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In-Line Monitoring of Vinyl Acetate/Acrylic Acid Batch Copolymerizations through Near Infrared Spectroscopy

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Summary: Near infrared spectroscopy (NIRS) is widely used for determination of polymer properties through in line and real time monitoring of polymerization reactions. Experimental runs were performed to evaluate whether NIRS can be used to monitor vinyl acetate/acrylic acid (VAc/AA) copolymerizations carried out in suspension reactors. It is shown that NIRS can be used successfully to monitor the evolution of VAc/AA suspension copolymerizations and that very good calibration models can be developed for monitoring of composition trajectories along the batch. Therefore, NIRS can be employed for real time monitoring and control of copolymer composition in VAc/AA copolymerizations performed in suspension reactors.

Keywords: acrylic acid; near infrared spectroscopy (NIRS); suspension copolymerization; vinyl acetate

Introduction

End-use properties of polymer materials depend strongly on the evolution of compositions during batch copolymerizations. For this reason, real time measuring of monomer and copolymer compositions can be of fundamental importance for implementation of advanced control procedures in batch copolymerizations. Therefore, development of techniques for monitoring of compositions in line and in real time in copolymerization processes constitutes a very important field of investigation.

Near infrared spectroscopy (NIRS) has been extensively used for monitoring of polymer properties and analysis of kinetic data in many polymerization systems. As a matter of fact, NIRS is a very powerful analytical tool, allowing for in-line and off-line evaluation of average particle sizes, monomer conversion, chemical compositions and average molecular weights in many distinct polymerization systems.[1–12] For instance, NIRS has been employed in suspension polymerization processes for monitoring and/or control of average particle sizes and morphological properties of the final polymer resin.[13–17] In this particular case, monitoring of morphological properties is possible because light is subject to distinct interactions with the polymer beads, including reflection, refraction and random scattering on the surface of the polymer particles. The large scattering/absorption ratio, usually regarded as a disadvantage for spectroscopy applications, plays a important role for analysis of the morphological features of polymer particles obtained in suspension polymerization systems.[7]

Regarding the use of NIRS in suspension polymerization reactors, it is very important to emphasize the pioneering studies developed by Santos et al,[13,14] who showed the possibility to monitor and

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control average particle sizes in real time during styrene polymerizations, through combination of NIRS data and proper manipulation of the agitation speed. Additional applications include detection of core-shell structures in simultaneous semi-batch suspension/emulsion processes[18] and prediction of bulk density (BD), cold plasticizer absorption (CPA) and average particle diameters (Dp) in batch PVC polymerizations.[15–17] Nevertheless, different authors reported that it can be very difficult to build good calibration models for monomer and copolymer compositions in suspension processes, as the spectral signal is largely dominated by scattering phenomena.[13,14]

Due to the complex nature of NIR spectra, empirical calibration models are usually built to correlate the observed spectral changes with variations of the polymer properties during the polymerization reaction. Linear multivariate calibration techniques are used most often, being assumed that there is a linear relationship between the monitored parameters and the intensities of the NIR spectra (or the first or second derivatives of the NIR spectra) at specified wavelengths.[19] In this case, the calibration model can be represented in the form $y = x^T b + e$, where y is a process response, x represents the spectral data, e is the residual and b contains the regression coefficients. Several standard regression techniques, such as multiple linear regression (MLR, normally employed when the user defines the particular set of wavelengths used for model calibration), principal component regression (PCR, which searches for directions that concentrate the maximum variability of the spectral data, generally employed when the user does not define the particular set of wavelengths used for model calibration) and partial least squares (PLS, which searches for directions that lead to maximum correlation between the spectral data and the response variables, also employed when the user does not define the particular set of wavelengths used for model calibration), can be used to estimate b.[7]

In the present work, it is shown for the first time that NIRS can be used successfully to monitor monomer and copolymer compositions in copolymerizations of vinyl acetate/acrylic acid (VAc/AA) performed in batch suspension processes. VAc/AA copolymers find important uses in different biotechnological applications, as a substitute for alginate materials.[20–22] In this process, AA is partitioned between the aqueous and the organic phases, which makes scattering phenomena less important, as significant part of the signal is related to the AA absorption in the aqueous phase. As a consequence, very good partial least squares (PLS) calibration models can be obtained for monitoring of the AA and VAc concentrations during the copolymerization reactions. Besides, based on the AA aqueous concentration values provided by NIRS, a phenomenological copolymerization model can also be used as reference for computation of the concentrations of the remaining species in both aqueous and organic phases during the reaction and for optimization of monomer feed and temperature profiles.[20–22]

Experimental Part

The experimental setup and procedures used to carry out the copolymerization reactions were similar to the ones described by Machado et al.[21] Due to lack of space, the reader must refer to this publication for more detailed description of reactor apparatus and analytical procedures.

Poly(vinyl alcohol) (PVA, used as the suspending agent) with a degree of hydrolysis of 85% and benzoyl peroxide (BPO, used as initiator) with a minimum purity of 98% were supplied by VETEC Química Fina (Rio de Janeiro, Brazil). Nitrogen was supplied by AGA S. A. (Rio de Janeiro, Brazil) with minimum purity of 99.9%. Monomers acrylic acid and vinyl acetate were supplied by Tedia Brasil (Rio de Janeiro, Brazil), with a minimum purity of 99.9%. Distilled water was used as the suspending medium. Unless stated other-

wise, chemicals were used as received, without additional purification.

VAc/AA copolymerizations were performed in a 1-L jacketed glass reactor (FGG Equipamentos Científicos Ltda, São Paulo, Brazil) with the organic load of 30 wt% and under inert atmosphere. Initially, the reactor was fed with distilled water, containing the specified amount of suspending agent (0.1 wt%, unless stated otherwise). When the desired temperature of 70 °C was achieved, the solution containing monomers and initiator (0.8 wt% of BPO, unless stated otherwise) was added. The system was kept under constant and vigorous agitation of 1000 rpm at isothermal conditions. Samples were taken every 15 minutes for characterization of monomer compositions (through gas chromatography and aqueous phase conductivity) and copolymer compositions (through NMR analyses).

In-situ NIRS measurements were performed in the range between 400 nm and 2500 nm with a spectrophotometer equipped with a stainless steel interactance probe with length of 30 cm, diameter of 1.905 cm and path length of 3 mm (Monochromator model 6500-On line supplied by NIRSystems, Inc., USA). Light was transmitted through a fiber optics cable of 3 m. Sampling time was equal to 1 min. 32 spectra were scanned, averaged, recorded and used for analysis automatically at each sampling time. The NSAS® (Near Infrared Spectral Analysis System) software was used for data acquisition and spectral data treatment.[23]

Results and Discussion

Figure 1 shows typical temperature and conversion profiles during VAc/AA batch copolymerizations. As one can observe, the reaction presents remarkable nonlinear features, including the existence of a maximum attainable conversion limit and strong autoacceleration, induced by the significant increase of the viscosity of the reacting medium during the reaction (characterizing the well-known glass effect and gel effect of free-radical polymerizations). Figure 1 also shows that reaction temperatures may increase a bit during the autoacceleration period, because of the significantly higher rates of heat generation.

As described by Machado et al.,[21] monomer conversion profiles can be divided into three main stages during VAc/AA batch copolymerizations. The first stage lasts for approximately 50 min and is characterized by the preferential consumption of the most reactive monomer

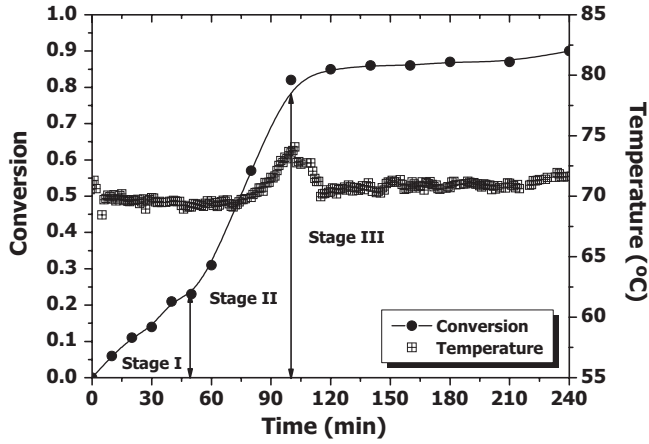

Figure 1.
Characteristic Dynamic Behavior of VAc/AA Batch Copolymerizations.

(AA). The second reaction stage also lasts for approximately 50 min and is characterized by the strong acceleration of the reaction rates, with the preferential polymerization of VAc. The third stage is characterized by the low reaction rates and existence of severe diffusive limitations, caused by the increase of the viscosity of the reaction medium (the lengths of the characteristic time intervals depend on several operation parameters, such as the reaction temperature, and concentrations of monomers and initiator). It is important to emphasize that both glass and gel effects take place during the three characteristic stages of the copolymerization, although the gel effect is more important in the first moments of the reaction, while the glass effect is more important at the final stages of the reaction. It is also important to observe that significant copolymer composition drifts occur during the batch because of the preferential consumption of AA in the first reaction stage.

Figure 2 shows the spectra of pure monomers and water, which are very different in the whole range of wavelengths analyzed. Figure 3 and Figure 4 illustrate

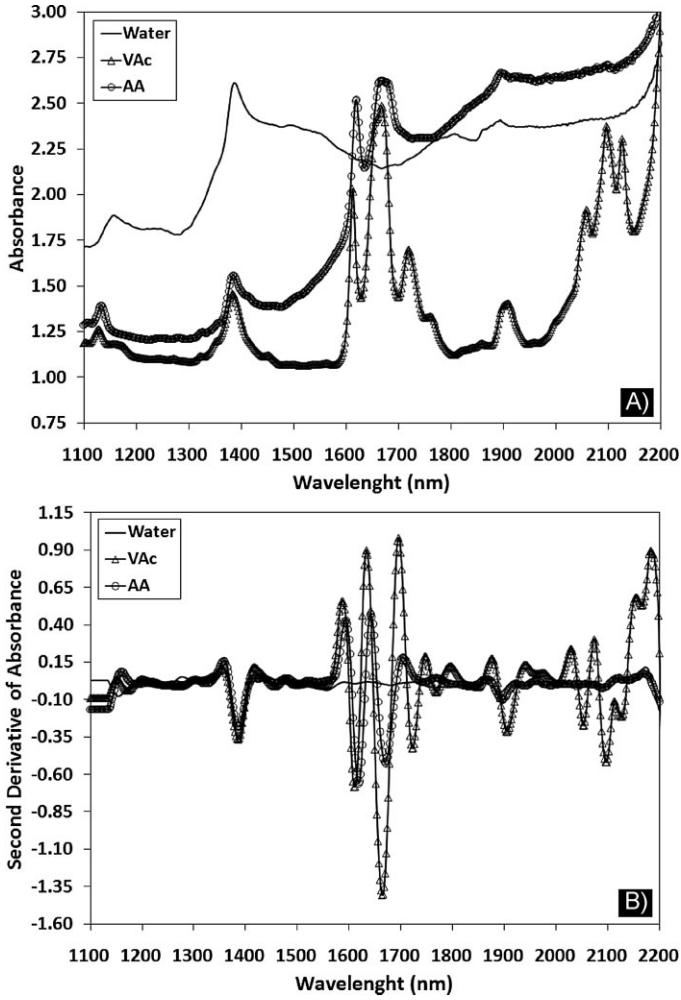

Figure 2.
Spectral Data for Monomers and Water. (A) Crude Spectra; (B) Second Derivatives of Crude Spectra.

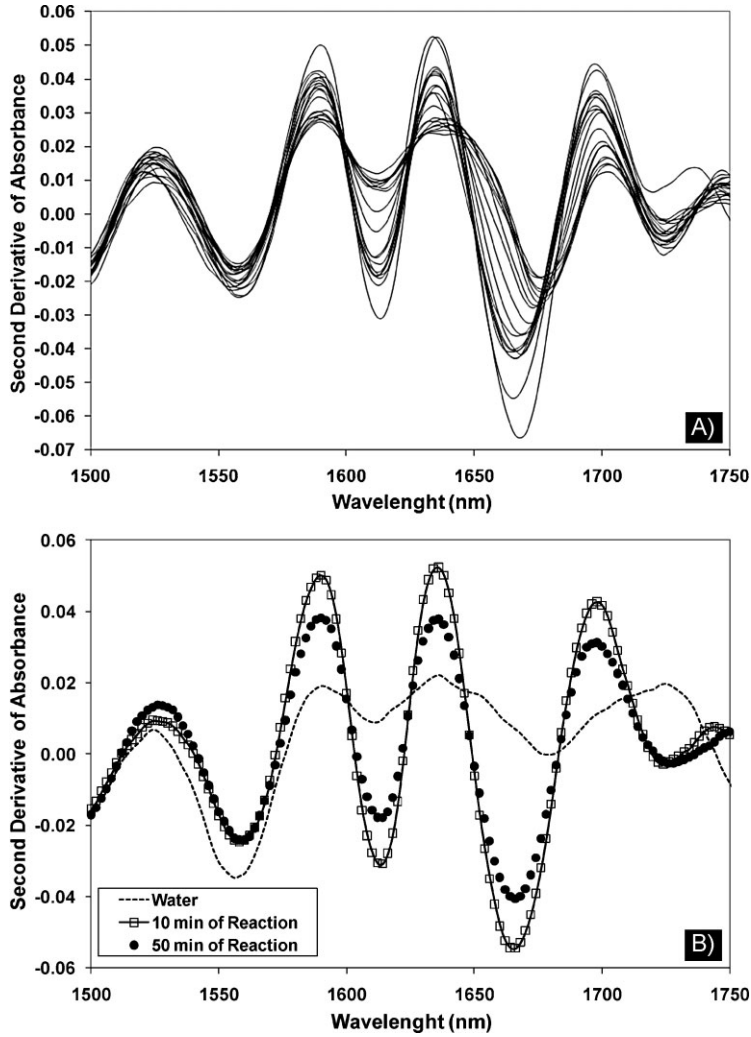

Figure 3.
Spectral Changes During VAc/AA Batch Copolymerizations (10 wt% of AA). (A) Second Derivatives of Crude Spectra. (B) Second Derivatives of Crude Spectra at Specified Reaction Times.

the evolution of the NIR spectra collected during the batch suspension copolymerization, when the monomer feed contains 10 wt% and 20 wt% of AA, respectively. It can be observed that appreciable changes take place along the batch and from one batch to the other, encouraging the development of calibration models for monitoring of the reaction.

Reactions were performed for distinct initial AA feed compositions, ranging from 2.5 to 20 wt%. The collected set of experimental data was divided into two main groups. The first group (containing 80% of the experimental data) was used to build the calibration models, while the second group (containing 20% of the experimental data) was used for independent model validation. Calibration models were built with the help of partial least squares (PLS) procedures, based on the second derivatives of the crude spectra in order to remove baseline variations.[19,24–29] PLS modeling presents several practical advantages. For

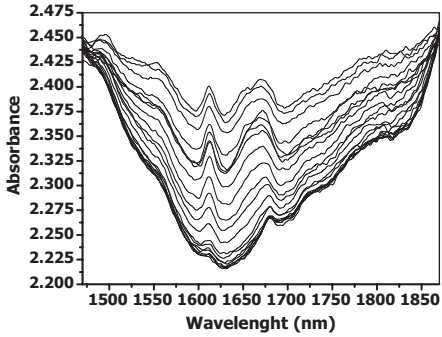

Figure 4.
Spectral Changes During VAc/AA Batch Copolymerizations (20 wt% of AA).

example, PLS models can be utilized when process responses are functions of multiple process disturbances, correlating more than one predicted variable with different state variables.[24–27] Additionally, PLS models can be based on spectral information available in the whole spectral region, so that the user does not have to determine the particular wavelengths to be used for multivariate calibration.[7] The number of PLS factors was increased to reduce the average squared residuals observed in the validation set of experimental data. Selected models (see Table 1) were the ones which led to the minimum average squared residuals of the validation set. Model performances are presented in Figures 5 and 6. Spectral data were treated with the help of the NSAS software,[23] which was also used to construct the PLS regression models. Cross-validation was performed by leaving one experiment aside at each time.

Table 1.
Performances of the Obtained PLS Calibration Models.

	Acrylic Acid	Vinyl Acetate	VAc in Copolymer
Calibration			
R	0.98	0.95	0.97
SEC	0.0030	0.1812	0.1565
Factors	4	2	2
Validation			
Bias	0.0028	0.0703	0.0045
R	0.95	0.90	0.96
SEP	0.0049	0.252	0.199

R represents the correlation factor between experimental and predicted data. SEC represents the standard error of calibration (M). Bias represents the average deviation between experimental and predicted data in the validation set. SEP represents the standard error of prediction (M).

According to Figure 5, the concentrations of the main constituents of the reaction can be monitored successfully with the help of the PLS calibration models, based on the available NIR spectra. As one can observe in Table 1, no more than four factors are necessary for model calibration, which indicates that the calibration models are very simple and robust. Calibration results are slightly better for AA than for VAc concentrations, due to the scattering effect, as AA is homogenously distributed in the homogeneous aqueous phase, while VAc monomer is placed inside the organic droplets. In spite of that, model performances can be regarded as very good.

According to Figure 6, the concentrations of the main constituents of the reaction can be monitored fairly well with the help of the PLS calibration models in the validation set, although the model performances are not so good as in the calibration set (as one might already expect). Despite that, the obtained results clearly show that model predictions capture the changes of AA and VAc concentrations inside the reaction system, allowing for implementation of advanced monitoring and control procedures based on the available NIR data, as shown elsewhere.[22] Based on the AA and VAc concentration values provided by NIRS, a phenomenological copolymerization model can be used afterwards as reference for computation and optimization of the concentration trajectories during the batch.

Conclusion

It was shown here that the NIRS technique can be successfully used to monitor the evolution of monomer and copolymer concentrations during batch VAc /AA suspension copolymerizations, as good calibration models can be developed to

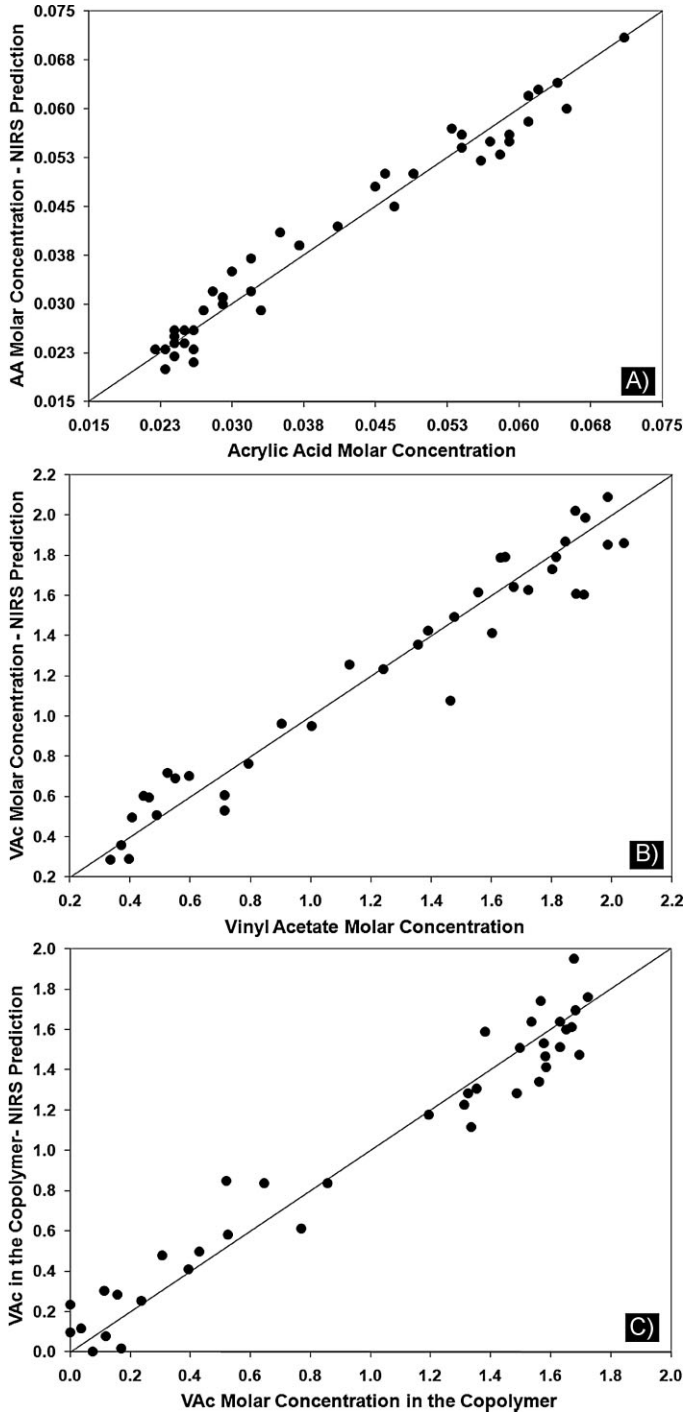

Figure 5.
Performance of the PLS Calibration Models in the Calibration Set. (A) Acrylic Acid; (B) Vinyl Acetate; (C) VAc in the Copolymer.

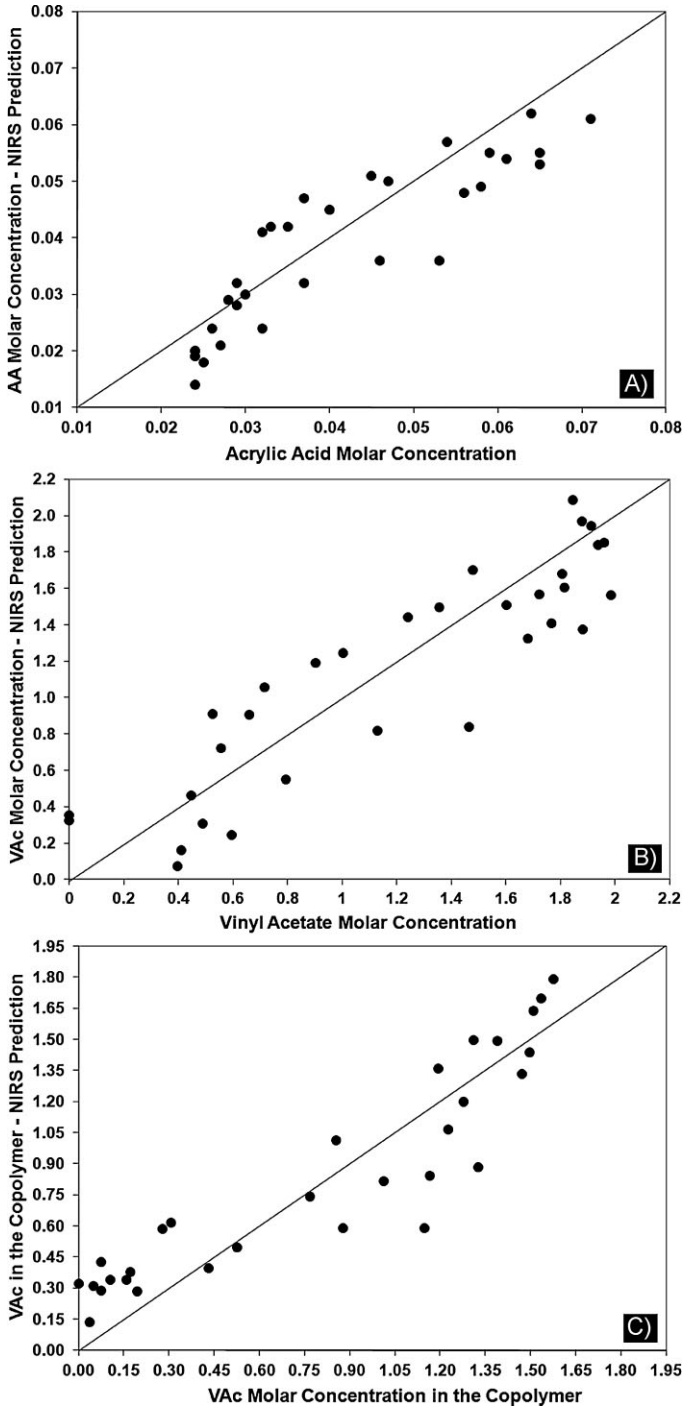

Figure 6.
Performance of the PLS Calibration Models in the Validation Set. (A) Acrylic Acid; (B) Vinyl Acetate; (C) VAc in the Copolymer.

describe how concentration profiles depend on the available NIR data. Thus, implemented calibration models can be employed for monitoring and control of VAc/AA copolymerizations performed in suspension reactors.

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