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Organobase-Catalyzed Carboxyl-yne Click Polymerization

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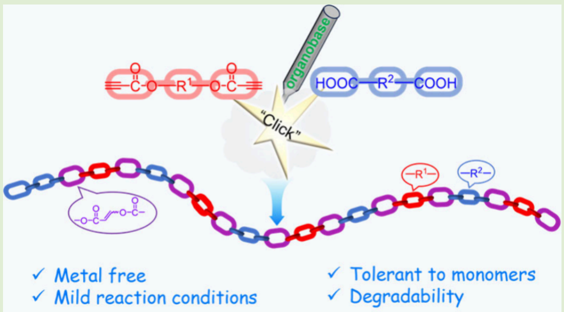
ABSTRACT: Polyesters have been widely used in the biological and engineering fields. However, the polycondensations used require high reaction temperatures and long reaction times, and the ring-opening polymerizations are generally intolerant to functional groups. Therefore, the development of a new polymerization toward polyesters under mild reaction conditions will further promote their development. In this work, we established a new organobase-catalyzed click polymerization of ester-activated alkynes and bis(carboxylic acid)s under mild reaction conditions, and regio- and stereoregular poly(β-acyloxyacrylate)s with weight-average molecular weights up to 24200 were obtained in yields up to 96%. The resultant polymers show versatile properties. The aliphatic poly(β-acyloxyacrylate)s exhibit crystalline behavior, whereas the aromatic polymers demonstrate high thermal stability. The polymer containing tetraphenylethene units exhibits the trade-off of high refractive index and Abbé Number. Thanks to the dynamic nature of β-acyloxyacrylate units, the resultant polymers could be quickly degraded upon addition of phenol derivatives and organobase, which could be applied in the fabrication of fluorescent photopatterns. Thus, this work not only provides a powerful polymerization toward polyesters and a facile reaction for postmodification of the materials containing carbonyl groups, but also enriches the family of X-yne click polymerization.



Polyesters are among the most significant polymers owing to their excellent mechanical properties and processability. Among this class of polymers, aliphatic polyesters exhibit excellent biocompatibility and biodegradability, so they are widely applied in diverse areas, such as absorbable surgical sutures, tissue engineering scaffolds, and food packaging, among others.[1−3] Furthermore, aromatic polyesters can be employed to manufacture fibers with high modulus and strength.[4]

Generally, polyesters are synthesized via three primary pathways. The first is the transesterification of dimethylesters with diols to form an intermediate diesters and oligomers, followed by polycondensation to generate the polymers; the second is the direct esterification of bis(carboxylic acid)s/diacyl chloride and diols, followed by polycondensation.[5−11] The third is the ring-opening polymerization of lactones, through which polyesters with high molecular weights and block main-chains could be obtained under relatively mild reaction conditions.[12−22] It is worth mentioning that polycondensation requires high reaction temperatures and long reaction times, and the monomers used for ring-opening polymerization need to be purified in advance by recrystallization or distillation. Furthermore, to avoid unnecessary side reactions, some functional groups, such as hydroxyl and amino groups, need to be protected and deprotected during the polymerization. All of these factors complicate the synthetic procedures.[23−27] Therefore, it is highly desirable to develop a new method to prepare polyesters with simple procedures under very mild reaction conditions.

One of the promising strategies for preparing polyesters under mild reaction conditions is an alkyne-based polymerization, as the rich chemical reactivity of alkynes enables the formation of diverse polymer structures with versatile functionalities.[28−34] Generally, the polymerizations are developed on the basis of efficient organic reactions.[35,36] It has been reported that the reaction between alkynes and carboxylic acids in the presence of ruthenium, palladium, rhodium, iridium, cobalt, silver, and gold complexes provides an efficient tool to form enol esters. These compounds have found widespread applications in organic syntheses, the pharmaceutical chemistry, and in polymer construction.[37−45] However, transition metal complexes pose challenges due to their toxicity, high cost, and, in some cases, instability in reaction solvents. Furthermore, some reactions are poorly selective.

Our groups have been working on the development of new polymerizations based on triple-bond building blocks under mild reaction conditions. In recent years we have successfully established efficient alkyne-based click polymerizations, such as

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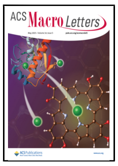

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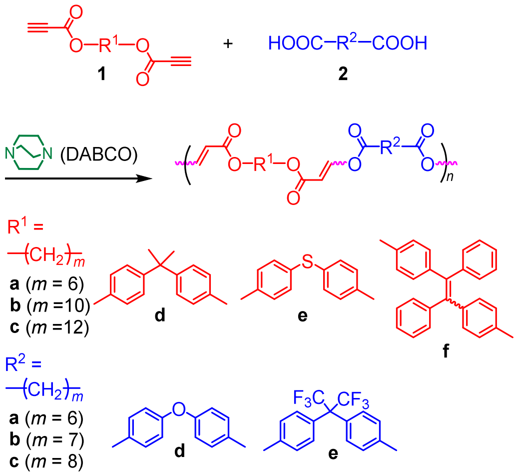
Cu(I)-, Ru(II)-, and Ni(II)-catalyzed alkyne−azide click polymerizations, as well as activated alkyne-based click polymerizations.[46−53] Notably, the activated alkyne-based click polymerizations, such as spontaneous amino-yne click polymerizations and organobase-catalyzed hydroxyl-yne click polymerizations, could be conducted under very mild reactions and generate regio- and stereoregular polymers with high molecular weights in high yields. Consequently, we have termed them as X-yne click polymerization,[54] which has been widely applied in different areas.[55−60]

Inspired by our previously developed DMAP (4-dimethylaminopyridine)-catalyzed phenol-yne and DABCO (1,4-diazabicyclo[2.2.2]octane) catalyzed hydroxyl-yne click polymerizations,[47,48] we were curious whether the carboxyl groups, which are weaker nucleophiles than the aromatic and aliphatic hydroxyl groups, could be utilized to polymerize with activated alkynes under mild conditions. Given the vast array of carboxylic acid sources, including natural amino acids, oxalic acid, and malonic acid, the successful implementation of such polymerizations would facilitate the conversion of carboxylic acid into functional polyesters and significantly enrich the realm of activated alkyne-based click polymerizations.

With this idea in mind, after systematically optimizing reaction conditions, we successfully established a DABCO-catalyzed click polymerization of bis(carboxylic acid)s and activated diynes under ambient conditions (Scheme 1). Regio- and stereoregular poly(β-acyloxyacrylate)s with weight-average molecular weights (M_w) up to 24200 were obtained in yields up to 96%. These polyesters demonstrate versatile properties, such as bright luminescence, high refractivity, and facile degradation, along with diverse applications, including high-resolution fluorescent patterning. Thus, the DABCO-catalyzed carboxyl-yne click polymerization represents an innovative approach within the realm of X-yne click polymerization, significantly enhancing the methodological toolbox for the synthesis of polyesters under exceptionally mild reaction conditions.

Scheme 1. DABCO-Catalyzed Click Polymerization of Bis(carboxylic acid)s and Dipropiolates toward the Poly(β-acyloxyacrylate)s



To establish a new polymerization, systematic screening of reaction conditions is necessary. Herein, the diyne **1a** and bis(carboxylic acid) **2a** were chosen as the representative monomers to study the polymerization conditions. First, the reaction solvent was optimized given its critical influence on polymerization. As detailed in Table S1, polymerization in dichloromethane (DCM) yielded no polymer due to the poor solubility of **2a**. Similarly, polymerizations in chloroform and tetrahydrofuran (THF) can produced only a trace amount of products. Delightfully, moderate yields were achieved in *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), and dimethyl sulfoxide (DMSO). Notably, DMSO provided the highest M_w (22200) and yield (72%) of the product and was thus selected as the optimal solvent.

Second, the effect of monomer concentration on click polymerization was investigated (Table S2). Varying the monomer concentration from 0.1 to 0.5 M had no significant impact on the M_w and yields. A concentration of 0.1 M yielded the highest M_w (23000), which was used as the optimized monomer concentration in subsequent studies.

Third, the influence of the DABCO amount on the click polymerization was examined (Table S3). At a DABCO/monomer ratio of 5 mol%, no product was obtained. However, increasing the ratio to 10 mol% resulted in a product with a M_w of 21600 and a yield of 74%. Further increases in the catalyst ratio resulted in no significant enhancement of the M_w or yields, likely due to the dynamic nature of the product.[61] Therefore, a ratio of 10 mol% was selected.

Fourth, the effect of the reaction temperature on the polymerization was studied (Table S4). Increasing the temperature from room temperature (25 °C) to 40 °C slightly enhanced the M_w and yield. However, the temperature increases led to a decrease in these values, again likely due to the products dynamicity. Consequently, reactions were conducted at 40 °C in the following experiments.

Fifth, the reaction time was optimized (Table S5). With a prolonged reaction time, the M_w remained relatively constant while yields increased slightly. A polymer with a M_w of 26000 was obtained in the highest yield of 90% at 4 h. Thus, we chose 4 h as the optimal reaction time.

Finally, other organic bases were used to catalyze the polymerization. As shown in Table S6, only DABCO could successfully catalyze the polymerization to give satisfactory results, while other bases failed to initiate the reaction. These results demonstrate that both the nucleophilicity and the basicity of the organic base are critical factors for this polymerization.

Utilizing these optimized reaction conditions, other diynes and bis(carboxylic acid)s were subjected to polymerization to assess its universality and robustness. As detailed in Table 1, the polymerizations propagated smoothly, yielding polymers **P1a2a**−**P1f2d**, with M_w values reaching up to 24200, produced in satisfactory yields up to 96%. These findings confirm the efficacy of the DABCO-catalyzed carboxyl-yne click polymerization.

The resulting polymers are soluble in low-polar solvents, including DCM, THF, and chloroform, yet remain insoluble in highly polar solvents, such as DMSO. This solubility behavior can be attributed to the conversion of polar bis(carboxylic acid)s into less polar polymeric structures during the polymerization process. Consequently, these solubility properties facilitated the characterization of the polymer structures utilizing "wet" spectroscopic techniques.

To facilitate structural elucidation of the polymers, a model compound, **M1** (Figure S1), was rationally designed and synthesized. Detailed synthetic procedures are provided in Supporting Information. Figure 1 presents the FT-IR spectra of

Table 1. DABCO-Catalyzed Click Polymerization of 1 and 2a[a]

entry	monomer	polymer	yield (%)[b]	M_w[c]	$Đ$[c]
1	**1a** + **2a**	P**1a2a**	82	20800	2.14
2	**1a** + **2b**	P**1a2b**	92	14600	2.02
3	**1a** + **2c**	P**1a2c**	86	14000	1.83
4	**1b** + **2a**	P**1b2a**	96	19900	1.98
5	**1b** + **2b**	P**1b2b**	82	15100	1.98
6	**1c** + **2a**	P**1c2a**	93	15200	1.72
7	**1c** + **2b**	P**1c2b**	86	13600	1.84
8[d]	**1d** + **2c**	P**1d2c**	80	22300	2.72
9[d]	**1d** + **2d**	P**1d2d**	79	15700	2.26
10[d]	**1d** + **2e**	P**1d2e**	70	24200	2.83
11[d]	**1e** + **2d**	P**1e2d**	80	16500	2.46
12[d]	**1f** + **2d**	P**1f2d**	78	15500	2.42

[a] Carried out in DMSO at 40 °C in air in the presence of DABCO for 4 h. [**1**] = [**2**] = 0.10 M, [DABCO] = 0.01 M. [b] Yield = m_p/m_{1+2}; m_p refers to the weight of the polymer after processing; m_{1+2} represents the sum of the weights of the corresponding monomers **1** and **2**. [c] Estimated by APC in THF on the basis of a PS calibration; M_w = weight-average molecular weight; $Đ$ = dispersity (M_w/M_n, M_n = number-average molecular weight). [d] Carried out in THF.

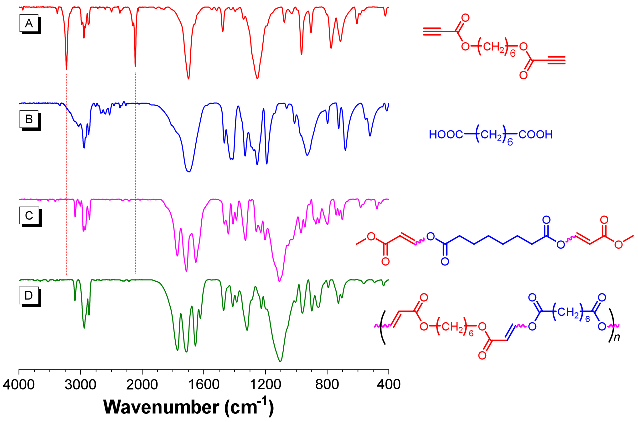


Figure 1. FT-IR spectra of monomers **1a** (A) and **2a** (B), model compound **M1** (C), and polymer P**1a2a** (D).

monomers **1a** and **2a**, the model compound **M1**, and the polymer P**1a2a**. The absorption peaks of **1a** associated with ≡C–H and C≡C stretching vibrations are observed at 3228 and 2112 cm^{-1}, respectively. However, C≡C stretching vibrations disappeared, and the absorption of the C=C stretching vibration appeared at 1622 cm^{-1} for P**1a2a**, indicating the consumption of the ethynyl groups of **1a** and the hydroxyl groups of **2a** during the polymerization process. Analogous results were observed for other polymers (Figures S2 and S3).

To further verify the polymer structures, ^1H and ^{13}C NMR spectra were measured. ^1H and ^{13}C NMR spectra of **1a** and **2a**, the model compound **M1**, and the polymer P**1a2a** are shown in Figure 2 as examples. Since the bis(carboxylic acid) **2a** could not be dissolved in $CDCl_3$, we used DMSO-d_6 as the deuterated solvent to measure the spectrum. The resonance of the ethynyl protons of **1a** in $CDCl_3$ was observed at δ 2.88, and the resonance of the carboxyl protons of **2a** in DMSO-d_6 was observed at δ 11.96. The resonant signal assigned to the vinyl protons of **M1** in $CDCl_3$ appeared at δ 8.31, 7.55, 5.71, and 5.30. The peaks at δ 8.31 and 5.71 could be assigned to the resonance of the *E* conformation of the vinyl protons, and those at δ 7.55 and 5.30 are for the *Z* conformation of the vinyl protons. Similar resonance peaks of the vinyl groups, as observed in **M1**, were also found at δ 8.30, 7.53, 5.71, and 5.29 in P**1a2a** in $CDCl_3$. Comparable results were obtained for other polymers (Figures S4–S6). Notably, the ratio of *E*-isomeric units in the polymers could be calculated from their integrals, which could be as high as 100% (Table S7). These results unambiguously indicate that our developed DABCO-catalyzed carboxyl-yne click polymerization is regio- and stereoselective and is a new kind of X-yne click polymerization given its mild reaction conditions. The ^{13}C NMR spectra further substantiate the conclusions drawn from ^1H NMR spectral analysis (Figure 2). The resonant peaks of the carbon atoms of the ethynyl groups of **1a** at δ 74.86 and 74.69 could not be observed in the spectrum of P**1a2a**. Instead, the resonance peaks of the vinyl carbon atoms at δ 149.64 and 105.92 appeared, suggesting that it was converted by the polymerization. Similar results were observed for other polymers (Figures S7–S9).

The thermal stability of the resultant polymers was assessed by using thermogravimetric analysis (TGA, Figure S10). The results indicated that the temperatures for 5% weight loss (T_d) of the poly(β-acyloxyacrylate)s are all above 215 °C. Notably, polymers derived from monomers containing an aromatic unit exhibited even higher T_d (>240 °C), attributed to the enhancement of decomposition temperatures by the aromatic units. Additionally, aliphatic poly(β-acyloxyacrylate)s, containing both ester groups and long alkyl chains that facilitate chain packing, exhibit crystallization behavior. Consequently, we analyzed the DSC curves of aliphatic poly(β-acyloxyacrylate)s. As depicted in Figure S11, these polymers exhibit obvious distinct crystal melting behaviors, with crystallization-melting temperatures ranging from 70 to 100 °C. The crystallization property was further confirmed by wide-angle X-ray diffraction (WAXD, Figure S12). Meanwhile, poly(β-acyloxyacrylate)s containing aromatic units exhibited only glass transitions in DSC analysis, with no observable crystallization or melting behaviors. This apparent suppression of crystallinity can be rationalized by the chain-packing disruption caused by bulky aromatic units, as further confirmed by WAXD analysis (Figure S13).

Optical materials exhibiting high refractive indices (n) and low dispersion possess significant potential for applications in the fields of optical lenses, liquid crystal displays, and organic light-emitting diodes, among others. Thanks to the advantages of low cost, good impact resistance, thermal stability, high mechanical properties, chemical corrosion resistance, etc., polymeric materials have progressively replaced inorganic optical materials in various applications. Nevertheless, conventional optical materials with high n values often result in low Abbé Numbers. Consequently, there is a compelling need to develop optical materials that concurrently exhibit high n values and high Abbé Numbers. The resultant poly(β-acyloxyacrylate)s, which incorporate polar groups, such as esters and aromatic units, are expected to demonstrate high n values. Indeed, the experimental results confirm that P**1d2d**–P**1f2d** have a trade-off of a high n value (≥1.6) and large Abbé Numbers (26.7–53.1) at 589 nm (Figures 3 and S14, and Table S8). The n values of poly(β-acyloxyacrylate)s are markedly higher than those of commonly used plastics, such as poly(methyl methacrylate) (PMMA, 1.49) and polycarbonate (PC, 1.59). Moreover, these polymer films exhibit a high transparency in the visible region (Figure S15). It is worth

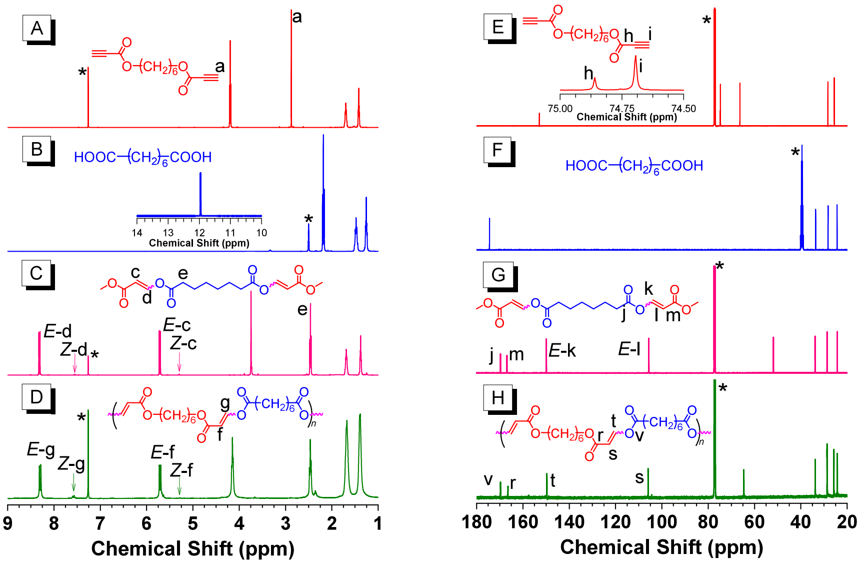


Figure 2. ^{1}H NMR spectra of **1a** (A), **2a** (B), **M1** (C), and P**1a2a** (D). ^{13}C NMR spectra of **1a** (E), **2a** (F), **M1** (G), and P**1a2a** (H). Since **2a** could not be dissolved in $CDCl_3$, it was dissolved in DMSO-d_6 to measure the spectrum. The others were dissolved in $CDCl_3$ for the measurement. The solvent peaks are marked with asterisks.

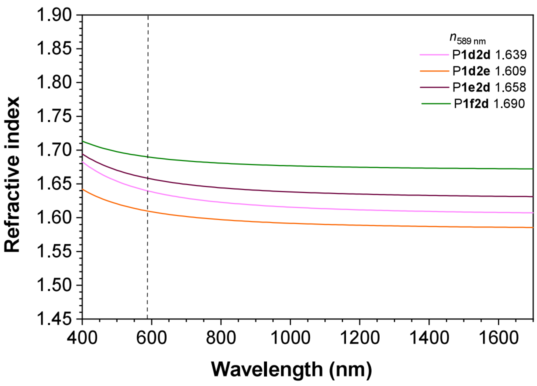


Figure 3. Light refraction spectra of thin solid films of polymers P**1d2d**–P**1f2d**.

noting that polymer P**1f2d** containing a tetraphenylethene (TPE) unit exhibits an *n* value of 1.690 and an Abbé Number of 53.1, which is of great significance for achieving the compatibility of a high *n* value and high Abbé Number.

Similar to the products generated by amino-yne and hydroxyl-yne click polymerizations, the *β*-acyloxyacrylate units in poly(*β*-acyloxyacrylate)s also show dynamic behavior. For instance, upon the addition of *p*-methylphenol to a DMSO solution of P**1f2d** in the presence of DMAP at room temperature, its M_w value rapidly dropped from 15500 to 1200 (Figure S16) via the transesterification reaction. Afterward, the M_w values remained virtually unchanged. Notably, the degradation products could be separated and thoroughly characterized (Figures S17–S19).

By incorporating the classical aggregation-induced emission (AIE) unit TPE into its backbone, polymer P**1f2d** exhibits the AIE activity (Figure S20). The photoluminescence quantum yield (Φ_F) of P**1f2d** increases from 7.3% in solution to 18.1% in the film state, confirming its aggregation-enhanced emission (AEE) feature.

Leveraging the above unique properties, a two-dimensional fluorescent pattern of P**1f2d** was fabricated via transesterification. Specifically, a DMSO solution containing *p*-methylphenol and DMAP was sprayed onto a masked polymer film for 5 min, followed by washing to remove degraded low-molecular-weight products. Alternatively, fluorescent photopatterning was achieved by UV irradiation (365 nm) through a photomask for 20 min. The irradiated regions became nonemissive due to photo-oxidation, while the masked areas retained their fluorescence (Figure 4).

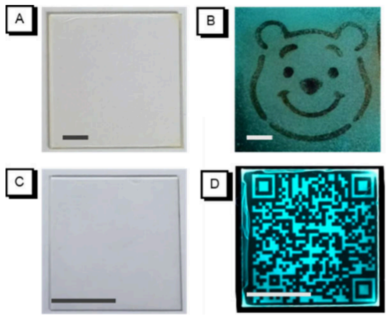


Figure 4. Two-dimensional fluorescent pattern generated by the transesterification reaction and UV irradiation of a thin film of P**1f2d** in air. Chemical patterning under daylight (A) and UV lamp at 365 nm (B). Photopattern under daylight (C) and UV lamp at 365 nm (D). Scale bar: 1 cm.

In conclusion, in this work, a new DABCO-catalyzed click polymerization of ester-activated diynes and bis(carboxylic acid)s was successfully established under mild reaction conditions. Under optimal reaction conditions, regio- and stereoregular poly(*β*-acyloxyacrylate)s with M_w values up to 24200 were obtained in yields up to 96%. The resultant aliphatic poly(*β*-acyloxyacrylate)s are crystalline. The polymer containing TPE units is AEE-active and shows a high *n* value of 1.690 and a high Abbé Number of 53.1. Moreover, the *β*-acyloxyacrylate units in the polymers show a dynamic nature, making the polymers degradable upon addition of *p*-methylphenol and DMAP through a transesterification reaction. Taking this feature, a two-dimensional fluorescent photopattern could be constructed. Moreover, the fluorescent photopattern could also be fabricated by a photo-oxidation reaction. Thus, the established DABCO-catalyzed carboxyl-yne click polymerization represents new progress toward an activated alkyne-based click polymerization and will find wide application in the preparation of new functional polymers and postmodification of materials containing carbonyl groups.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.5c00123.

> Chemicals, instrumentation, synthetic procedures, ^{1}H and ^{13}C NMR spectra, and the thermal and photophysical spectra (PDF)

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Author Contributions

[#]H.S. and J.Z. contributed equally to this work. A.Q. and B.Z.T. conceived and designed the experiments and supervised the research. All authors discussed the results and commented on the manuscript.

Notes

The authors declare no competing financial interest.

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