Polymerization of Bicyclic Acetals. III.* Cationic Copolymerization of 6,8-Dioxabicyclo[3.2.1]octane with Styrene

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ABSTRACT: 6,8-Dioxabicyclo[3.2.1]octane (DBO) was copolymerized with styrene in methylene chloride, 1-nitropropane, and toluene at various temperatures ranging from −78 to 25°C. Boron trifluoride etherate was used as an initiator. Sequence distributions of the monomeric units in the copolymers were determined by NMR analysis. It was found that the copolymerization in methylene chloride and 1-nitropropane gave copolymers with relatively short sequence lengths at higher temperatures, while it provided products with a highly block-like character at lower temperatures. In toluene solution, however, preferential polymerization of DBO occurred over the entire temperature range, yielding in most cases only the homopolymer of DBO. On the basis of these results, the structure and reactivity of the cationic growing chain-end of DBO were discussed.

KEY WORDS 6,8-Dioxabicyclo[3.2.1]octane / Styrene / Copolymerization / Cationic Polymerization / Sequence Distribution / Solvent Effect /

In previous papers,[1,2] we have reported that the cationic polymerization of 6,8-dioxabicyclo[3.2.1]octane (DBO) was affected markedly by polymerization temperature and solvents; a highly stereoregular polymer was produced at low temperatures such as −78°C and in solvents of low polarity, while a stereoirregular polymer was formed at higher temperatures and in polar solvents. In a continuation of the series of the studies on the polymerization of bicyclic acetals, the cationic copolymerization of DBO with styrene has been investigated in methylene chloride, 1-nitropropane, and toluene at different temperatures from −78 to 25°C. This paper describes the effects of solvent and temperature on the microstructure of the copolymer of DBO with styrene in relation to the structure and reactivity of the cationic growing species of DBO.

EXPERIMENTAL

Materials

DBO was prepared from 3,4-dihydro-2*H*-pyran-2-carboxaldehyde (acrolein dimer) by the method

of Sweet and Brown,[3] and purified as described in a previous paper.[2] Styrene was washed with 5-% aqueous potassium hydroxide and water successively, dried over calcium hydride, and fractionally distilled under reduced pressure. Methylene chloride, 1-nitropropane, and toluene were purified by the usual methods.[2] Boron trifluoride etherate was distilled just before use.

Polymerization Procedures

The copolymerization of DBO with styrene was carried out in an evacuated sealed tube at various temperatures from −78 to 25°C. The copolymerization was terminated by the addition of a few m*l* of ammoniacal methanol, and the reaction mixture was poured into a large excess of methanol to precipitate the polymer. It was reprecipitated repeatedly by using methylene chloride and methanol as a solvent—precipitant pair. Methanol-soluble polymer was recovered by adding water to the methanol solution in such an amount that the volume ratio of water to methanol became approximately 1 to 2. These products were dried under vacuum at room temperature to constant weight.

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Characterization

The copolymer composition was determined from the relative peak area of phenyl protons using NMR spectroscopy. NMR spectra of the copolymers were measured at 60°C in deuteriochloroform solutions with a Japan Electronics Model JNM-4H-100 working at 100 MHz. Tetramethylsilane was used as an internal standard.

The number-average molecular weight of the copolymers was determined with a Hewlett Packard Vapor Pressure Osmometer Model 302 using benzene solutions at 37°C.

RESULTS

Copolymerization in Methylene Chloride

Some of the results of the copolymerization of DBO with styrene, which was carried out in methylene chloride by using boron trifluoride etherate as the initiator, are listed in Table I. The products were fractionated into methanol-soluble and -insoluble parts. The difference in solubility was found to arise from the molecular weights, but in a few cases, the DBO content in the methanol-soluble part was slightly higher than that in the methanol-insoluble part. Furthermore, the distribution of the monomeric units in the polymer chain determined by NMR analysis was essentially the same in both the methanol-soluble and -insoluble parts. Hereafter, we will deal with the methanol-insoluble part

unless otherwise specified.

Figure 1 shows the NMR spectra of the copolymerization products obtained at 0°C (A) and −78°C (B). Although the compositions of both samples are alike, there are remarkable differences between these spectra: in the phenyl proton region, there appears a single peak at τ 2.90 in
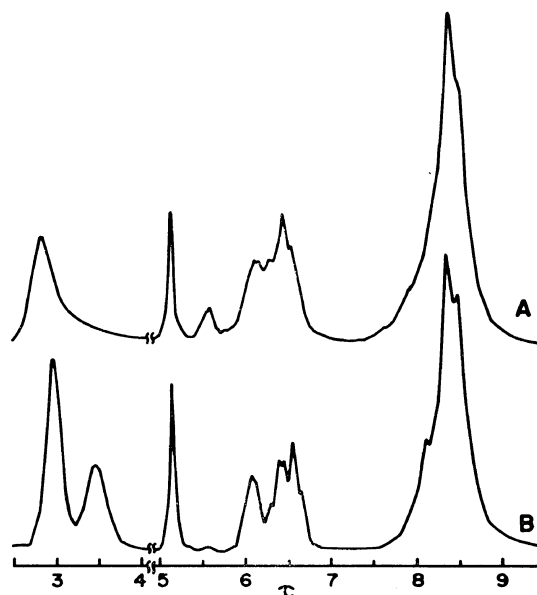

Figure 1. NMR spectra of DBO—styrene copolymer: Polymn temp, 0°C (A), −78°C (B); DBO content, 59 mol% (A), 54 mol% (B).

Table I. Cationic copolymerization of DBO with styrene in methylene chloride[a]

Exptl no.	{DBO}feed[b]	BF₃OEt₂, mol%	Temp, °C	Time, day	Yield, %		$M_n \times 10^{-3}$ [e]	
					Sol[c]	Insol[d]	Sol[c]	Insol[d]
DS-8	0.40	0.5	0	1	5.7	8.5	1.4	2.4
DS-3	0.30	0.5	0	2	8.1	2.3	1.6	3.6
DS-21	0.40	0.5	−20	2	13.3	3.8	1.8	4.0
DS-12	0.20	0.5	−20	2	4.8	3.1	1.4	2.6
DS-13	0.40	1.0	−40	1	5.8	41.0	2.7	8.6
DS-14	0.20	1.0	−40	1	5.3	7.6	1.6	7.6
DS-5	0.40	2.0	−78	2	trace	71.2	—	—[f]
DS-6	0.20	2.0	−78	2	trace	66.7	—	—[f]

[a] Total monomers, 0.02 mol; methylene chloride, 2.5—3.1 ml.
[b] Mole fraction of DBO in monomer feed.
[c] Methanol-soluble part.
[d] Methanol-insoluble part.
[e] By vapor pressure osmometry in benzene at 37°C.
[f] Insoluble in benzene.

spectrum A, while there are two peaks at τ 2.95 and 3.40 with peak area ratio of 3 to 2 in spectrum B. These characteristic shapes of the signals demonstrate that the copolymer obtained at 0°C contains short sequences of styrene units, and conversely, the product at −78°C has long sequences of styrene units, in other words, it is a block copolymer or a mixture of homopolymers. Another marked difference in the spectra can be seen in the acetal proton region: in spectrum A, there are two peaks at τ 5.15 and 5.60 which are ascribable to the equatorial and axial methine protons of the tetrahydropyran ring of DBO unit, respectively.[4] On the contrary, there appears a singlet peak due to the equatorial acetal methine proton in spectrum B. This feature is in accord with that observed in the homopolymer of DBO and is closely related to the stereoregularity of DBO units in the polymer chain.[2]

In order to acertain whether the reaction product at −78°C is a block copolymer or a mixture of homopolymers, elution fractionation by cyclohexane was carried out at 42°C on a thin film cast from a chloroform solution of the sample (DS-50). For comparison, a film of a mixture of poly-DBO and polystyrene (MDS-3) was treated under the identical conditions. The results are presented in Table II. From the homopolymer mixture, more than 60% of the polystyrene which had been contained initially in the film was eluted by this procedure, while no poly-DBO was extracted. On the other hand, a smaller amount of polymer consisting of styrene

and DBO units with a molar ratio of approximately 2 to 1 was found in the cyclohexane extract of the copolymerization product. These results, together with the fact that the copolymerization product obtained at −78°C only swells in benzene, seem to indicate that a block copolymer consisting of poly-DBO and poly-styrene sequences was formed as a major product, probably mixed with poly-DBO and a smaller amount of polystyrene, in the copolymerization at −78°C.

In order to begin to elucidate the formation of the block copolymer, three series of copolymerizations in which the initial mole fractions of DBO in feed were 0.2, 0.4, and 0.6 were undertaken in methylene chloride at −78°C, and the products obtained at different conversions were analyzed. Figure 2 shows the conversion dependence of the mole fraction of styrene unit, {B}, in the products. Interestingly, the {B} values increase abruptly near the conversions which correspond to the weight percents of the charged DBO monomer to the total monomers. The {B} values of the products obtained before these critical conversions are extremely low, especially for the series of the mole fraction of DBO in feed of 0.6. These results suggest strongly that the preferential polymerization of DBO takes place first, followed by the polymerization of styrene after most of the charged DBO monomer has been consumed, thus leading to the formation of the block copolymer in methylene chloride at −78°C.

Table II. Elution fractionation of copolymerization product (DS-50) and homopolymer mixture (MDS-3)[a]

Sample no.	Original polymer		Extracted polymer		Residue, g
	g	{DBO}[b]	g	{DBO}[b]	
DS-50[c]	0.413	0.53	0.065	0.33	0.359
MDS-3[d]	0.491	0.48	0.154	0.00	0.336

[a] Solvent, cyclohexane; temperature, 42.0±0.2°C; time, 204 hr.
[b] Mole fraction of DBO in polymer.
[c] Prepared at −78°C in 1-nitropropane.
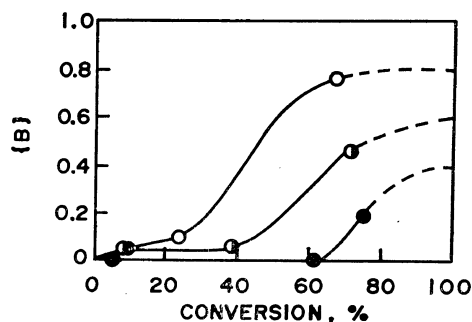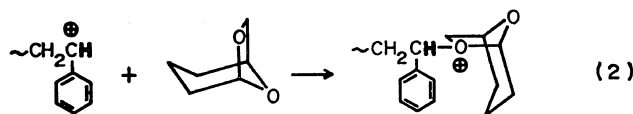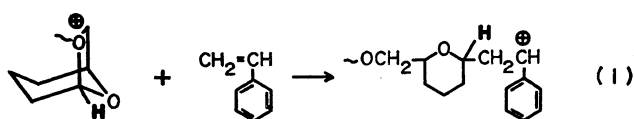[d] Poly-DBO and polystyrene used were prepared at −78°C in methylene chloride.

Figure 2. Conversion dependence of mole fraction of styrene, {B}, in DBO—styrene copolymer: Solvent, methylene chloride; initiator, BF_3OEt_2; polymn temp, −78°C. Mole fraction of DBO in monomer feed: ○, 0.2; ◑, 0.4; ●, 0.6.

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The sequence distribution of DBO and styrene units in a copolymer chain can be estimated from the NMR spectrum. When a cationic chain-end of DBO unit attacks a styrene monomer to form a DBO—styrene crossover diad, the acetal methine proton of the DBO monomer unit in this diad no longer shows its NMR signal in the acetal proton region, but instead in the ether proton region (1). On the other hand, when a styryl cation adds to a DBO monomer to form a styrene—DBO crossover diad, the methine proton of the styrene unit in this diad exhibits its NMR signal at τ 5.8 (2). Accordingly, the fraction of DBO—DBO consecutive diad, which is expressed by {AA}, can be estimated directly from the relative peak area of the acetal protons, and then the fraction of DBO—styrene cross-over diad, {AB}, is given by {A}—{AA}, where {A} is the mole fraction of DBO unit in the copolymer. The fraction of styrene—DBO cross-over diad, {BA}, can be determined, in principle, from the relative area of the signals appearing in the region of τ 7.8—9.0, $A_{7.8-9.0}$.

$$A_{7.8-9.0} = [6\{A\} + 3\{B\} - \{BA\}]/[10\{A\} + 8\{B\}]$$

However, such an estimate of {BA} seems less accurate, because it is calculated only indirectly from the relative areas of the overlapped complex peaks originating from protons of different types, as the above equation shows.

In an ordinary copolymer, unless it is of a low molecular weight, it is statistically valid to say that the diad fraction of M_1-M_2 is equal to that of M_2-M_1. If this relation holds in our copolymer, {AB} equals {BA}, and {BB} is given by {B}—{BA}. Although this assumption is invalid for the copolymerization products at $-78°C$ because of their highly block-like character described above, the {BB} values of all the copolymers were tentatively estimated as {B}—{AB}.

Table III summarizes the composition and diad fractions of the copolymers thus determined. The {AB} values tend to increase with the rise in polymerization temperature; in other words, the sequence distribution of the monomeric units in the copolymer chain changes gradually from block type to random type, as represented by the run number R in the last column, which is defined as the number of sequences per 100

Table III. Composition and diad fractions of the copolymers obtained in methylene chloride[a]

Exptl no.	Polymn temp, °C	{A}	{B}	{AA}	{AB}	{BB}[b]	R
DS-8	0	0.89	0.11	0.82	0.07	0.04	14
DS-3	0	0.58	0.42	0.45	0.13	0.29	26
DS-21	−20	0.84	0.16	0.77	0.07	0.09	14
DS-12	−20	0.47	0.53	0.39	0.08	0.45	16
DS-13	−40	0.80	0.20	0.78	0.02	0.18	4
DS-14	−40	0.63	0.37	0.59	0.05	0.32	10
DS-5	−78	0.54	0.46	0.54	0.00	0.46	—
DS-6	−78	0.23	0.77	0.22	0.01	0.76	2

[a] Methanol-insoluble part.
[b] Calculated as {B}—{AB}.

monomeric units in a copolymer chain. This tendency is clearly demonstrated in Figure 3.
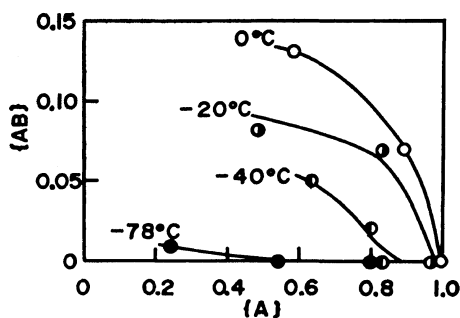

Figure 3. Relationship between mole fractions of DBO, {A}, and crossover diad, {AB}, in the copolymers obtained in methylene chloride. Polymn temp, °C: ○, 0; ◑, −20; ◐, −40; ●, −78.

Copolymerization in 1-Nitropropane

The results of the copolymerization of DBO with styrene in 1-nitropropane and of the NMR analysis of the microstructure of the copolymers are given in Tables IV and V, respectively. The {BA} values which were estimated independently in the aforementioned manner are included in Table V. The agreement between the {AB} and {BA} values appears fairly satisfactory. The temperature dependence of the relationship between {AB} and {A} in Figure 4 shows that also for the copolymers obtained in 1-nitropropane, the {AB} values of the copolymers at a fixed value of {A} increase with polymerization temperature, although the tendency is less noticeable than that observed for the copolymerization in methylene chloride.

Table IV. Cationic copolymerization of DBO with styrene in 1-nitropropane[a]

Exptl no.	{DBO}$_{feed}$[b]	BF$_3$OEt$_2$, mol%	Temp, °C	Time, day	Yield, %		$M_n \times 10^{-3}$ [e]	
					Sol[c]	Insol[d]	Sol[c]	Insol[d]
DS-43	0.40	0.25	0	3	16.3	1.9	1.3	5.3
DS-45	0.20	0.25	0	3	7.4	3.8	1.0	2.0
DS-31	0.40	0.5	−20	1	6.7	13.7	—	6.7
DS-32	0.20	0.5	−20	1	6.3	18.1	—	4.5
DS-47	0.20	0.5	−40	1	4.3	22.0	2.4	7.0
DS-48	0.20	0.5	−40	3	4.3	26.9	—	7.4
DS-49	0.40	0.5	−78	3	trace	34.9	—	—[f]
DS-50	0.20	0.5	−78	3	trace	29.3	—	—[f]

[a] Total monomers, 0.02 mol; 1-nitropropane, 2.3—2.9 m*l*.
[b] Mole fraction of DBO in monomer feed.
[c] Methanol-soluble part.
[d] Methanol-insoluble part.
[e] By vapor pressure osmometry in benzene at 37°C.
[f] Insoluble in benzene.

Table V. Composition and diad fractions of the copolymers obtained in 1-nitropropane[a]

Exptl no.	Polymn temp, °C	{A}	{B}	{AA}	{AB}	{BA}	{BB}[b]	R
DS-43	0	0.81	0.19	0.75	0.06	0.04	0.13	12
DS-45	0	0.34	0.66	0.27	0.07	0.09	0.59	14
DS-31	−20	0.73	0.27	0.67	0.06	0.06	0.21	12
DS-32	−20	0.44	0.56	0.38	0.06	0.08	0.50	12
DS-47	−40	0.34	0.66	0.30	0.04	0.07	0.62	8
DS-48	−40	0.35	0.65	0.31	0.04	0.06	0.61	8
DS-49	−78	0.71	0.29	0.70	0.01	(−0.03)	0.28	2
DS-50	−78	0.53	0.47	0.51	0.02	(−0.01)	0.45	4

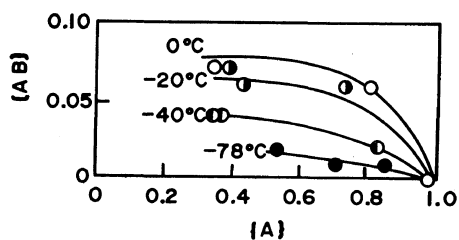[a] Methanol-insoluble part.
[b] Calculated as {B}−{AB}.

Figure 4. Relationship between mole fractions of DBO, {A}, and crossover diad, {AB}, in the copolymers obtained in 1-nitropropane. Polymn temp, °C: ○, 0; ◑, −20; ◐, −40; ●, −78.

Copolymerization in Toluene

The copolymerization of DBO with styrene was attempted in toluene at −78, 0, and 25°C for the monomer mixtures with mole fraction of DBO in feed of 0.20, 0.40, and 0.60. However, the reactivity of styrene was depressed so greatly in this solvent that only the homopolymer of DBO or, at best, the copolymer containing a very small amount of styrene unit was formed even at higher temperatures. From the comparison of the data in Tables III and V (for example, DS-8 vs. DS-43, and DS-21 vs. DS-31), it follows that the apparent relative reactivity of DBO in the copolymerization with styrene increases in the following order: 1-nitropropane < methylene chloride < toluene.

DISCUSSION

In a cationic copolymerization of structually different monomer pairs such as styrenes and vinyl ethers, the monomer reactivity ratios are affected significantly by solvents,[5−8] while those for monomer pairs with analogous structures are practically unaltered by solvents.[9] For example, in the cationic copolymerization of 2-chloroethyl vinyl ether with styrene derivatives, the relative reactivity of the former, a more reactive monomer, increases with decrease in the polarity of solvents.[8] In our present copolymerization, a similar trend was observed: the apparent relative reactivity of DBO increased in the order of 1-nitropropane < methylene chloride < toluene. This phenomenon is interpreted satisfactorily in terms of a preferential solvation of growing chain-ends by DBO monomer. The strength of the solvation of this type can be related to the nucleo-

philicity of monomers and solvents. As a measure of nucleophilicity, the infrared shift value of ν_{O-D} from the reference ν_{O-D} in benzene when a small amount of methanol-d is mixed with monomer or solvent is frequently adopted.[10] The $\Delta\nu_{O-D}$ value for DBO was found to be 66 cm^{-1}, much higher than the reported value of 2 cm^{-1} for styrene.[11] The $\Delta\nu_{O-D}$ values for toluene, methylene chloride, and nitroethane are reported as 2, −12, and 8 cm^{-1}, respectively.[11] (The $\Delta\nu_{O-D}$ value for 1-nitropropane is unavailable in the literature but is presumably very close to that for nitroethane.) Therefore, it is quite reasonable to ascribe the formation of the homopolymer of DBO, or, at best, a copolymer with minimum content of styrene unit in the copolymerization in toluene to the preferential solvation of growing chain-ends by the most powerful nucleophile, DBO.

Inspection of the data given in Tables III and V discloses that the enhanced reactivity of styrene in the copolymerization in 1-nitropropane compared with that in methylene chloride mostly arises from the acceleration of homopropagation of styrene in the former solvent, as the {BB} values show.

The {AB} values of the copolymers obtained in 1-nitropropane are in general smaller than those of the copolymers prepared in methylene chloride under similar conditions. This means that the crossover propagation from DBO to styrene occurs less frequently in 1-nitropropane than in methylene chloride, presumably because in the former solvent, solvation of the growing cation of DBO by 1-nitropropane molecules having appreciable nucleophilicity as well as by DBO monomer makes the addition of styrene to the growing chain-end of DBO unfavorable.

There are two possible ways to interpret the observed increase in the {AB} values with the rise in temperature, compared at a fixed value of {A}, as shown in Figures 3 and 4. The first is the concept that the growing chain-end of DBO consists of a cyclic trialkyloxonium ion, I, and an oxycarbenium ion, II, which are in equilibrium, and that the former ion is predominant at lower temperatures, the latter at higher temperatures. By analogy with the observations that cyclic ethers which undergo cationic polymerization through cyclic trialkyloxonium ions

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I   II
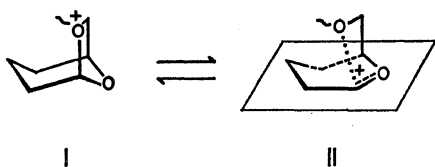
generally do not copolymerize cationically with vinyl monomers,[12-14] it is postulated that **I** is very reluctant to copolymerize with styrene, while **II**, whose structure resembles that of the cationic growing chain-end of vinyl ether, is capable of copolymerizing with styrene.

The second explanation is that the cationic growing-species of DBO is **II** regardless of the polymerization temperature, and that a higher activation energy for the crossover propagation from DBO to styrene than that for the homopropagation of DBO is responsible for the increase in the {AB} values with the rise in temperature. In addition to the difference in activation energy, the effect of the reversibility of the homopropagation of DBO must be taken into consideration. The homopolymerization of DBO involves an equilibrium between monomer and polymer as in the polymerization of monocyclic formals. The monomer concentrations of DBO in equilibrium were found to be 0.46 and 0.086 mol/l at 0 and −40°C, respectively, in methylene chloride.[15] Accordingly, it is expected that in the present copolymerization, particularly with the molar fraction of DBO in feed of 0.20 which corresponds to an initial monomer concentration of *ca.* 0.9 mol/l, the homopropagation of DBO would be retarded considerably at 0°C. Thus, the crossover propagation from DBO to styrene becomes relatively favorable at higher temperatures, with a consequent increase in the {AB} values of the resulting copolymers.

In view of the limited amount of information deducible from the data presented in the foregoing section, it would be difficult to decide conclusively which of the alternative explanations is more adequate. The first concept satisfactorily accounts for the temperature dependence of the stereoregularity of the polymers obtained in the cationic polymerization of DBO.[2] On the other hand, our recent NMR study has shown that an ionic species produced in the reaction of 1,3-

dioxane with triethyloxonium tetrafluoroborate is an oxycarbenium ion rather than a cyclic trialkyloxonium ion over the entire temperature range from −109 to 21°C.[16] This finding seems to support the second explanation. Therefore, more elaborate experiments will be required to determine definitely the structure of the cationic growing-species of DBO.

In summary, the cationic copolymerization of DBO with styrene gave rise to copolymers with relatively short sequence lengths at higher temperatures in methylene chloride and 1-nitropropane, particularly in the former solvent. However, at lower temperatures, the copolymerization provided the copolymers with a highly block-like character, probably mixed with homopolymers of DBO and styrene in both solvents. In toluene solution, preferential polymerization of DBO occurred over the entire range of polymerization temperatures examined, thus leading to the formation of only the homopolymer of DBO in most cases. These results suggest that proper selection of reaction conditions (*i.e.*, solvent of moderate polarity and low nucleophilicity, and relatively higher temperature) is a prerequisite to perform random copolymerization of cyclic acetals with vinyl monomers.

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