Adsorption of polymer/solvent complexes on silica surfaces

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SUMMARY: In this work local chain conformation, polymer/solvent interactions and particle size of different PMMA/solvent or PMMA/surfactant/solvent systems were investigated by dynamic light scattering, infrared spectroscopy and capillary viscosimetry. Aggregation can be forced, in the chlorinated solvents, through mixing with a small amount of PEG non-ionic surfactants. Nano-gel particles can also be formed by stereocomplexation of i- and s-PMMA in certain solvents.
The adsorption of stereoregular PMMA on silica was investigated by ^{1}H NMR. The strong relative lowering of the peak ascribed to isotactic sequences has provided evidence of a stereospecific adsorption of the isotactic segments. The conformation and the secondary structure induced by the PMMA stereoregularity may, therefore, be considered as a significant factor in the adsorption process. According to the miscibility of the components, PMMA/PEG mixtures are shown to increase the amount of polymer adsorbed and also to modify the stereoselectivity of the adsorption. Aggregative adsorption is assumed to deeply influence the organisation of the polymer at the silica/solvent interface. Finally, adsorption of aggregates of stereocomplexes can be used to pattern surfaces in thin films.

Introduction

Stereoregular PMMA are known to form aggregates or stereocomplexes1) in many organic solvents whereas other solvents, such as chloroform, dichoromethane or benzoic alcohol are known to be non aggregating2). According to Vacatello and Sundararajan3,4) Rotational Isomeric State (RIS) calculations conformational differences between isotactic and syndiotactic PMMA may exist for single molecules in the theta state. If the most stable conformation of the backbone is trans-trans in the two cases, the probability to find trans bond is 0,89 in syndiotactic PMMA and 0,72 in the isotactic form. This stereoisomer contains also trans-gauche (tg) and gauche-trans (gt) conformations These results are consistent with those obtained by O'Reilly and al.5) from FT-IR investigations. The RIS calculations but also experimental results6) converge to demonstrate a

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higher chain stiffness of the i-PMMA in theta conditions which leads to higher radius of gyration and consequently to higher intrinsic viscosity for that isomer as compared to the s-PMMA. The characteristic ratio, C_∞, of the i- and s-PMMA are 10.2 and 7.2, respectively. Kamijo et al(6), have pointed out differences in the expansion factor according to the PMMA tacticity by carrying out viscometric and light scattering experiments at temperature of 25°C in good solvents such as acetone or chloroform. At this temperature, the difference in the expansion factor becomes noticeable only for relatively high molecular weights, namely, above 20000 to 30000 g/mol

In addition, some solvents are known to favour the formation of associated structures of PMMA through self-aggregation1). Much efforts have been devoted over the past 40 years to the elucidation of the structure of stereocomplexes or aggregates obtained from isotactic and syndiotactic PMMA or the mixture of the two. The first tentative proposal of a structure of the stereocomplexes at the molecular level was provided by Liquori et al.7) who claimed that only the isotactic chains were of helical conformation. These assumptions were contradicted some time ago by Spevacek et al.8) and Challa et al.9) who suggested a double stranded helix structure of the stereocomplex which is more consistent with the possible template polymerisation of stereoregular PMMA10). At the nanometer scale the internal structures of the aggregates and physical gels formed by conventional (atactic) PMMA are constituted of cylinder-like structures as highlighted11) by neutron scattering. Stereocomplex association forms aggregates which consist of arrays of rigid rods connected to one other and described by the so-called fringed-micelle model12).

Extensive work has been published on the conformation and aggregation of water soluble polymers13) or proteins14) mixtures with ionic surfactants in water. In contrast, the behaviour of non charged polymers and non-ionic surfactant in organic solvents was much less investigated15). Nevertheless, aggregation can occur in these systems through interactions such as H-bonds, hydrophobic or van der Waals interactions. In comparison to the extensive works published on stereocomplexes, the conformation of steroreoregular polymers aggregated with surfactants was, to our knowledge, not yet investigated.

Many studies can be found in the literature about the influence of molecular weight16) and solvent17) on adsorption but fewer take into account the polymer stereoregularity18). Several authors have shown that the adsorption energy decreases with an increase in chain stiffness19) because stiff polymers loose less entropy on adsorption than flexible ones since they have fewer configurations available. Molecular simulation studies have shown, first, that the tacticity influences the dynamics of an isolated adsorbed PMMA chain[20)] and, second, that the relaxation time of an adsorbed s-PMMA chain is larger than that of an i-PMMA chain.

In this paper, we addressed the question of the significance of the conformation of polymer chains near a hard wall. We reported investigations carried out on the conformation of free stereoregular polymers and on polymer/surfactant aggregates in solution. Results concerning the adsorption of chains and aggregates at an interface in the presence of solvent were reported. The fate of stereocomplex nano-particles in dry thin films was also studied.

Experimental

The PMMA used here were purchased from Polymer Source Inc. Their characteristics are given in table 1.

PMMA	*Tacticity (%) i : h : s*	M_n $(10^{-3}g/mol)$	M_w/M_n	*Tg (°C)*
i-PMMA	97:03:0	37	1,21	61
s-PMMA	0:20:80	33	1,05	131

Table 1 : Characteristics of the PMMA used. i, h and s represents the isotactic, heterotactic and syndiotactic triads, respectively.

The non-ionic surfactants are POE 1000 (POE) which is an oligomer with hydroxyl groups at both ends and PEG diolate (d-PEG) is a telechelic oligomer terminated by alkyl short chains. Their hydrophilic to lypophilic balance (HLB) is 20 and 8, respectively.

Polymers and aggregates in solution. In our experiments, the concentrations of the solutions were varied between 0.1 to 10 g/l and were equilibrated for 1h or 20h at room temperature. Dynamic light scattering was used to evaluate the size of the aggregates in acetone. Viscosity of the solution was measured with an Ubbelohde viscosimeter at 25°C. Fourier transform infra-red spectrometer (FT-IR) was a Bruker IFS-66 equipped with a mercury-cadmium-telluride (MCT) detector. Curve-fitting and spectral subtraction have been performed using Bruker software.

Adsorption investigations "in situ" in solution. For the adsorption experiments, several techniques were used. Pyrogenic silica is amorphous, non porous Aerosil 130 and purchased from Degussa in Germany. The average particle size is 16 nm, the specific surface determined by BET is 105 m^2/g and the average density of silanol groups at the surface is 4 OH/nm^2 [10]. Bruker AC250 NMR spectrometer operating at 250 MHz was used in ^1H NMR measurements. The tubes were initially filled with a 3g/l PMMA solution in $CDCl_3$, the reference spectra was recorded and then, a given amount of SiO_2 was added

Adsorption experiments in solution were done with a spectroscopic ellipsometer Sopra operating in the UV-visible spectral domain. Silicon wafers were immersed in a quart prism containing 5 ml of the PMMA solution at a given concentration. A stabilisation time of one hour was waited before recording the ellipsometric angles. FilmWizard software was used for curve-fitting and determination of the thickness of the adsorbed layer d and the refraction index n. The Feijter formula$^{21)}$ was used to convert d and n in an adsorbed amount A.

Experiments on dry thin films. The solutions were spin-cast onto silicon wafers which have been UV-Ozone treated prior to the polymer deposition.

AFM experiments were made with a NanoScope IIIa /Dimension 3000 (Digital Instruments). They were performed in the Tapping Mode at ambient conditions, using the electronic extender modulus allowing simultaneously the phase detection and height imaging. Image treatments was performed using the Digital Instrument software. The pictures were binarized at the same level and the size of the aggregates calculated using the Grain Size function. The fractal coefficient D was determined by using Scion Images software on the binarized AFM pictures from the equation $N \sim R^D$. Concentric circles with varying radius R were drawn and the number of particles N in each concentric circles were measured.

Results and discussion

Conformation of stereoregular PMMA in chloroform: From dynamic light scattering and capillary viscosimetry, the radius of gyration of the PMMA coils in chloroform was measured in good agreement. At room temperature, Rg is 15 nm and 12 nm for i- and s-PMMA, respectively. The backbone conformation is *trans-trans* for both isomers whereas the side chain conformation differs from *trans-trans* to *trans-gauche* for the i- and s-PMMA, respectively. The packing and arrangement of the side groups may then lead to differences in the accessibility of the solvent molecules to the polar carbonyls groups. These assumptions can be supported by the study of the specific PMMA/$CHCl_3$ interaction with the temperature. Indeed, figure 1 shows that the fraction of acid-base bonded carbonyl $f_{(C=O)}{}^{ab}$ can be obtained from the curve-fitting of the carbonyl peak.

The free carbonyl vibration located at 1732 cm^{-1} and the bonded carbonyls at 1714 cm^{-1} are consistent with the wavenumbers given by Fowkes et al.[22)]. It should be noticed that $f_{(C=O)}^{ab}$ is higher for s-PMMA than for i-PMMA indicating that more syndiotactic chains segments are swollen than for isotactic chains. This observation made at room temperature but also at higher temperatures can be interpreted in terms of solvent permeability of the coil . Thus, i -PMMA is assumed to be an homogenous coil with polymer solvent contacts predominantly taking place in the external part of the coil whereas s-PMMA chain is likely to be constituted of densely packed chain segments (perhaps of helicoidal structure) and disordered parts leading to an density heterogeneous coil more easily swollen by chloroform. Therefore, an increase of temperature increases linearly $f_{(C=O)}^{ab}$ for the i-PMMA by a gradual expansion of the coil which allows more polymer/solvent contacts. s-PMMA chains maintain their $f_{(C=O)}^{ab}$ value at approximately 0.35 up to 35°C and then the density of acid-base interactions raises sharply. It is assumed that the disordered segments of syndiotactic isomer are totally swollen even at room temperature, while the chain segments involved in helicoidal intramolecular structures require to reach the temperature of conformational transition to reorganise themselves by taking into account the surrounding solvent molecules.

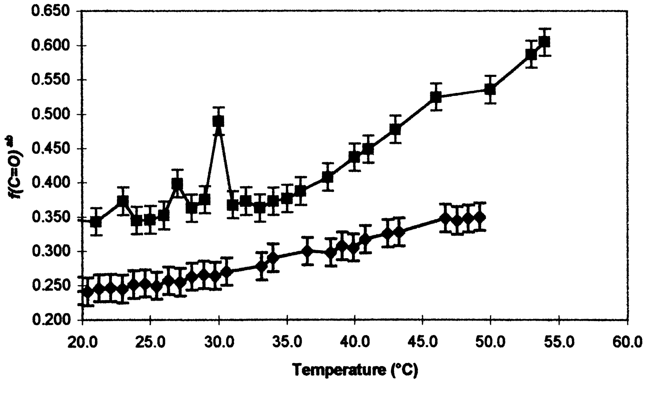

Figure 1 : Fraction of acid-base bonded carbonyls $f_{(C=O)}^{ab}$,calculated from the infrared carbonyl peak as a function of temperature, in $CHCl_3$. ◆ represents the i-PMMA solutions and ■ represents the s-PMMA solutions.

Aggregation in PMMA/PEG mixtures in solution: Strong specific interactions between two molecular species can lead to restriction in the mobility of the bonded groups[18)]. In high resolution liquid state ^{1}H NMR spectroscopy the immobilised segments will, therefore, escape the detection and will no more contribute to the recorded signal. Therefore, a decrease of the relative intensity of a peak ascribed to a particular stereoregular triad indicates a stereospecific aggregation of the PMMA and the surfactant. In other words, according to the tacticity of the PMMA and to the chemical structure of the surfactant, added in amount below the cmc, association of PEG oligomers can occur with specific part of the PMMA chain. We believe that this effect is due to the conformation adopted by stereoregular chain sequences (helix for instance) which are likely to modify the polarity or hydrophilic/hydrophobic character of these sequences and, therefore, their affinity for the surfactant. Table 2 shows that d-PEG aggregates stereospecifically on the organised sequences of i or s-PMMA whereas POE is associated with stereoregular syndiotactic sequences but homogeneously distributed on i-PMMA chains. The particle size systematically increases in presence of additive as compared to the Rg of the PMMA alone in solution. This is the evidence of PEG/PMMA aggregation in chloroform. Moreover, larger aggregates are formed with the d-PEG. Low HLB is likely to be significant parameter to favour aggregation, but this should be further investigated in forthcoming work.

Mixtures	Relative lowering of the intensity of NMR peak (%)	Particle size (nm)
i-PMMA/d-PEG	20 % isotactic sequences	34
i-PMMA/POE	No effect	19
s-PMMA/d-PEG	25% syndiotactic sequences	28
i-PMMA/POE	25 % syndiotactic sequences	17

Table 2: Relative lowering in the intensity of the ^{1}H NMR α-methyl peaks ascribed to isotactic, syndiotactic or heterotactic triads after addition of 2.5% (w/w relative to the polymer) of surfactant. The particle size is measured by dynamic light scattering in chloroform.

Adsorption isotherm of stereoregular PMMA and mixtures: Figure 2 shows the adsorption isotherm of i-PMMA and the aggregated structures on silicon wafer in chloroform calculated from ellipsometric data. It clearly turns out from these investigations that the shape of the curve corresponds to a Langmuir isotherm for i-PMMA whereas the adsorption process of the aggregates developed in solution exhibit a much more complex behaviour with the existence of a maximum on the isotherm. According to Lipatov et al.[23)] , who first described this particular adsorption isotherm, a mechanism of adsorption called aggregative adsorption was proposed. When aggregates are present in solution together with free polymer chains, the aggregates are first preferentially transferred on the surface, because of their lower solubility, increasing rapidly the adsorbed amount with the concentration of the solution. After this first regime, when the maximum of the isotherm is reached, adsorption decreases due to two possible effects : the formation of a physical network in solution which prevents the adsorption of the aggregates and/or a modification of the equilibrium between isolated and aggregated molecules (diminishing the number and size of the aggregates with an increase in the solution concentration). Another explanation, that we propose, is that at the maximum of the isotherm, the concentration of isolated chains is sufficient to build a monolayer at the surface, preventing the adsorption of the aggregates because of the larger fraction of bound segments per chains of the isolated coils as compared to the aggregates. The same kind of particular adsorption isotherm is obtained with PMMA stereocomplex in acetone, for instance.

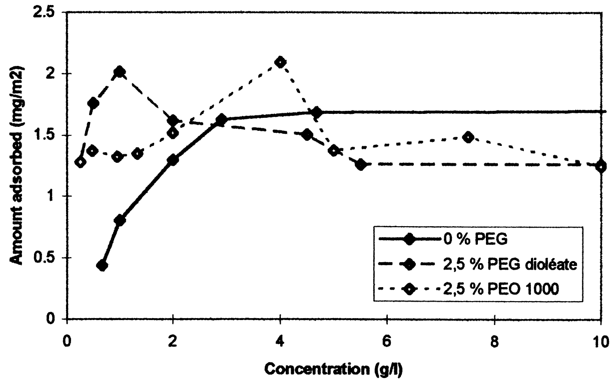

Figure 2 : Adsorption isotherms of i-PMMA and mixtures with surfactants in $CHCl_3$ on silicon wafer calculated from spectroscopic ellipsometry.

Stereospecific adsorption of PMMA on silica: Strong specific interactions discussed elsewhere$^{22)}$ in terms of acid-base interactions are likely to involve the PMMA carbonyl groups and the silanol surface groups. As discussed above, strong interactions cause restrictions in the mobility of the segments directly bonded to the surface which in turn lower the intensity of the ^1H NMR peak. Spectra A on figure 3 clearly shows the high content of isotactic mm triads of the i-PMMA sample in $CDCl_3$ solution. After SiO_2 adding (spectra B) two new peaks appear due to the impurities desorbed from the silica surface, namely, methylene and methyl groups at 1.25 and 0.88 ppm, respectively. However, the most interesting feature is that the peak assigned to the isotactic sequences exhibits a strong reduction comparatively to that of the syndiotactic triads (spectra D). The integrated intensity of mm triads relative to the other triads decreases from 95 to 42 or 51 %, depending on the PMMA to silica ratio, after adsorption. Since no change in the chain tacticity is allowed, the only explanation for the observed effect is that the NMR lines of the polymer segments directly bonded to the substrate are so broad that they escape detection in high resolution spectrum. This effect was already reported in earlier studies[18)] Therefore, the large decrease of the relative amount of isotactic triads observed in this study by ^1H NMR after adsorption can be attributed to a preferential adsorption of these sequences at the SiO_2 surface. Thus, the only sequences which still sensitively contribute to the NMR peaks are the non adsorbed chains and also the free segments belonging to the physisorbed chains, namely, loops and tails. Furthermore, the increase after adsorption in the amount of syndiotactic triads from 1 to 26 or 58%, according to the ratio of PMMA to silica, is somewhat unexpected for a highly isotactic sample. However, these sequences can be viewed as ''defects'' in the chain stereoregularity highlighted here since they may concentrate in loops and tails which are the only part of the adsorbed layer contributing significantly to the NMR signal.

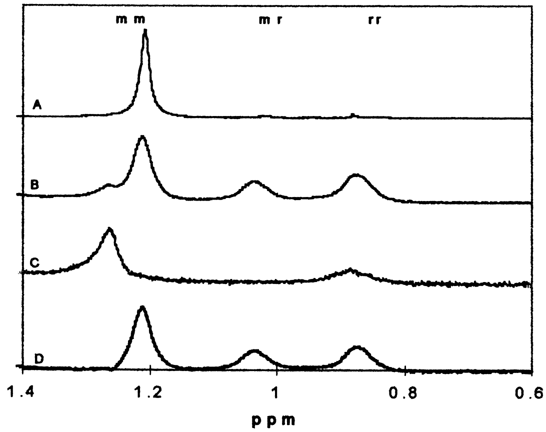

Figure 3 : α-Methyl peaks of ^1H NMR spectra of isotactic PMMA in $CDCl_3$. (A) represents the i-PMMA in solution, (B) represents the i-PMMA after silica adding (0.12 g of PMMA for

1g SiO_2), (C) represents the silica alone and (D) represents the resulting spectra after spectral subtraction (D = B - C).

Besides, the isotacticity of the a-PMMA decreases from 13 to 5% after silica adding. Thus, stereospecificity in the adsorption is still noticeable for that isomer, however its extent becomes lower than for i-PMMA. Selectivity in the adsorption of s-PMMA can still be deduced from the integrated intensity of the NMR peaks. Indeed, the percentage of isotactic sequences decreases from 7 to 0 % after silica adding. However, no definitive conclusion can be drawn from these last results since the intensity of the NMR signal is close to the range of experimental error.

The same ^{1}H NMR experiments were carry out with addition of 2.5 % of surfactant before adsorption on silica. While stereospecific adsorption remains for the i-PMMA/d-PEG mixture, it vanishes for the i-PMMA/POE system. The results obtained for s-PMMA are much more striking. Indeed, while s-PMMA did not exhibit any preference of its syndiotactic sequences for the silica surface, both s-PMMA/surfactant mixtures segregate syndiotactic segments at the interface. Actually, stereospecific aggregation of surfactant oligomers on the PMMA chains allow stiffening or modification of the hydrophilic/hydrophobic character of segments which are, therefore, driven to the interface by enthalpic or entropic forces.

Patterning of surfaces through adsorption of aggregates: The behaviour of the gel nanoparticles of stereocomplexes at an interface, as observed in figure 4, is close to that of colloidal particles. This is obvious from the observation of the complex random dendritic clusters obtained by other workers with colloidal systems such as gold microparticles at a surface$^{24)}$ or PS particles at the water/air interface$^{25)}$. The mechanism of the aggregates formation is discussed by introducing the concept of diffusion-limited aggregation (DLA) developed by Witten and Sander$^{26)}$. This model assumes that the particles originate far away from the developing immobile structure and perform a random walk in the surrounding space. Once a particle encounters the structure, it sticks to it.

Changing the ratio of isotactic to syndiotactic isomer from the 1:2 to the 4:1 ratio leads to a decrease in the size and the degree of branching of the aggregates at the surface as well as to an increase in the size dispersion of the clusters. The average diameter of the clusters is 204, 244, 118 and 87 nm for 1:2, 1:1, 2:1 ; 4:1 i/s-ratios, respectively. The largest size of the aggregates was observed for the 1:1 ratio. The stoiechiometry of PMMA stereocomplex is often cited as being equal to 1:2 or 1:1, or in-between these values, depending on the stereoregularity of the PMMA and the technique of investigation . The depression in the size of the aggregates is correlated to a decrease of the associated fraction p, calculated as described elsewhere[1)], from 0.67 for the i:s=1:2 ratio, to 0.23 for the 4:1 ratio. Finally, we can notice that the density of the clusters regarded individually, strongly decreases for the i:s=2:1 and 4:1 ratios. Moreover, coalescence or compact aggregation of the stereocomplex particles occurs at surfaces from the 2:1, 4:1 ratios. The fractal exponent D equal to 1.35 for the 1:2 ratio is lower than for the other i:s ratios which are 1.46, 1.61, 1.82 for 1:1, 2:1 and 4:1 ratios, respectively. These calculated values are consistent with those reported by other workers[24)] for 2D cluster-cluster DLA. The low values of the fractal dimension D are indicative of a fast aggregation process where the probability of cluster-cluster sticking on collision is very high. The shape of the aggregates is rather open in that case. Higher values of D correspond to a slow aggregation process where the probability of sticking is low and

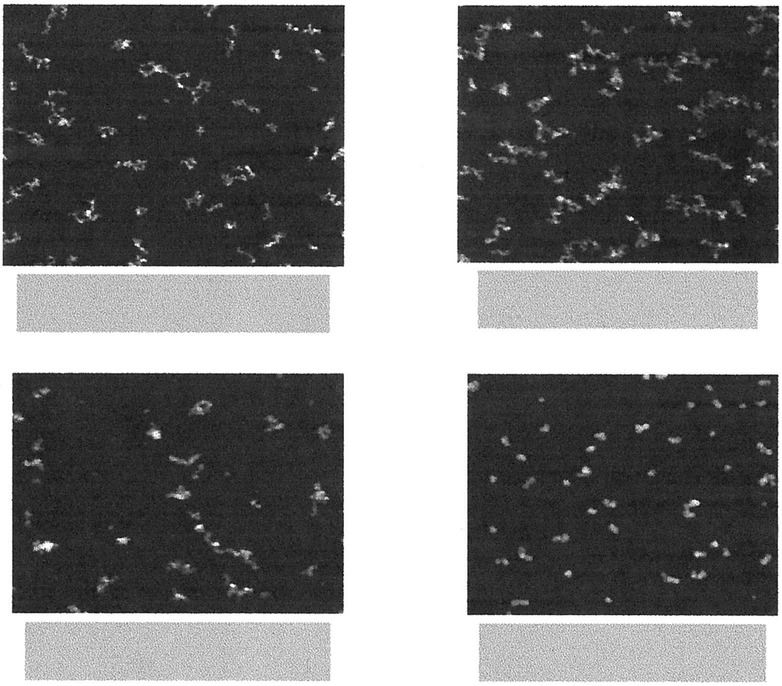

Figure 4 : PMMA stereocomplex nano-particles spin cast from dilute acetone solution (0.2 g/l) on silicon wafer. 1-2, 1-1, 2-1, 4-1, represents the isotactic to syndiotactic ratio in the complex.

provides more compact structure of the aggregates. These observation can be correlated with the structure of the aggregates in solution. Indeed, the fraction of associated segments per chain is likely to influence the self-association of the helix sequences and the swelling of the resulting gel nano-particles in the solvent. Thus, it is stated that the association of the helix rigid sequences acts as physical cross-links between macromolecules. At high values of p, the particles are rather compact while at low p the particles are surrounded by segments dangling in solution. The compaction of the particles in solution influences the surface-particle interactions as well as the inter-particles interactions. Indeed, the steric repulsion between particles is increased by the dangling segments while the specific interactions with the substrate are favoured. It turns out that diffusion and particle sticking at the surface is restricted for less compact particles (2:1, 4:1 ratio) inducing a slow aggregation process indicated by high fractal dimension ($D<1.5$). In contrast, the compact stereocomplex particles with i:s ratio close the stoechiometry aggregate faster at a surface as suggested by lower D values ($D>1.5$).

Conclusion

The aim of this work was to point out that the formation of polymer/solvent complexes is of huge importance in the behaviour of the chains at an interface. The stereoregularity enables to vary of the local conformational entropic of the polymer. Thus, parameters such as chain stiffness, solvating through specific interactions or formation of aggregates strongly influence the conformation, the arrangement and the packing of the chains at an interface. The persistence of conformation in polymer chains in the vicinity of an interacting surface can be highlighted in certain cases. The control of the organisation of macromolecules at interfaces is of great interest in the fields of thin film technologies or rheology of polymer stabilised dispersions.

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