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Polymerization Kinetics of Water-Soluble *N*-Vinyl Monomers in Aqueous and Organic Solution

Sandhya Santanakrishnan,[1] *Robin A. Hutchinson,**[1] *Lucia Učňová,*[2] *Marek Stach,*[2] *Igor Lacík,*[2] *Michael Buback*[3]

Summary: Free-radical batch polymerization (FRP) of *N*-vinyl pyrrolidone (NVP) and *N*-vinyl formamide (NVF) monomers in aqueous solution as well as NVP polymerization in organic (*n*-butanol) solution has been studied. The differences found in rate of monomer conversion with monomer and solvent choice correlates well with the differences in values of the propagation rate coefficients (k_p) and their variation with monomer concentration measured in independent pulsed-laser polymerization studies, a result demonstrating that a generalized understanding of water-soluble vinyl monomers can be obtained once their k_p differences have been accounted for. A reasonable representation of polymer molecular mass averages and the complete molecular mass distributions for the three systems was obtained by assuming that the rate coefficient for transfer to monomer, polymer, and organic solvent also vary as a function of monomer concentration.

Keywords: kinetics (polym.); modeling; *N*-vinyl formamide; *N*-vinyl pyrrolidone; radical polymerization

Introduction

Water-soluble vinyl polymers, usually produced via free-radical polymerization (FRP) of water-soluble monomers in aqueous solution, are an important class of free-radical polymers finding application in a variety of fields, such as pharmaceuticals,[1] waste water treatment,[2] consumer products, paper manufacturing, and cosmetics.[3] Despite their importance, the understanding of aqueous systems has lagged behind that of their organic counterparts, due to the influence of water on the reaction kinetics. A review of previous literature is contained in recent studies of methacrylic acid (MAA)[4] and *N*-vinyl pyrrolidone (NVP)[5] batch and semibatch polymerizations in aqueous solution, and will not be repeated here. In most of the earlier studies, little specific information was presented about the kinetic peculiarities of aqueous-phase polymerization, predominantly due to the non-availability of independent values of rate coefficients. It was only after the advent and application of specialized techniques such as PLP-SEC (Pulsed Laser Polymerization-Size Exclusion Chromatography) and SP-PLP-NIR (Single Pulse-Pulsed Laser Polymerization-Near Infrared), which have enabled the determination of individual propagation (k_p) and termination (k_t) rate coefficients, has the understanding of these systems improved.

The groups of Buback and Lacík have jointly conducted extensive PLP-SEC studies[6–8] on MAA polymerization, finding that both monomer concentration and degree of ionization have a significant influence on k_p in aqueous solution. PLP experiments conducted in the temperature range of 20 to 80 °C showed k_p to decrease

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[1] Department of Chemical Engineering, Dupuis Hall, Queen's University,Kingston, Ontario K7L 3N6, Canada
E-mail: robin.hutchinson@chee.queensu.ca

[2] Polymer Institute of the Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava 45, Slovak Republic

[3] Institute of Physical Chemistry, University of Göttingen, Tammannstraße 6, D-37077 Göttingen, Germany

by almost one order of magnitude as the monomer concentration was changed from very dilute (1 wt% MAA) to bulk.[7] This enormous change in k_p could not be explained by any of the existing explanations proffered in literature such as dimerization, difference in bulk and local monomer concentrations or specific association of MAA to poly(MAA). The behavior, uniquely observed in water-soluble systems, was attributed to the interaction between the transition structure (TS) for propagation and the surrounding environment resulting in an enhanced friction on the TS in the presence of increased monomer concentration, thereby affecting its internal rotation.[7–9] The resistance to internal rotation decreases with reduced monomer concentration, thus causing an increase in k_p with increasing dilution or increasing conversion in a batch reaction, the latter result demonstrated by a follow-up PLP study[10] with added poly(MAA) to simulate higher conversion levels. Degree of ionization (α) had a similar influence on k_p as monomer concentration, with the influence of α being more pronounced at low initial MAA concentration $\left(w^0_{\mathrm{MAA}}\right)$ of about 5 wt% and weaker at higher w^0_{MAA}.[7] The influence of MAA content was most pronounced at $\alpha = 0$ (non-ionized) and gradually decreased with increasing α with only a slight increase in k_p at $\alpha = 1$ (fully ionized). Other PLP studies include those on non-ionized[11] and ionized[12] acrylic acid (AA), NVP,[9] and *N*-vinyl formamide (NVF).[13] In all cases, a significant increase in k_p was found with decreasing monomer concentration (or increasing monomer conversion) in aqueous solution.

Once the non-idealities in k_p are properly accounted for, the k_t behavior for these monomers can be better understood, as established using the SP-PLP-NIR technique. The k_t of MAA showed a significant dependence on conversion (similar to methacrylates), with the value controlled by segmental diffusion at low conversion levels of up to about 20%, followed by translational diffusion and reaction diffusion control at high conversion levels.[14] The k_t of NVP, however, showed a negligible change over the conversion range studied (up to 60%) for aqueous solutions containing up to 40 wt% NVP, with the k_t value in this predominantly segmentally-controlled regime found to vary with the initial weight fraction of NVP.[15]

The k_p and k_t coefficients determined from these specialized techniques were shown to provide a good description of continuously-initiated aqueous-phase batch polymerization of MAA[4] and batch and semibatch polymerization of NVP,[5] including polymer molecular mass (MM) averages and molecular mass distributions (MMD). In addition, differences in NVP and NVF batch polymerization rates in aqueous solution correlated well to the measured differences in k_p values determined by PLP-SEC.[13] The goal of the current work is to extend this rate comparison to NVP in organic solution, as well as compare MMs and MMDs obtained in NVP and NVF polymerizations. Simple mechanistic models have been developed in order to explain the kinetic differences based on the understanding gained from the PLP-SEC k_p studies.

Experimental Part

N-vinyl pyrrolidone (>99%, Aldrich), *N*-vinyl formamide (98%, Aldrich), *n*-butanol (99.9%, Sigma-Aldrich) and the thermal initiators 2,2′-azobis(2-methylpropionamidine) dihydrochloride (V-50, Fluka, ≥98%) and 2,2′-azobis(2-methyl butyronitrile) (Vazo-67, DuPont) were used as received. Polymerizations were carried out isothermally in a 1 L automated (MT Autochem) stirred reactor under nitrogen blanket. Conversion was tracked online using a MT-Autochem React-IR system and off-line using gravimetry and NMR analysis, as detailed previously.[5,13] Molecular mass (MM) analysis was carried out by size-exclusion chromatography (SEC) at the Polymer Institute of the Slovak Academy of Sciences, the details of which are also

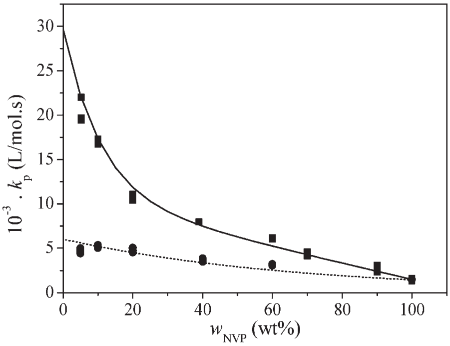

Figure 1.
The influence of *N*-vinyl pyrrolidone concentration (w_{NVP}) on the propagation rate coefficient (k_p) for polymerization in aqueous[9] and butanol[16] solution, as measured by PLP-SEC experiments at 40 °C. Additional PLP-SEC experiments of NVP in *n*-butanol are underway.[16]

discussed in earlier publications.[5,9,13] The MM averages obtained using the refractive index detector with respect to polystyrene calibration were shifted by correction factors of 1.17 and 1.53 for the aqueous and organic-phase polymerized NVP and 0.41 for aqueous-phase polymerized NVF, based upon the measure of absolute MMs by light scattering of the samples prepared in this work.

Results and Discussion

Aqueous versus Organic-Phase NVP Polymerization

The kinetic model for NVP polymerization, built using Predici©, includes the basic free-radical polymerization mechanisms of initiation, propagation, transfer and termination. The rate coefficients and model parameters for aqueous-phase NVP polymerization are as previously published,[5] with k_p[9] and k_t[15] expressions developed from PLP studies. Both the aqueous and organic models for NVP use identical rate expressions, with the only differences being the k_p expressions (fit to PLP-SEC experimental data), the introduction of chain transfer to *n*-butanol (for organic phase polymerization), and the initiator decomposition expressions, as two different initiators (V-50 in aqueous phase and Vazo-67 in organic phase) were used due to the insolubility of V-50 in *n*-butanol.

The influence of monomer concentration on k_p is more pronounced in water than in *n*-butanol as can be seen from Figure 1, which summarizes an extensive PLP-SEC study of NVP in aqueous[9] and organic[16] solution. The variation of NVP k_p in *n*-butanol as a function of initial weight percent of NVP in solution (w^0_{NVP}), temperature, and fractional conversion of monomer to polymer (x_p) is captured by Equations 1 and 2.

$$\frac{k_p}{k_{p,max}} = 0.02 + 0.98\exp\left(-\frac{0.015 \cdot w^0_{NVP} \cdot (1 - x_p)}{1 - w^0_{NVP} \cdot x_p}\right) \tag{1}$$

$$k_{p,max}/\left(\mathrm{L \cdot mol^{-1} \cdot s^{-1}}\right) = 1.42 \times 10^7 \exp\left(-\frac{2.43 \times 10^3}{(T/\mathrm{K})}\right) \tag{2}$$

Note that these expressions may be slightly modified, as additional PLP-SEC experiments of NVP in *n*-butanol are underway.[16]

The thermal initiators V-50 and Vazo-67 decompose by a first-order reaction with half-lives of 16 min[17] and 54 min[18] at 85 °C, respectively. This difference in the decomposition rates was compensated for by adjusting the moles of initiator added, in order to achieve equal initial radical flux in the two solvents, assuming equivalent initiator efficiencies:

$$\left(k_d[\mathrm{I}]_0\right)_{\text{Vazo-67}} = \left(k_d[\mathrm{I}]_0\right)_{\text{V-50}} \tag{3}$$

At the lower NVP concentrations used in batch polymerizations ($w_{NVP} < 20\%$), it is expected that the significantly lower k_p values in *n*-butanol should result in a conversion rate significantly lower than that in aqueous solution, assuming that k_t is similar in the two systems. This difference was indeed found experimentally, as seen from the comparison of monomer conversion profiles in Figure 2a, obtained from batch polymerizations at 85 °C with 12.5 vol% NVP in solution. (MM results, shown as Figure 2b will be discussed later.) Previous work showed that aqueous-phase NVP batch and semibatch polymerizations conducted over a range of initial monomer and initiator concentrations at 70 and 85 °C are well-represented by the FRP model parameters summarized in ref. 5. A similar set of experiments in *n*-butanol has been completed at 85 °C, with conversion profiles shown in Figure 3. The effect of NVP concentration on polymerization rate was found to be negligible in *n*-butanol, in agreement with the PLP-SEC results shown in Figure 1. Moreover, the model developed to describe aqueous-phase NVP polymerization also provides a good description of the conversion profiles measured in *n*-butanol over a range of monomer and initiator concentrations, once the difference in k_p behavior is accounted for. The slight mismatch between model predictions and experimental results in Figure 3 may indicate a small difference in NVP k_t behavior for the two solvents. From these results it can be concluded that the k_p expressions determined from independent pulsed laser investigations capture the differences observed for the experimental conversion profiles of NVP in aqueous and organic solution.

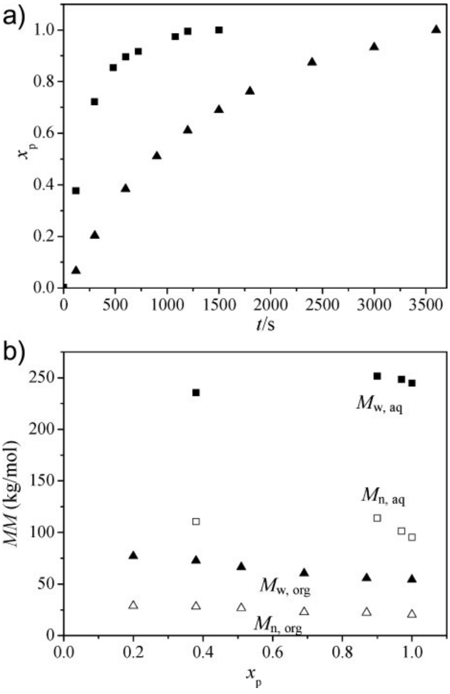

Figure 2.
(a) Conversion profiles and (b) polymer weight and number molecular-mass averages (M_w filled symbols, M_n open symbols) plotted as a function of conversion for batch polymerization of 12.5 vol% NVP at 85 °C in water (■) and butanol (▲) with the same initial radical flux.

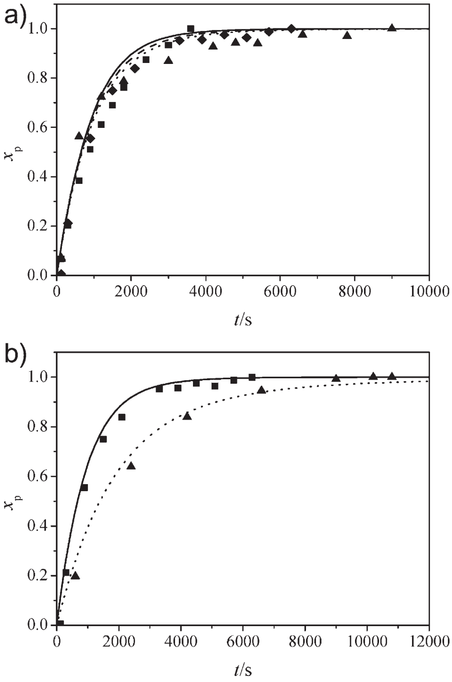

Figure 3.
Conversion profiles for organic-phase batch polymerizations of NVP at 85 °C. (a) Influence of NVP concentrations of 12.5 (■, –––), 20 (◆, – – –) and 30 (▲, ·······) vol% at an initiator concentration of 0.093 wt% Vazo-67. (b) Influence of initiator concentrations of 0.023 (▲,·······) and 0.093 (■,–––) wt% Vazo-67 with initial NVP level of 20 vol%. The lines represent the simulations and the symbols represent the experimental results.

The significantly lower k_p values for polymerization in organic compared to aqueous solution also affects polymer MM. As shown in Figure 2b, MM averages of polymer produced in *n*-butanol are significantly lower than polymer produced in water. Most of the difference in the data can be explained by the differences in k_p values; however, a small amount of chain transfer to *n*-butanol ($k_{tr}^{sol}/k_p = 1.5 \times 10^{-4}$ at 85 °C) was added to the model to better match the experimental data, with the transfer to monomer and transfer to polymer ratios set to the values determined from the aqueous-phase study of NVP polymerization.[5] A comparison of simulation and experimental MM averages and complete MMDs for aqueous-phase batch and semibatch polymerizations has been presented previously.[5] As shown in Figures 4 and 5, the same model provides a good description of how MM averages and full distributions vary with conversion for NVP polymerization in *n*-butanol.

Comparison of Aqueous-Phase NVP and NVF Polymerization

The previous section illustrates that the large differences observed in NVP polymerization rate and polymer MM in organic and aqueous solution are not at all surprising, as long as a-priori knowledge of k_p behavior is known. A second example illustrating this point is provided by comparing aqueous-phase batch polymerization of NVP and NVF. A recent PLP-SEC study of NVF in aqueous solution indicates that, while the same general behavior is observed, the absolute value of NVF k_p is lower than that of NVP under identical conditions and the increase with decreasing monomer concentration is not as large.[13] Although no PLP studies of NVF k_t have been conducted, preliminary batch polymerization experiments indicated that observed differences in the initial rates of monomer conversion correlated well to the measured differences in k_p values.[13] We have completed a larger number of NVF batch experiments, and have applied the0 aqueous-phase NVP polymerization model[5] to represent the results, only changing the monomer density and k_p expressions[13] and assuming that termination and chain-transfer rate coefficients are identical for the two monomers. The influence of initial monomer concentration on NVF conversion data is shown in Figure 6. The incomplete conversion is due to the depletion of initiator, as V-50 has a half-life of 16 min at 85 °C.[17] NVP reacts at a much faster rate compared to NVF, with the initial rates of reactions at identical conditions summarized in Table 1. The experimental differences compare very well to their respective differences in k_p ($k_{p,NVP} = 3 \times k_{pNVF}$) measured by PLP-SEC,[13] suggesting that k_t values for the

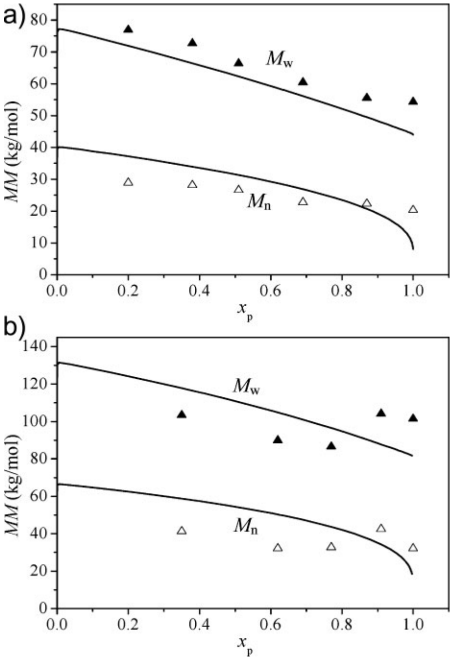

Figure 4.
Polymer molecular-mass averages plotted as a function of conversion for batch experiments conducted in *n*-butanol at 85 °C with (a) 12.5 vol% NVP and 0.093 wt% Vazo-67 and (b) 20 vol% NVP and 0.023 wt% Vazo-67. The lines represent the simulation results and the closed and open symbols represent the experimental results for M_w and M_n, respectively. The simulations were carried out with $k_{tr}^{mon}/k_p = 6 \times 10^{-4}$, $k_{tr}^{pol}/k_p = 6 \times 10^{-5}$ and $k_{tr}^{sol}/k_p = 1.5 \times 10^{-4}$.

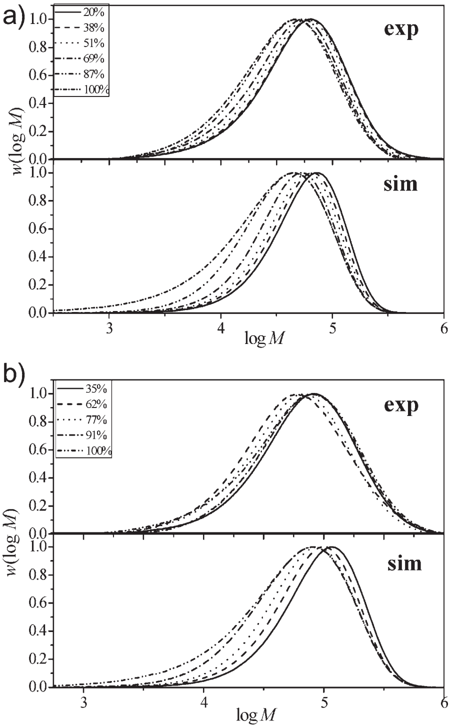

Figure 5.
Comparison of simulation and experimental molecular-mass distributions obtained for (a) 12.5 vol% NVP and 0.093 wt% Vazo-67 and (b) 20 vol% NVP and 0.023 wt% Vazo-67 at 85 °C in *n*-butanol. Polymer conversions as indicated in the figure legends. The simulations were carried out using $k_{tr}^{mon}/k_p = 6 \times 10^{-4}$, $k_{tr}^{pol}/k_p = 6 \times 10^{-5}$ and $k_{tr}^{sol}/k_p = 1.5 \times 10^{-4}$.

two monomers must be similar in magnitude. In addition, the polymerization model developed for NVP (but utilizing the known k_p behavior of NVF) provides a reasonable representation of the conversion profiles in Figure 6. The small difference between k_p values for 12.5 and 20 vol% NVF is counteracted by the corresponding changes in k_t;[15] subsequently, the difference in initial rates becomes negligible, as can be seen from the values in Table 1.

Polymer MM averages obtained in the NVP and NVF polymerizations are compared in Figure 7 for two different levels of initial monomer concentration. Clearly, poly(NVF) MMs are much lower compared

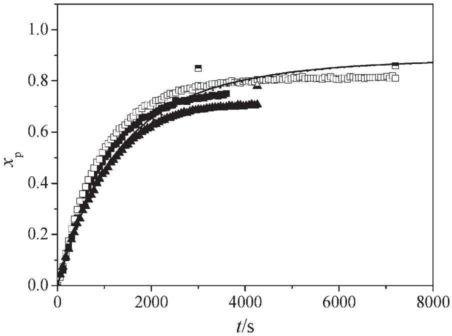

Figure 6.
Conversion profiles for batch polymerization of NVF at 85 °C for initial NVF concentrations of 12.5 (■, —) and 20 (▲, ······) vol% at an initiator concentration of 0.02 wt% V-50. The lines represent the simulations and the symbols represent the experimental results; open symbols represent repeat results and the partly filled symbols represent conversion determined by NMR.

to poly(NVP). The absence of data at higher conversion levels for NVF makes it difficult to comment on the importance of chain-transfer to polymer in the system. However, the small increase in poly(NVF) weight-average MM values observed with increasing conversion for the experiment with 20 vol% NVF (Figures 7b) is consistent with the upswing seen for NVP at high (>80%) conversion levels.[5] Moreover, the reasonable model predictions of the NVF MM averages using the NVP model coefficients (only correcting for the differences in k_p) suggests that the relative transfer rate coefficients of the two *N*-vinyl monomers must be of similar magnitude.

Table 1.
Comparison of initial rates of monomer conversion for aqueous-phase batch polymerizations of NVP and NVF at 85 °C with 0.02 wt% V-50 initiator.

Monomer level, vol%	Initial conversion rate (dx_p/dt)		NVP/NVF ratio	
	NVP	NVF	Average	
20	0.00176	0.00060	2.94	2.93
		0.00175	2.92	
12.5	0.0020	0.00060	3.32	3.07
		0.00070	2.83	

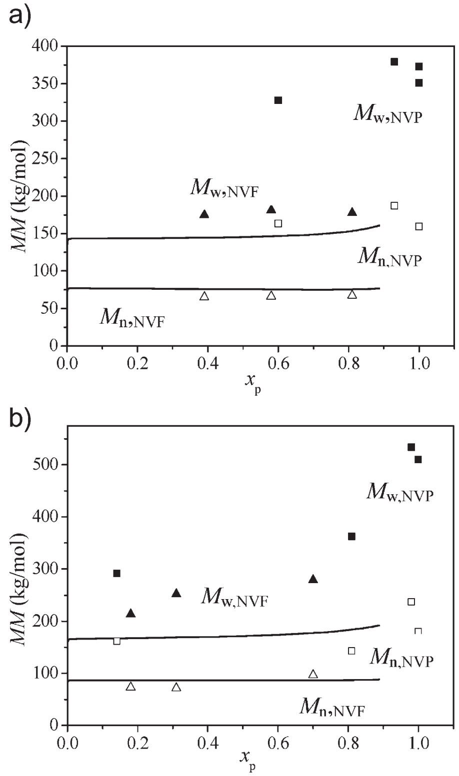

Figure 7.
Comparison of the evolution of number and weight molecular-mass averages (M_w, M_n) with monomer conversion for NVP (■) and NVF (▲) batch experiments conducted with monomer concentrations of (a) 12.5 vol% and (b) 20 vol% with an initiator concentration of 0.02 wt% at 85 °C. The closed and open symbols represent the experimental results for M_w and M_n, respectively, and the lines represent simulation results for the NVF system (see text).

Conclusion

The polymerization behavior of NVP in aqueous and organic (*n*-butanol) solution and that of NVF in aqueous solution has been studied. A significant decrease in both rates of monomer conversion and polymer MM averages is found for NVP polymerization in *n*-butanol compared to aqueous-phase polymerization at the moderate monomer contents under investigation. Similarly, it is found that NVF aqueous-phase polymerization is slower and produced lower-MM polymer compared to NVP polymerization under identical conditions. The differences in both polymerization rates and polymer MMs correlate very well with the effect of monomer and solvent choice on k_p measured in independent PLP-SEC experiments. Indeed, a single model can represent all three experimental data sets reasonably well, changing only the k_p expressions and introducing a small amount of chain transfer to *n*-butanol. These results suggest that a generalized understanding of the kinetic behavior of water-soluble *N*-vinyl monomers can be obtained once their k_p differences have been accounted for. Experiments on other systems are underway to further test this finding.

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