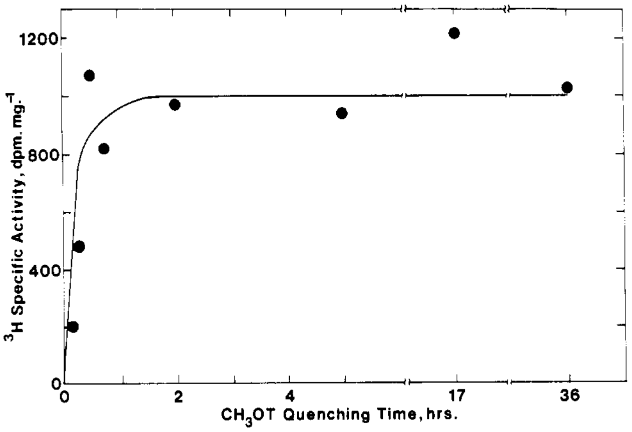

Figure 1. Specific activity of tritium in polyacetylene as a function of time of reaction with tritiated methanol. The reaction conditions are described in the text.

for polypropylene obtained by radioassay and by fractionation were in excellent agreement.[15]

Studies in our laboratories had shown that the active species derived from $Ti(OBu)_4$ and $AlEt_3$ are one or more aluminum alkyl complexes of $EtTi(OBu)_2$.[16] The propagation reaction produces polyacetylene chains bound to Ti (Ti-P). Chain transfer with $AlEt_3$ led to chains bound to Al (Al-P). Termination by oxidative coupling produced P-Ti-CH=CH-Ti-P. For this polymerization, I_2^* cannot be used for radiotagging because it is a well-known dopant for polyacetylene. In fact, I_2^* has been used to study ppm-level doped $[CH]_x$.[17] Use of radioactive $AlEt_3$ is impractical because of the large quantities of catalysts required for the acetylene polymerizations. Therefore, CH_3OH^* was the reagent of choice.

For the radioquenching method to be valid, all the metal-polymer bonds must react completely with methanol. The rates of reaction between CH_3OH^* and metal-polymer bonds have been determined at room temperature. A number of acetylene polymerizations were carried out under identical conditions: 2.5×10^{-5} mol of $Ti(OBu)_4$, 10^{-4} mol of $AlEt_3$, 20 mL of toluene, 530 torr of acetylene, 295 K, 2 h. An excess of tritiated methanol (5×10^{-3} mol) was added to each polymerization mixture and the polymer worked up after various times of reaction. Figure 1 shows the increase of specific activity in the polymer with time of reaction with CH_3OH^*. A constant specific activity was attained for reaction times of 0.5 h or longer. Therefore, the reactions are complete in about 30 min. In all subsequent experiments, 2 h was allowed for the quenching reaction.

The quenching reactions are

$$\text{Ti-P} + CH_3OT \rightarrow TiOCH_3 + PT \tag{1}$$

$$\text{Al-P} + CH_3OT \rightarrow AlOCH_3 + PT \tag{2}$$

$$\text{P-Ti-CH=CH-Ti-P} + 2CH_3OT \rightarrow (\text{CH-TiOCH}_3)_2 + 2PT \tag{3}$$

Each of reactions 1–3 has the analogous one for CH_3OH, which has a faster rate than the corresponding ones for CH_3OT due to the kinetic isotope effect. So far no ingenious method has been conceived to determine k_H/k_T separately for the Ti-P and Al-P bonds. Instead, an average kinetic isotope effect was determined by two methods, both based on the simple principle that when the number of moles of CH_3OH^* added is equal to the number of moles of reactive metal–carbon bonds, then both the CH_3OH and CH_3OT in the CH_3OH^* react equally without the isotopic effect. In the first method, the polymerization of a 20-mL mixture containing 20 μmol of $Ti(OBu)_4$ and 80 μmol of $AlEt_3$ was stopped by removing the monomer and the mixture was titrated with 78-μmol aliquots of CH_3OH^*. One hour of contact time was allowed between the addition of each aliquot. The experiment took a total of 36 h, and the total amount of CH_2OH^* added was in excess of the total number of potential metal–ligand bonds. The tritium specific activity of polyacetylene radiolabeled thusly was 3 times larger than that obtained for an idential polymerization but quenched by a single addition of an excess of CH_3OH^*. Therefore, $k_H/k_T \sim 3.0$. In the second method, a number of identical polymerizations were stopped by monomer removal, and different amounts of CH_3OH^* were added to each reaction. Figure 2a shows data for a polymerization at 263 K using a low catalyst concentration. From the ratio of maximum specific activity to the constant specific activity with an excess of CH_3OH^*, a value of $k_H/k_T = 3.4$ was obtained. In this experiment, only P-type $[CH]_x$ was formed. At higher catalyst concentration and 195 K, both G and F $[CH]_x$ were produced as shown in Figure 2b and c, respectively; the kinetic isotope effects are 2.7 for G and 2.3 for F. Therefore, both polymerization conditions and the morphology of $[CH]_x$ seem to influence k_H/k_T, which is taken to have an average value of 2.8 ± 0.4. Kinetic isotope effects have been reported to be 3.5 and 1.3 for CH_3OH^* quenching of $TiCl_4/(i\text{-}Bu)_2AlH$-catalyzed ethylene polymerization[18] and $\alpha\text{-}TiCl_3/AlEt_2Cl$-catalyzed propylene polymerization,[19] respectively.

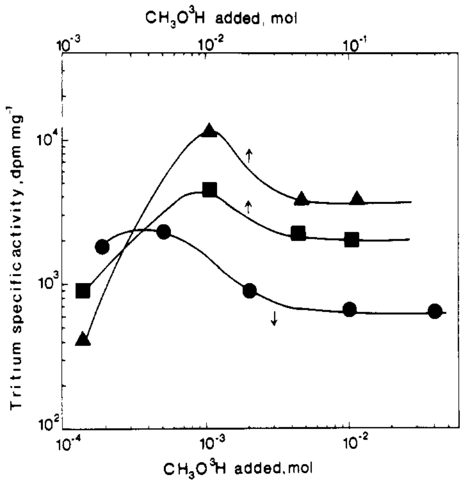

Figure 2. Specific activity of tritium-labeled $[CH]_x$ as a function of CH_3OT added: (a) (●) $[Ti]_0 = 2.0 \times 10^{-5}$ mol, temperature = 263 K, $p_{C_2H_2}$ = 460 torr, time = 2 h, powdery product; (b) (■) $[Ti]_0 = 2 \times 10^{-3}$ mol, temperature = 195 K, $p_{C_2H_2}$ = 460 torr, time = 2 h, film product; (c) (▲) same as in b, gel product.

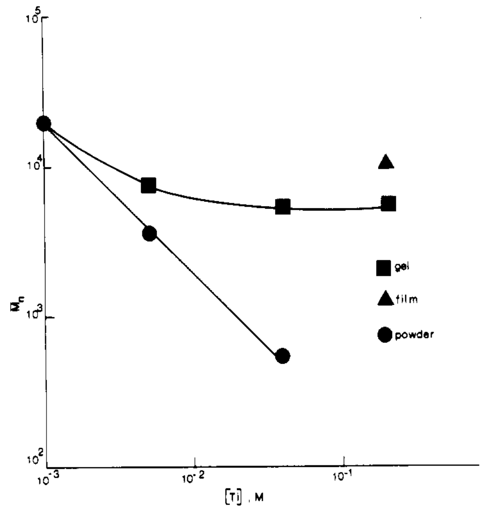

Figure 3. Variation of $\bar{M}_n$ of $[CH]_x$ with catalyst concentration for polymerization at 195 K and 460 torr of acetylene: (●) powder; (■) gel; (▲) film.

The $\bar{M}_n$ is obtained from the tritium specific activity of polyacetylene in dpm·mg^{-1}, A_{CH_x}, and specific activity of methanol ($A_{CH_3OH^*}$):

$$\bar{M}_n = \frac{A_{CH_3OH^*}(2.22 \times 10^6)}{A_{CH_x}(k_H/k_T)} \tag{4}$$

Results and Discussion

Variation of catalyst concentration was found to have strong influence on the molecular weight of polyacetylene. Figure 3 shows the $\bar{M}_n$ values obtained over a 200-fold change in the catalyst concentration. At 10^{-3} M $[Ti]_0$, only

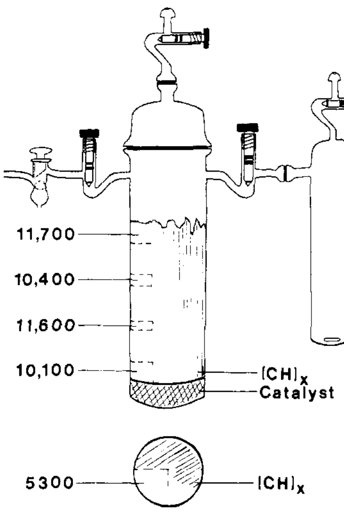

Figure 4. Molecular weight of specimen cut at various heights of the polyacetylene film and of the polymer gel.

$[CH]_x$ P was obtained with $\bar{M}_n \sim 20000$. At 0.2 M $[Ti]_0$, both G and F forms of $[CH]_x$ were obtained with $\bar{M}_n$ values of 5400 and 11 000, respectively. At intermediate $[Ti]_0$, both P and G forms of $[CH]_x$ resulted; $\bar{M}_n$ of the P polymer reached as low as 500, whereas the $\bar{M}_n$ values of the G polymers were much larger. In general the polyacetylene molecular weights in a given polymerization decrease in the order F $\sim$ G > P. This is due to two factors. The accessibility of monomer to the catalyst follows the same order. In fact the polymer gel at the surface of the catalyst solution acts as a barrier for the replenishment of depleted acetylene in the reaction medium beneath it. The second factor is chain transfer and termination, which occur much more frequently in the reaction medium because the catalyst components are present in abundance. Consequently, the P polymers formed in the catalyst solution have very low $\bar{M}_n$. In contrast, on the reactor wall, only a small amount of catalyst is deposited and most is adsorbed on the glass surface and more or less immobilized, thus greatly reducing the occurrence of the chain length limiting processes.

Since most investigations reported were made on the polyacetylene films, we carried out a study of the uniformity of such materials. Acetylene was polymerized using the conditions [Ti] = 0.20 M, Al/Ti = 4, $p_{C_2H_2}$ = 630–560 torr, and temperature = 195 K for 30 min and quenched by CH_3OH^*. These are the conditions employed commonly by researchers of the field to obtain high-quality *cis*-polyacetylene films. A 1-cm-wide specimen was cut from the free-standing film immediately above the surface of the catalyst solution. Then 0.5-, 0.5-, and 1-cm-wide sections of the film were cut at heights of 3, 5.5, and 8 cm, respectively, from the surface of the catalyst solution as shown in Figure 4. Each sample was radioassayed in quadruplicates. Virtually identical $\bar{M}_n$ values were found for the three lower specimens; the average value was 10 500 ± 1500 with a very small standard deviation. The top-most specimen had nearly the same molecular weight also, but a greater variation in the specific activity of the quadruplicates: $\bar{M}_n = 11\,700 \pm 3200$. The polyacetylene formed at the surface of the catalyst, i.e., the gel material, has a much lower $\bar{M}_n$ value of 5300 ± 1200. Consequently, the polyacetylene film is quite uniform in molecular weight.

The effect of temperature is shown in Figure 5. Above 263 K the $\bar{M}_n$ decreases with increasing temperature. This is due to different temperature dependences for the individual processes in Ziegler–Natta polymerizations. For instance, above 273 K polyethylenes obtained with the $(\pi\text{-}C_5H_5)_2TiCl_2/2AlMe_2Cl$ catalyst showed a 2.6-fold decrease of $\bar{M}_n$ for a 30 K increase in temperature,[14] and a similar effect was observed in the α-$TiCl_3/AlEt_2Cl$-catalyzed polymerization of propylene.[15] In the present case there is a threefold decrease of $\bar{M}_n$ for about a 70 K increase in temperature. Molecular weight decreases with decreasing temperature below 263 K. Our kinetic study[13] showed this to be due entirely to slow rate of propagation at low temperatures. Polymerizations of olefins by Ziegler–Natta catalysts were seldomly carried out at such low temperature.

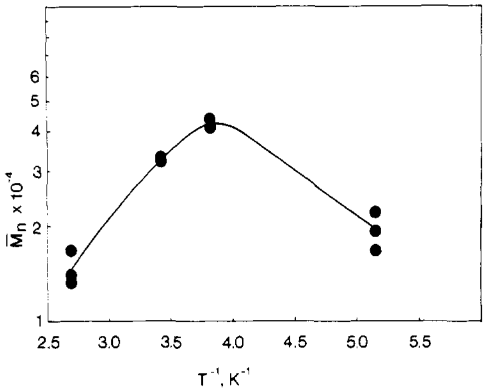

Figure 5. Variation of $\bar{M}_n$ with temperature of polymerization: $[Ti]_0 = 2.0 \times 10^{-5}$ mol, time = 2 h, $p_{C_2H_2}$ = 460 torr.

Table I
Effect of Monomer Concentration on $[CH]_x$ Molecular Weight[a]

$P_{C_2H_2}$, torr	$[C_2H_2]$, M	polym time, h	polymer morphology	$\bar{M}_n$
190	1.33	2	P	8 500, 11 600
380	2.66	2	P	18 700, 19 200
760	4.26	2	G	100 000, 40 000
760	4.26	2	G	85 100
760	4.26	0.33	G	105 000
760	4.26	1.25	G	122 000
760	4.26	4	G	120 000

[a] $[Ti]_0$ = 1 mM, temperature = 195 K.

The influence of pressure on polymerization at 195 K is shown by the results summarized in Table I. As expected, the increase of monomer concentration increases $\bar{M}_n$. The two sets of $\bar{M}_n$ values in the table are for duplicate polymerizations.

The Al/Ti ratio can affect acetylene polymerization in two ways. The first is the activation of $Ti(OBu)_4$ by reducing it to a trivalent complex. Thus, no acetylene polymerization occurred for Al/Ti < 2. At higher Al/Ti ratios the frequency of chain transfer increases, resulting in lowering of the polymer molecular weight. For polymerizations using $[Ti]_0 = 10^{-3}$ M, $p_{C_2H_2}$ = 760 torr, temperature = 298 K, and time = 2 h, the polyacetylenes obtained with Al/Ti ratios of 4, 7, and 10 have $\bar{M}_n$ values of 40 000, 6200, and 3050, respectively.

Finally, the variations of $\bar{M}_n$ with time of polymerization are shown in Figure 6 at both 195 and 298 K. The polymer chain grew rapidly at first, reaching maximum $\bar{M}_n$ values in about 30 min. There was no further increase in $\bar{M}_n$ with time at 195 or 298 K even though more polymer was formed. Thus, chain-transfer processes limit the chain growth. At 195 K there was no additional polymerization after 50 min.

Several reactions, which if they occur to a significant extent, could introduce errors to the present method of

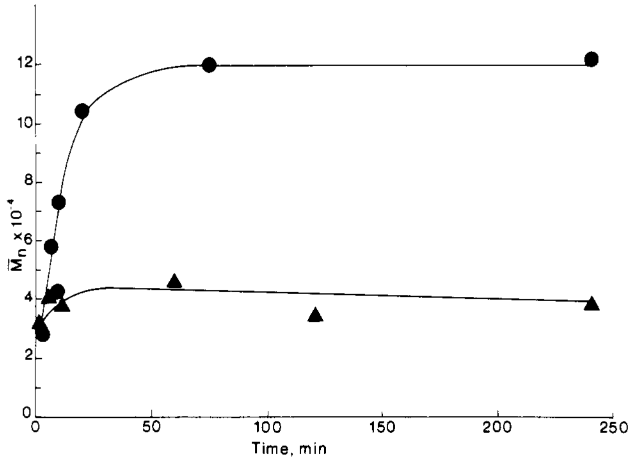

Figure 6. Variation of $\bar{M}_n$ with time of polymerization: (●) 195 K; (▲) 298 K. $[Ti]_0 = 1 \times 10^{-3}$ mol·L^{-1}, $p_{C_2H_2} = 760$ torr.

molecular weight determination. These are transfer to monomer

$$Ti\text{-}P + C_2H_2 \rightarrow Ti\text{-}C{\equiv}CH + P_{\text{-}H} \qquad (5)$$

transfer by β-hydrogen elimination

$$Ti\text{-}P \rightarrow TiH + P_{\text{-}H} \qquad (6)$$

reductive terminations

$$2Ti\text{-}P \rightarrow 2Ti + P_{\text{-}H} + P_{+H} \qquad (7)$$

and other less probable reactions having similar consequences. All of these processes yield free polyacetylene molecules which will escape labeling and make the measured $\bar{M}_n$ values higher than they actually are. Our results showed reaction 7 to be unimportant because it will tend to increase apparent $\bar{M}_n$ or leave $\bar{M}_n$ unaffected by the increase of catalyst concentration. In fact, Figure 3 showed a decrease of $\bar{M}_n$ with increasing [Ti] for the powdery polymer. With regard to the transfer processes 5 and 6, they will normally be seen as $\bar{M}_n$ independent of monomer concentration or first-order dependent on it. The present technique will have $\bar{M}_n$ increasing with acetylene pressure whether these transfer reactions are important or not. Furthermore, kinetic results to be published elsewhere[13] showed reactions 5–7 to be indeed unimportant in acetylene polymerization.

In conclusion, we have shown that radioquenching can be used to determine the $\bar{M}_n$ of $[CH]_x$. Once the polyacetylene chain is properly labeled, no subsequent reactions will alter the result. Furthermore, as the labeling was done to end the polymerization, there was no opportunity for any side reaction to occur. The technique can determine the molecular weights of polymers formed in different reaction zones. The important contribution of this work is to show how the experimental variables affect the molecular weight of $[CH]_x$. The results point the ways to prepare polyacetylene over a wide range of $\bar{M}_n$ for the purpose of establishing relationships between $\bar{M}_n$ and polymer crystal structure and morphology, soliton concentration, spin dynamics,[20] and transport properties of undoped and doped $[CH]_x$.

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Registry No. Polyacetylene (homopolymer), 25067-58-7; *cis*-polyacetylene (homopolymer), 25768-70-1; CH_3OT, 20982-51-8.

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