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H. R. Kricheldorf^a; G. Behnken^a; M. Sell^a

^a Institut für Technische und Makromolekulare Chemie, Hamburg, Germany

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Influence of Isosorbide on Glass-Transition Temperature and Crystallinity of Poly(butylene terephthalate)

H. R. KRICHELDORF, G. BEHNKEN, and M. SELL

Institut für Technische und Makromolekulare Chemie, Hamburg, Germany

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Copolyesters of isosorbide and 1,4-butane diol were prepared by Ti(OBu)₄-catalyzed transesterifications with dimethyl terephthalate in bulk at temperatures up to 250°C. The content of isosorbide was considerably lower than expected from the feed ratio and the molar masses were low, so that no DSC measurements were conducted. Copolycondensations of isosorbide and 1,4-butane diol with terephthaloyl chloride were either performed in dichloromethane at 40°C or in toluene at 100°C. The second method gave the higher molar masses. However, both series of polycondensations had the content of isosorbide roughly paralleled the feed ratios in common. The DSC measurements revealed that even 6 mol% of isosorbide is sufficient to raise the glass-transition temperature (T_g) by 10–12°C (up to 55°C). With 50 mol% of isosorbide, the T_g reaches 100°C. Yet, incorporation of isosorbide also reduces the melting temperature T_m and the degree of crystallinity, and a mol percentage above 30% prevents crystallization completely. In summary, incorporation of isosorbide allows for fine-tuning of T_g and T_m of poly(butylene terephthalate) over a wide range.

Keywords: poly(butylene terephthalate); isosorbide; polycondensation; glass-transition

1 Introduction

Long term problems for mankind is warming of the climate and exhaustion of oil resources. One answer (of course not the only one) is the production and application of materials from renewable resources. In the field of polycondensates only few difunctional monomers are available which can be produced at sufficiently low costs. One of these monomers is isosorbide (anhydrosorbitol) which is technically produced from glucose. This situation has prompted numerous research groups to study syntheses and properties of various types of homopolymers based on isosorbide. A review article (1) summed up the pertinent literature up to 1996. Meanwhile, at least fourteen more papers and patents have appeared (2–15).

Incorporation of isosorbide into known polymers may be of interest for three reasons. First, isosorbide introduces chiral centers as an effect which is particularly interesting for the preparation of cholesteric materials. Second, the thermal stability and stability against oxidation is higher than that of α,ω -dihydroxy- or diaminoalkanes. Third, isosorbide units may raise the glass-transition temperature (T_g) compared to polymers derived from α,ω -dihydroxyalkanes. In cases

such as poly(ethylene terephthalate), PET, or poly(ethylene-1,6-naphthalene dicarboxylate), PEN, where the T_g s are high, incorporation of isosorbide will only have relatively small effect. Nonetheless, four patents dealing with PET containing a low percentage of isosorbide have been disclosed (3, 4, 7, 8). However, in the case of poly(butylene terephthalate) PBT the T_g is relatively low (around 45°C) and thus, incorporation of isosorbide may cause a considerable enhancement of the T_g in as much, as the T_g of the homopolymer poly(isosorbide terephthalate) PIT is known to be as high as 195–200°C (1). Therefore, it was the purpose of the present work to study the influence of isosorbide as comonomer on T_g and crystallization of PBT. Since reactivity of isosorbide is quite different from that of 1,4-butane diol it is not a triviality to synthesize copolyesters with a random sequence of both monomers and a broad variation of the composition. Therefore, two different synthetic methods were used and compared.

2 Experimental

2.1 Materials

Isosorbide 1,4-butane diol, dimethyl terephthalate and terephthaloyl chloride were purchased from ACROS Organics (Geel, Belgium). Isosorbide was recrystallized from acetone and dried over P₄O₁₀. 1,4-butane diol was azeotropically dried with toluene and distilled *in vacuo*. Pyridine was

Address correspondence to: H. R. Kricheldorf, Institut für Technische und Makromolekulare Chemie, Hamburg, Germany. E-mail: kricheld@chemie.uni-hamburg.de

distilled over freshly powdered calcium hydride. Dichloromethane and toluene were distilled over P_4O_{10} .

2.2 Polycondensations

(A) Transesterification of dimethyl terephthalate (DMT, No. 5, Table 1). Isosorbide (60 mmol), 1,4-butanediol (60 mmol) and DMT (60 mmol) were weighed into a cylindrical glass reactor equipped with mechanical stirrer, and gas-inlet and gas-outlet tubes. $Ti(OBu)_4$ (0.06 mmol) was injected in the form of a 0.5 M solution in toluene. The reaction vessel was placed into an oil bath preheated to 150°C and the temperature was rapidly raised to 180°C. The temperature was then raised to 190, 200, 220 and 240°C in time intervals of 0.5 h. At 240°C, vacuum was applied for an additional 15 min. Finally, the reaction mixture was stirred at 250°C for 1 h *in vacuo*. The crude product was characterized. Analogous polycondensations were conducted with variation of the feed ratio. (B) Acylation with terephthalate chloride in toluene (No. 6, Table 3). Isosorbide (20 mmol), 1,4-butanediol (20 mmol) and terephthaloyl chloride (40 mmol) were weighed into a 150 mL three-neck round bottom flask (equipped with mechanical stirrer) and dry toluene (40 mL) was added. After heating to 100°C, pyridine (100 mmol) was added via a syringe under an atmosphere of dry nitrogen. Stirring at 100°C was continued for 2 d, and after cooling, the reaction mixture was poured into methanol (500 mL) and the precipitated polymer was isolated by filtration.

Analogous polycondensations were conducted with a variation of the feed ratio.

2.3 Measurements

The inherent viscosities were measured in dichloromethane containing trifluoroacetic acid (volume ratio 4:1) with an automated Ubbelohde viscometer thermostated at 20°C. The

Table 1. Thermal copolycondensation^a of isosorbide and 1,4-butane diol (BD) with dimethyl terephthalate (DMT) in bulk catalyzed by $Ti(OBu)_4$

Exp. no.	DMT/Isos./ 1,4-BD ^b	mol% Isosorbide in feed	mol% ^c Isosorbide (found)	η_{inh}^d (dL/g)
1	10.0/10.0/25.0	29	11	0.13
2	10.0/10.0/25.0	29	9	0.08
3	10.0/10.0/17.0	37	22	0.09
4	10.0/10.0/13.5	43	25	0.10
5	10.0/10.0/10.0	50	23	0.37
6	10.0/5.0/10.0	33	21	0.17
7	10.0/10.0/ - 0.0	100	100	0.11

^aTemperature/time program: 0.5 h at 180°C, 190°C, 200°C, 220°C, 240°C + 0.25 h at 240°C with vacuum + 1 h at 250°C with vacuum.

^bMolar feed ratio.

^cContent of isosorbide units as determined by 1H NMR spectroscopy.

^dMeasured at 20°C with $c = 2$ g/L in CH_2Cl_2 /TFA (volume ratio 4:1).

400 MHz 1H NMR spectra were recorded on a Bruker "Avance 400" FT spectrometer in 5 mm o.d. sample tubes. $CDCl_3$ containing trifluoroacetic acid (volume ratio 4:1) served as solvent and internal TMS for shift referencing. The DSC measurements were performed on a Mettler Toledo Md 821 at a heating rate of 10°C/min. The T_g s were determined from the second heating. The T_m s and melting enthalpies were determined from the first heating after annealing for 6 d at 150°C. The MALDI-TOF mass spectra (m.s.) were measured on a Bruker Biflex III equipped with a nitrogen laser ($\lambda = 337$ nm). All m.s. were recorded in the reflection mode with an acceleration voltage of 20 kV.

3 Results and Discussion

3.1 Copolycondensations with Dimethyl Terephthalate

The standard method for the technical production of PBT and also for the preparation of PBT on the laboratory scale consists of the polycondensation of 1,4-BD with DMT in the presence of a transesterification catalyst (Equation (1)). The most efficient and most widely used catalyst for such polycondensations is $Ti(OBu)_4$, which may be used as a neat compound or in combination with additives slightly enhancing its reactivity (16, 17). Yet, it is also well known that $Ti(OBu)_4$ -based catalyst causes side reactions such as formation of cyclic ethers (e.g. tetrahydrofuran) or linear ethers (e.g. diethylene glycol) (18). Nonetheless, the first series of polycondensations studied in this work was based on the standard method using neat $Ti(OBu)_4$ as catalyst in a feed ratio of 1:1000 relative to DMT. The maximum temperature was limited to 250°C because higher temperatures accelerate side reactions considerably (18, 19). The feed ratio of isosorbide and 1,4-BD was varied, but one attempt was made to synthesize the homopolyester from neat isosorbide (experiment No. 7, Table 1). The results obtained from these polycondensations comprise two noteworthy aspects. First, the rate of incorporation of isosorbide was rather low. For instance, in experiment No. 5, Table 1, the percentage of isosorbide in the feed ratio was 50% (relative to the sum of both diols), but the copolyester contained only 25 mol%. A systematic variation of the content of isosorbide over a broad range (e.g. from 5 to 50 mol%) proved to be difficult. Second, with exception of experiment No. 5, the inherent viscosities of all PBIT(co)polyesters were low, so low, that it did not make sense to characterize their thermal properties.

3.2 Polycondensations with Terephthaloyl Chloride

A classical method for the preparation of polyesters on the laboratory scale is the polycondensation of diols with dicarboxylic acid dichlorides in the presence of tertiary amine which serves as catalyst and HCl acceptor (Equation (2)). Using pyridine as base and catalyst, one series of polycondensations was performed in dichloromethane at 40°C (Table 2).

Table 2. Copolycondensations of terephthaloyl chloride (TC) with isosorbide and 1,4-butane diol in CH₂Cl₂ at 40°C

Exp. no.	TC/Isos./ 1,4-BD ^a	mol% Isosorbide in feed	mol% ^b Isosorbide (found)	η_{inh}^c (dL/g)	T _g ^d (°C)	T _m ^e (kJ/mol)	ΔH_m^e (J/g)
1	10.0/1/9	10	6	0.24	55	212	40.4
2	10.0/2/8	20	15	0.15	60	197	21.0
3	10.0/3/7	30	25	0.25	68	181	11.7
4	10.0/4/6	40	36	0.32	84	—	—
5	10.0/5/5	50	46	0.33	97	—	—

^aFeed ratio in mmol.^bContent of isosorbide units as determined by ¹H-NMR spectroscopy.^cMeasured at 20°C with c = 2 g/L in CH₂Cl₂/TFA (volume ratio 4:1).^dDSC measurements with 10°/min, 2nd heating.^eDSC measurements with 10°C/min after annealing at 150°C, 1st heating.

It was hoped that this approach allows for the incorporation of isosorbide at a rate corresponding to the feed ratio. The results summarized in Table 2 indeed confirmed that the isolated polyesters contained a mol percentage of isosorbide which came close to the feed ratio, and thus, a systematic variation of the composition of the copolyesters was feasible. On the other hand, the inherent viscosities were again non-satisfactory, but slightly higher than those obtained before (Table 1). Nonetheless, the copolyesters resulting from these polycondensations were characterized by DSC measurements, which will be discussed below.

To obtain higher molar masses, a third series of polycondensations was performed, and three experimental parameters were changed. First, toluene was used as reaction medium and the temperature was raised to 100°C (Table 3). These conditions were selected, because another research group had reported on satisfactory results for polycondensations of isosorbide with terephthaloyl chloride (or other dicarboxylic acid dichlorides) (20). In this work, the polycondensation of

neat isosorbide with terephthaloyl chloride was repeated and a homopolyester with an inherent viscosity of 0.51 dL/g was obtained (No. 7, Table 3).

The third parameter, which was changed, concerned the stoichiometry. Two polycondensations were conducted with a feed ratio of 3/7 (Nos. 3 + 4, Table 3) and an exactly equimolar amount of terephthaloyl chloride (relative to the sum of both diols) or with an excess of one mol%. With this excess, the inherent viscosity was much lower than with perfectly equimolar stoichiometry. This result looks reasonable at first glance, but it was found in numerous previously studied polycondensations (21, 22) that an excess of the electrophilic monomer around 1–2 mol% is usually advantageous for optimization of the molar mass. However, the results of polycondensations Nos. 3 and 4 (Table 3) prompted us to perform all other experiments of this series with exactly equimolar stoichiometry. The positive outcome of all these changes were inherent viscosities which, on the average, were higher than those of both preceding series.

Table 3. Copolycondensations of terephthaloyl chloride (TC) with isosorbide and, 4-butane diol in toluene at 100°C

Exp. no.	TC/Isos./1,4-BD ^a	mol% ^b Isosorbide in feed	mol% ^b Isosorbide (found)	η_{inh}^c (dL/g)	T _g ^d (°C)	T _m ^e (kJ/mol)	ΔH_m^e (J/g)
0	Poly(butylene terephthalate)	0	0	0.	—	226	44.0
1	10.0/1/9	10	6	0.31	55	208	35.5
2	10.0/2/8	20	18	0.46	58	191	21.0
3	10.0/3/7	30	24	0.22	84	162	—
4	10.0/3/7	30	25	0.74	80	190	17.0
5	10.0/4/6	40	30	0.47	78	155	—
6	10.0/5/5	50	42	0.30	92	—	—
7	10.0/10/0	100	100	0.51	197.5	—	—

^aFeed ratio in mmol.^bContent of isosorbide units as determined by ¹H-NMR spectroscopy.^cMeasured at 20°C with c = 2 g/L in CH₂Cl₂/TFA (volume ratio 4:1).^dDSC measurements with 10°/min, 2nd heating.^eDSC measurements with 10°C/min after annealing for 6 d at 150°C, 1st heating.

The content of isosorbide was somewhat lower than expected from the feed ratio, but it paralleled the feed, so that a variation from 6 to 42 mol% was feasible.

Since in contrast to series 1, the polycondensations of terephthaloyl chloride are kinetically controlled or, in other words, irreversible polycondensations, the sequences of isosorbide and 1,4-butane diol are not necessarily random in nature and may depend on the reaction conditions. Different sequences may, in turn, have an influence on the thermal properties of PBITs as discussed below. Frequently, the ^{13}C -NMR signals of the CO-groups are best suited for NMR sequence analyses (23–25), but in the case of PBIT, the CO-signal is unfavorable because of the low signal-to-noise-ratio and because of an unfavorable position relative to the diol units. Therefore, the ^1H -NMR signals of the aromatic protons were studied in more detail. The signal pattern of the PIT homopolymer presented in Figure 1A, displayed indeed four strong signals resulting from the exo-exo, endo-endo and endo-exo combinations of the isosorbide units. The inner pair of peaks results from the endo-exo combination, which has the consequence that both pairs of terephthaloyl protons are not equivalent (the vicinal coupling is not taken into account). The signal pattern of the copolyesters proved highly complicated as exemplarily illustrated in

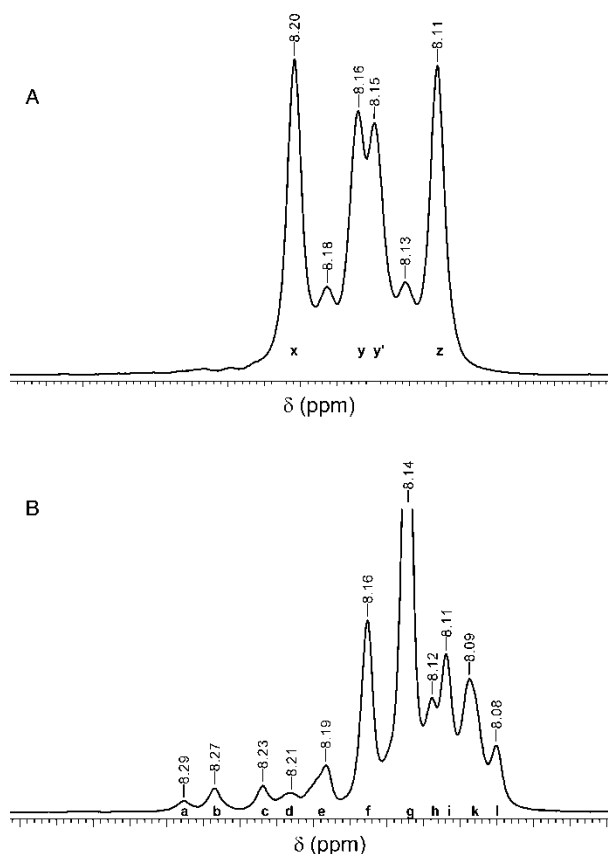


Fig. 1. 400 MHz ^1H NMR spectrum (segment 8.0–8.4 ppm) of: A) PIT homopolymer (No. 7, Table 3) and B) PBIT containing 25 mol% of isosorbide (No. 3, Table 3).

Figure 1B. The strongest peak (labeled “g” in Figure 1b) originates from terephthaloyl units flanked by two butylenedioxide units. However, unambiguous assignments of the other ten peaks were not feasible, in as much as the weakest peak may result from endgroups. Nonetheless, it was found that this signal pattern varies when the four samples, having identical compositions (No. 4, Table 1, No. 1, Table 2, and Nos. 3 + 4, Table 3), were compared. For instance, the signal “h” (8.12–8.13 ppm) is stronger in the spectrum of No. 3, Table 2, than in the spectra of Nos. 3 or 4, Table 3. These deviations suggest that the sequences of butanediol and isosorbide were, in fact, somewhat different, due to the higher reactivity of the butane diol.

3.3 DSC Measurements

The DSC measurements were performed with a heating rate of $10^\circ\text{C}/\text{min}$. The glass-transition temperatures (T_g s) were extracted from the second heating trace. The thermal data of a PBT sample prepared by $\text{Ti}(\text{O}i\text{Bu})_4$ catalyzed thermal transesterification were listed under experiment 0 in Table 3 and those of an isosorbide homopolymer under experiment No. 7. Both samples containing 6 mol% of isosorbide (No. 1, Table 2 and No. 2, Table 3) demonstrate that even this low content does suffice to raise the T_g of PBT to 55°C ($+10^\circ\text{C}$). As expected, the T_g increases further with higher contents of isosorbide and the samples No. 5, Table 2 and No. 6, Table 3 suggest that the T_g reaches a value of 100°C when the content of isosorbide approaches 50 mol%. This is certainly a significant increase, but a T_g of 100°C is still far below the T_g of the homopolymer PIT which has a T_g in the range of 196 – 200°C (depending on the molecular weight).

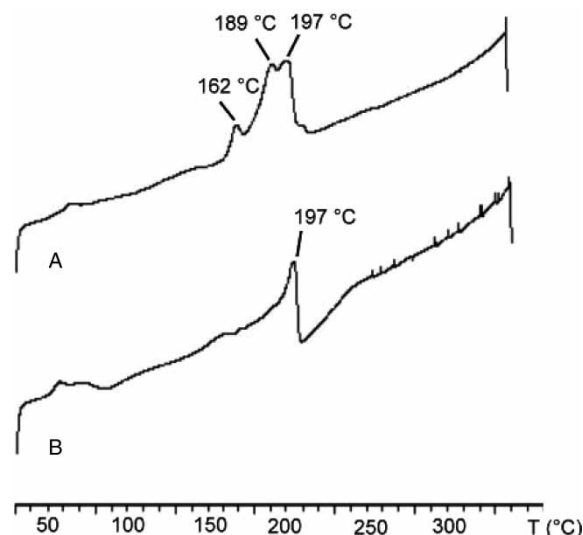


Fig. 2. DSC curves, 1st heating of PBIT No. 2, Table 2: A) after drying at 60°C , B) after annealing for 6 d at 150°C .

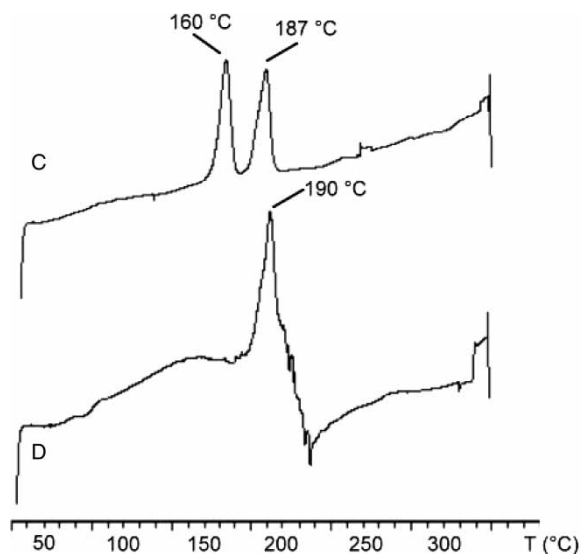
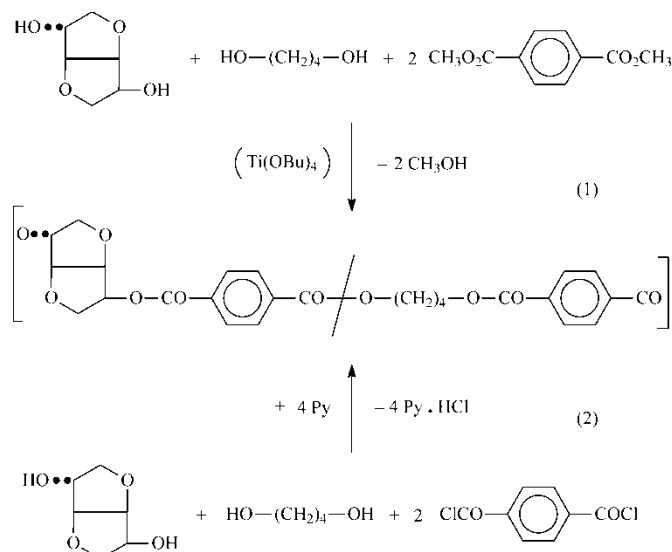


Fig. 3. DSC curves, 1st heating, of PBIT No. 4, Table 3: C) after drying at 60°C, D) after annealing for 6 d at 150°C.

In order to elucidate the influence of isosorbide on the crystallization, the copolyesters listed in Tables 2 and 3 were annealed for 6 d at 150°C. The influence of this annealing on the heating curves is ideally illustrated in Figures 2 and 3. The melting endotherms of the first heating trace was then evaluated. The thermal data obtained for the PBT prepared from terephthaloyl chloride in toluene were listed under experiment No. 0 in Table 3 as a basis for the comparison with the copolyesters. The data compiled in Table 2 indicate that the copolyesters are totally amorphous for a percentage of isosorbide around 36% or higher. With 25 mol% of isosorbide, the copolyester is still crystalline with a T_m around 180°C and a melting enthalpy around 25% of the value characteristic for PBTs. From the copolyesters prepared in toluene (Table 3), the following particularities were learned. The sample containing 30 mol% of isosorbide (No. 5) showed a broad flat endotherm around 155°C, suggesting, together with sample No. 4, Table 2, that the crystallinity fades away when the content of isosorbide falls into the range of 30–35 mol%. Second, the samples containing 24 or 25 mol% of isosorbide (Nos. 3 and 4, Table 2) proved quite different thermal properties. Whereas the high-molar mass sample displayed a relatively sharp endotherm at 191°C, a broad endotherm around 162°C was found for the low molar mass sample. Sample No. 3, Table 2, also containing 25 mol% isosorbide, displayed a T_m inbetween these extremes, although its inherent viscosity was quite similar to that of sample No. 3, Table 3. Hence, these three samples demonstrate that the thermal properties of copolyesters with an isosorbide content between 15 and 30 mol% depend immensely on the molecular weight and on slight differences in the sequence of the diols. When the samples containing 6 mol% of isosorbide are compared to PBT, it can be learned that an increase of the T_g from 45 to 55°C is

combined with the penalty that the T_m drops from 226°C to $210 \pm 2^\circ\text{C}$.



4 Conclusions

The comparison of two synthetic methods allows the conclusion that the standard method, the transesterification of DMT in the melt, is not suited for syntheses of copolyesters with a high concentration of isosorbide. In contrast, polycondensation of terephthaloyl chloride in solution yielded PIBT copolyesters with compositions close to the feed ratio. Even a rather low content of isosorbide (e.g. 6 mol%) has a significant influence on the thermal properties raising the T_g above 50°C and lowering the T_m to values $\leq 210^\circ\text{C}$. Therefore, incorporation of isosorbide into PBT allows for fine-tuning the thermal properties over a wide range. Yet, variation of the molecular weight and slight differences in the sequence of the diols (which are difficult to detect) also have a strong influence on the crystallinity of these copolyesters. Another interesting aspect is the finding that PBIT containing more than 50 mol% of isosorbide may be useful as amorphous transparent engineering plastics with T_g s above 100°C.

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