

Nitroxide-Mediated Radical Polymerization of 4-Vinylpyridine and Its Application on Modification of Silicon Substrate

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ABSTRACT: The poly(4-vinylpyridine) with hydroxyl end group and narrow polydispersity was synthesized by polymerization of 4-vinylpyridine by the use of nitroxide initiator based on 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl and azobisisobutyronitrile. The effects of different initiator amounts and reaction time on polymerization rate, molecular weight, and molecular weight distribution of the poly(4-vinylpyridine) were investigated at bulk polymerization. The experimental results have shown that the polymerization of 4-vinylpyridine is a controlled living free-radical polymerization; the molecular weight is proportional to reaction time; and the molecular weight and molecular weight

distribution are affected by molar ratios of [4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl]/[azobisisobutyronitrile]. By varying the ratio of 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl to azobisisobutyronitrile, the poly(4-vinylpyridine) with narrow polydispersity can be obtained. X-ray photoelectron spectroscopy results show that the synthesized poly(4-vinylpyridine) can be tethered on the surface of silicon wafer through the reaction between hydroxyl end of poly(4-vinylpyridine) and native silicon oxide layer on the wafer surface. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2687–2692, 2002

INTRODUCTION

Recently, accurate control of polymerization processes to give well-defined molecular weight, narrow polydispersity, and end-functionalized macromolecules has become an increasingly important aspect of polymer chemistry because these end-functionalized polymers can produce various types of block copolymers,¹ form networks,² and be anchored to silicon surface to adjust the surface characteristics of a substrate.³ Traditionally, the homopolymers or random copolymers with functional chain end and narrow polydispersity can be prepared by using either anionic,⁴ cationic,⁵ or group transfer polymerization techniques.⁶ While these procedures are undoubtedly successful, they do suffer from rigorous synthetic requirements. Free-radical polymerization requires less rigorous synthetic condition, and in some cases, can offer an alternative method for the preparation of end-functionalized polymers and copolymers.⁷ However, the major drawback of free-radical processes is that they cannot accurately control the molecular weight of products,

molecular weight distribution, and, more importantly, the number of chain ends.⁸

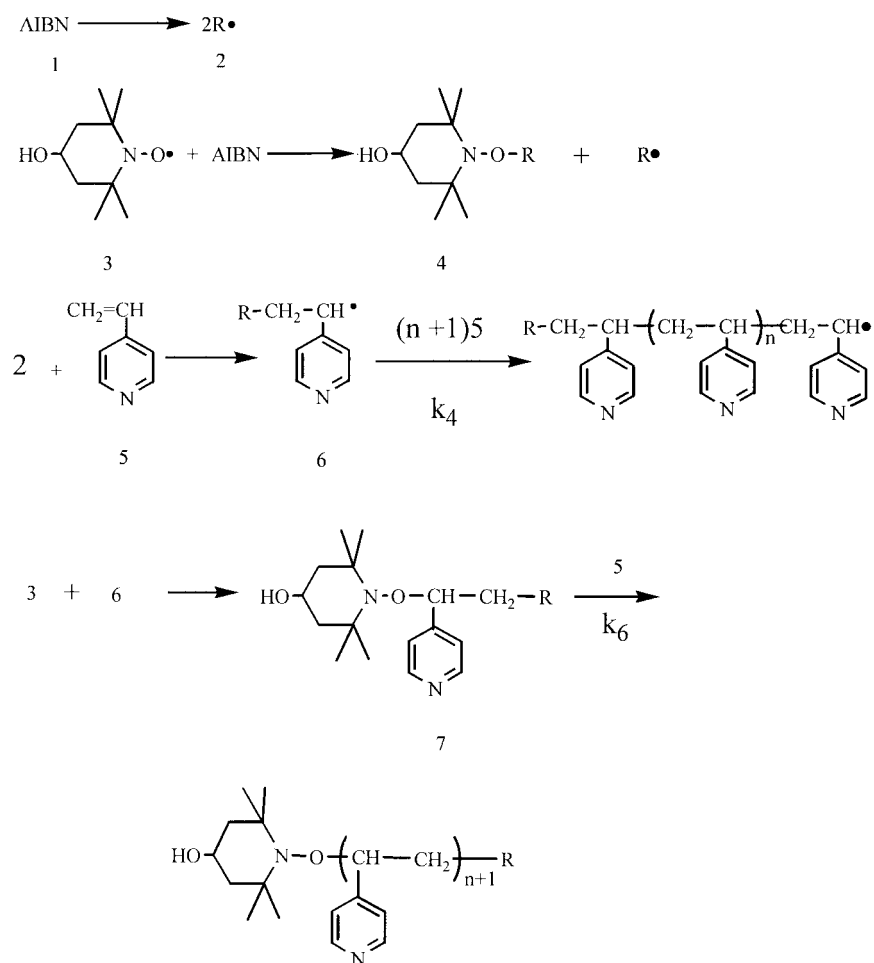
In 1993, Georges et al.⁹ first reported that a polystyrene with a narrow molecular weight distribution could be prepared by a living free-radical polymerization process. Then, a number of homopolymers, random copolymers, and block copolymers with narrow polydispersities were prepared by a living free-radical polymerization technique by using a nitroxide initiator based on 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) and benzoyl peroxide (BPO).^{10,11,12}

The homopolymer and copolymer that contain the pyridine group have attracted much interest in very recent years because of various applications such as water-soluble polymer and coordination reagents for transition metal.¹³ Conventional free-radical polymerization of 4-vinylpyridine is carried out in bulk or solvents by using common initiators such as BPO or azobisisobutyronitrile (AIBN),¹³ which often results in polymers with broad molecular weight distribution. For the living ionic polymerization of 4-vinylpyridine, its development is also limited by the difficulty in solubility because of insolubility of poly(4-vinylpyridine) (P4VP) above a certain molecular weight in the most common solvents, such as tetrahydrofuran (THF).^{14,15}

In this article, we report on the synthesis of P4VP with narrow molecular weight distribution by nitroxide-mediated free-radical polymerization using an ini-

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Scheme 1 Polymerization route of 4-vinylpyridine.

tiation system, 4-hydroxy-2,2,6, 6-tetramethylpiperidin-1-oxyl (HTEMPO) and AIBN, and the investigation of kinetic process of this polymerization. The covalently tethering P4VP with HTEMPO chain end on the silicon surface is also described.

EXPERIMENTAL

Materials

The materials used were as follows: 4-VP (Aldrich), which was dried by calcium hydride and then distilled under reduced pressure before use; AIBN (Shanghai 4th Factory of Chemicals, 99%), which was purified by recrystallization with absolute methanol; HTEMPO, which was prepared by oxidation of HTEMPO (Beijing Huashan Auxiliary Factory) with 30% hydrogen peroxide using sodium tungstate and ethylene diamine tetraacetic acid as catalyst.¹⁶ All unspecified chemicals were obtained from the Shanghai Chemical Reagent Co., Shanghai, China.

Polymerization of 4-vinylpyridine

The polymerization route of 4-vinylpyridine is displayed in Scheme 1. A typical synthesis procedure is

described as follows: 10.5 g 4-VP (0.1 mol), 28.5 mg AIBN (0.2 mmol), and 67.4 mg HTEMPO (0.36 mmol) were added to a single-necked flask and stirred with magnetic stirrer; after three cycles of freeze-pump-thaw, the single-necked flask was placed into an oil bath at 100°C for 2 h and then at 130 ± 2°C under argon atmosphere. At a desired time, the polymerization was stopped by cooling to -20°C. The polymers were recovered as precipitates from a large excess of toluene and then filtered and dried. The polymers were purified by way of reprecipitation in which the crude polymer samples were dissolved in ethanol first and then precipitated in a mixed solvent of ethanol and toluene (volume ratio of ethanol and toluene: 1/5). Finally, the obtained polymers were dried in a vacuum oven.

Grafting reaction on silicon wafer

The hydroxyl group of HTEMPO moiety in P4VP end was used to end-graft P4VP to the native silicon oxide layer. The silicon wafers that were cleaned in advance through immersing them in a solution of sulfuric acid (98%) and hydrogen peroxide (30%) (70 : 30 ratio by

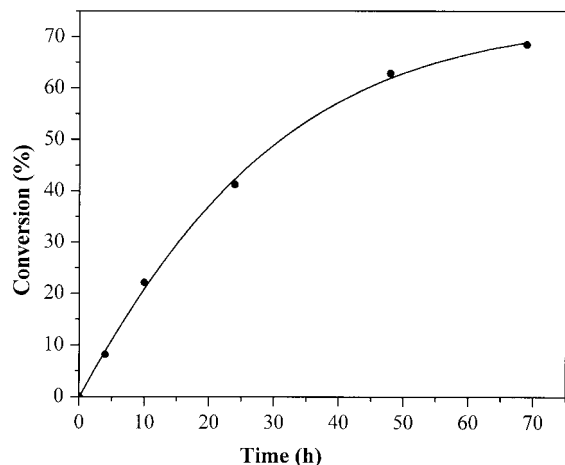


Figure 1 Conversion as a function of polymerization time; [HTEMPO] (●), 3.6×10^{-4} mol/L, [AIBN], 2.0×10^{-4} mol/L, [4-vinylpyridine], 0.2 mol/L; reaction temperature, $130 \pm 2^\circ\text{C}$.

volume) at 90°C for 2 h were washed with distilled water.¹⁷ The thin P4VP film on silicon wafer was prepared by spin-coating method. The polymer-coated substrates were heated under vacuum at 130°C for 48 h, to make the hydroxyl end group diffuse to and react with the native oxide layer. Then, the substrates were taken out of the oven and quenched to room temperature.

The ungrafted polymers were removed by way of repeated washing with *N,N*-dimethylformamide (DMF).

Measurements

The conversion of polymerization was determined by UV spectra measurement on UV-3100 spectrometer. $^1\text{H-NMR}$ spectra were obtained on a Bruker MSL-300 spectrometer with DMSO-d_6 as the solvent. The molecular weight measurements were carried out by a Waters 244 gel permeation chromatograph (GPC) with a UV detector using DMF as an eluant. Monodisperse polystyrene samples were used as standards for calibration. X-ray photoelectron spectroscopy (XPS) measurement was carried out on ESCA 850V with an MgK α X-ray source.

RESULTS AND DISCUSSION

Polymerization of 4-vinylpyridine

The polymerization of 4-vinylpyridine initiated with AIBN and HTEMPO was carried out at $130 \pm 2^\circ\text{C}$ under argon atmosphere. To investigate the mechanism of the polymerization of 4-vinylpyridine in the presence of HTEMPO, the reactions in different reactors were stopped at desired time intervals, and the UV spectra of the samples obtained at various poly-

merization times were measured. The conversion of monomer was calculated from UV spectra based on the peak absorption intensity of 228 nm (vinyl group) and the standard plot of peak absorption intensity of 228 nm with different concentration of 4-vinylpyridine monomer. Figure 1 gives the plot of conversion versus time for polymerization of 4-vinylpyridine in the presence of HTEMPO with a molar ratio of HTEMPO to AIBN and to monomer of 1.8 : 1 : 1000. It shows that the conversion of monomer increases with increasing polymerization time. In the initial stage, the conversion increased rapidly with the polymerization time because of the higher monomer concentration and lower viscosity of the system, and then the increased rate of the conversion slows down with the increase of viscosity and the decrease of monomer concentration.

Figure 2 gives the plot of molecular weight versus conversion for polymerization of 4-vinylpyridine. It shows that the molecular weight of the polymers increases with the polymerization time, exhibiting the basic character of living radical polymerization. A nice linear relationship between \bar{M}_n and conversion indicates that this polymerization is quite different from the common radical polymerization in which the molecular weight of polymer is independent of conversion.

Figure 3 shows the plot of $\ln([M]_0/[M]_t)$ versus time for the polymerization of 4-vinylpyridine at 130°C in the presence of HTEMPO with the molar ratio of HTEMPO to AIBN and to monomer of 1.8 : 1 : 1000. A nice linear relationship between $\ln([M]_0/[M]_t)$ and polymerization time was also observed, indicating that the reaction is a first-order reaction. Based on the reactions of monomers with monomer free radicals and dormant compounds with monomers in Scheme 1, the rate equation of monomer consumption can be given as follows:

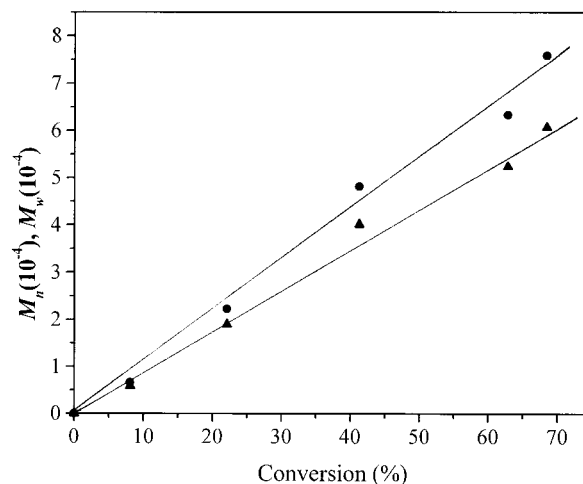


Figure 2 Polymer molecular weights (\bar{M}_w and \bar{M}_n) plotted with conversion for bulk polymerization with [HTEMPO]/[AIBN] = 1.8; temperature: $130 \pm 2^\circ\text{C}$; \bar{M}_w (●), \bar{M}_n (▲)

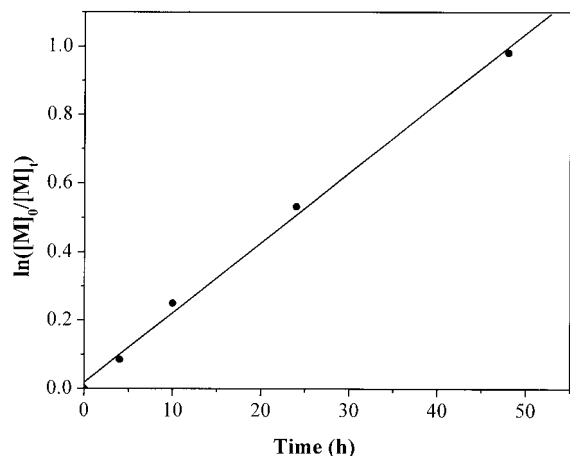


Figure 3 $\ln([M]_0/[M]_t)$ with time for bulk polymerization, [HTEMPO], 3.6×10^{-4} mol/L, [AIBN], 2.0×10^{-4} , [4-vinylpyridine], 0.2 mol/L; reaction temperature, 130°C.

$$d[M]/dt = k_4 \times [M] + k_6 \times [\text{HTEMPO-P}] \times [M] \quad (1)$$

where k_4 is the rate constant of reaction between monomers and monomer free radicals, k_6 is the rate constant of reaction between dormant compounds and monomers in Scheme 1, $[M]$ is the concentration of the monomer, and [HTEMPO-P] represents the concentration of dormant compound in reaction system. Because the polymers synthesized by this method have narrower polydispersity, it can be deduced that once the initiation is completed, the chain radicals will be trapped rapidly by HTEMPO radicals. Thus, the insertion of monomers into NO—C bond will be predominantly propagation (i.e., $k_4 \times [M] \ll k_6 \times [\text{HTEMPO-P}] \times [M]$); the rate of polymerization in the presence of stable radicals can be written as:

$$d[M]/dt = k_6 \times [\text{HTEMPO-P}] \times [M] \quad (2)$$

Since the concentration of dormant compound is nearly a constant throughout the polymerization, the equation can be simplified as:

$$d[M]/dt = K \times [M] \quad (3)$$

As a result, the $\ln([M]_0/[M]_t)$ versus time plot is a straight line where $K = k_6 \times [\text{HTEMPO-P}]$, and the reaction of monomer consumption is a first-order reaction. From Figure 3, K is calculated to be $6.35 \times 10^{-5} \text{ S}^{-1}$, which is consistent with the value obtained in polystyrene prepared by the nitroxide radical.¹⁸

Thus, it is reasonable to conclude that the polymerization of 4-vinylpyridine in the presence of HTEMPO is a controllable living free-radical polymerization. Compared with conventional free-radical polymerization, the polymerization of 4-vinylpyridine in the presence of nitroxide stable free radical has no self-accelerating effect, and the reaction of the inserting of monomers into the bond of C—ON in dormant compound is predominantly propagation.

Effect of molar ratio of HTEMPO to AIBN on the polymerization

Table I shows the data of polymerization of 4-vinylpyridine at two kinds of molar ratios of the HTEMPO to AIBN. From these data, we find that the molecular weight of P4VP increased with an increase in the polymerization time and that the molecular weight distribution index is in the range of 1.13 to 1.25. At same reaction time, the concentration of HTEMPO is lower, the molecular weight of resulting polymers is higher, and the distribution is broader.

According to Veregin et al.¹⁹ and our experiments, in the living free-radical polymerization of 4-vinylpyridine in presence of HTEMPO, the propagation of polymer chain was predominately carried out through inserting the monomer into NO—C of dormant compound. In the case of a higher concentration of HTEMPO, the propagation of polymer chain should be slower and the molecular weight lower, whereas the distribution is narrower. On the contrary, for lower concentrations of HTEMPO, the HTEMPO cannot cap all chain free radicals to form the dormant compounds in the initial stage, and there are considerable chain free radicals in the system that can initiate

TABLE I
Results of the Characterization of P4VP

[HTEMPO]/[AIBN]	Reaction time (h)	$\bar{M}_w (\times 10^{-4})$	$\bar{M}_n (\times 10^{-4})$	\bar{M}_w/\bar{M}_n	Conversion (%)
1.8	4	0.6593	0.5815	1.17	8.1
	10	2.2183	1.8896	1.13	22.1
	24	4.8115	4.0096	1.20	41.3
	48	6.3354	5.2359	1.21	62.8
	69	7.5321	6.0256	1.25	68.8
2.5	4	0.2465	0.2186	1.13	5.2
	10	0.9684	0.8421	1.15	17.5
	24	2.4000	2.0689	1.16	37.6
	48	3.7614	3.2149	1.17	56.3

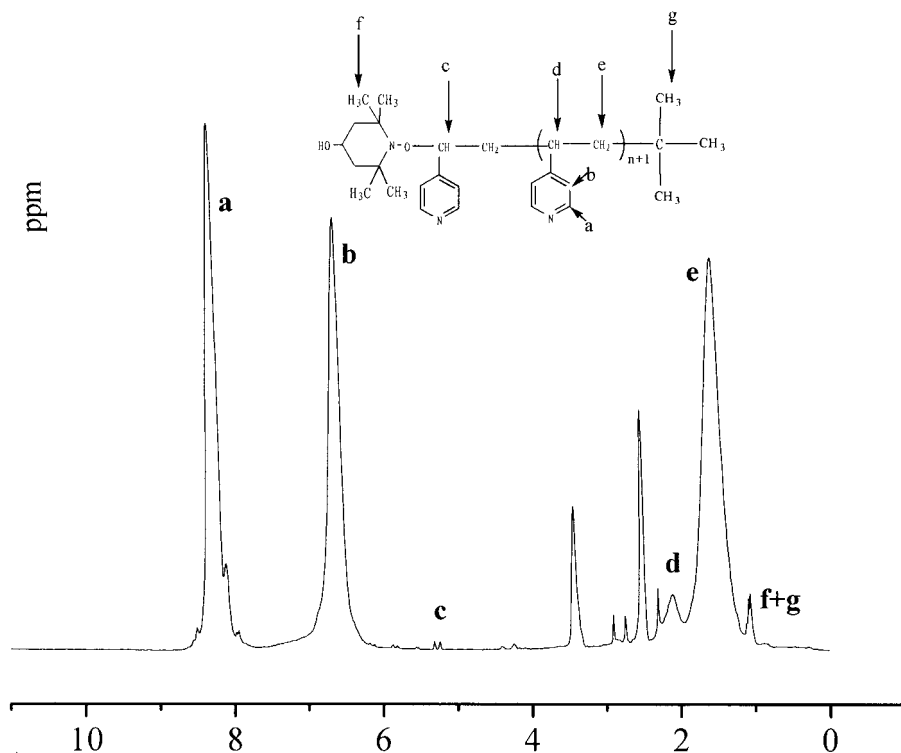


Figure 4 The ^1H -NMR spectrum of poly(4-vinylpyridine).

polymerization of 4-vinylpyridine with a common free-radical mechanism; thus, the molecular weight of copolymers is higher and the distribution is broader.

Structure of P4VP

Figure 4 gives the ^1H -NMR spectrum of the poly(4-vinylpyridine) with M_n of 18,896; the initiation system is HTEMPO and AIBN with the molar ratio of HTEMPO to AIBN of 1.8. The chemical shifts at 8.3 ppm (a) and 6.6 ppm (b) are assigned to second and sixth protons of pyridine rings, and third and fifth protons of pyridine rings, respectively. The small peak at 5.2 ppm (c) is assigned to the methenyl proton of 4VP moiety linked with HTEMPO moiety and the chemical shifts around 1.2 to 2.2 ppm (d + e) are due to the methylene protons and methine protons of main chain. Resonance of the methyl protons of HTEMPO at the chain end appears at 1.01 ppm (f). The signal at 0.9 ppm (g) is assigned to the methyl protons of AIBN fragment at another chain end. The ^1H -NMR spectrum suggests that HTEMPO moiety is capped at the end of the polymer chain.

The characterization of grafted P4VP on silicon substrate

To investigate the grafting ability of the P4VP with hydroxyl end group on silicon wafer, the solution of P4VP in DMF was spin coated onto treated silicon

wafers. The polymer-coated substrates were heated under vacuum at 130°C for 48 h to allow the hydroxyl end group to diffuse to and react with the native oxide layer. Unattached P4VP was removed by repeated rinsing with DMF. Figure 5 shows the XPS survey spectrum of polymer-grafted silicon wafer recorded at the emission angle of 45° . The molecular weight of polymer samples used in grafting reaction is 40K. The analytical depth ($d = 3\lambda \sin \theta$) was calculated by using the value of the inelastic mean free path (λ) evaluated from Ashley's equation.²⁰ The magnitude of d is 6.8 nm, corresponding to photoelectron emission angle of

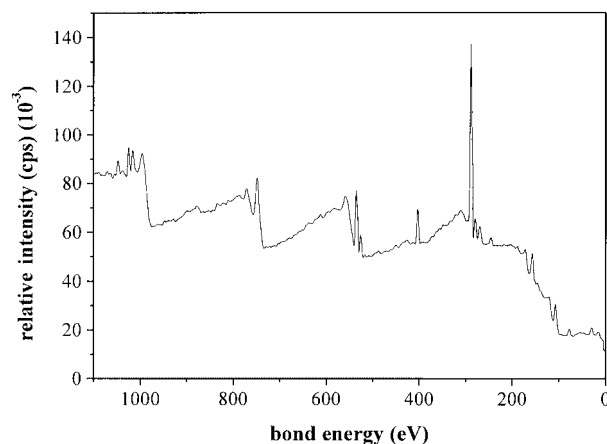


Figure 5 The XPS spectrum of the polymer grafted to silicon substrates.

45°. After grafting P4VP to silicon substrates, the characteristic peaks corresponding to N_{1s} at 400 eV, O_{1s} at 532 eV, C_{1s} at 285 eV, Si_{2s} at 152 eV, and Si_{2p} at 100 eV signals are detected. The appearance of the carbon at 285 eV, and nitrogen at 400 eV, demonstrate that P4VP has been chemically attached to the surface of silicon wafer. The presence of weak peaks of Si_{2s} and Si_{2p} in survey spectrum, which were attributed to the native oxide layer of substrate, implied that the grafted P4VP on substrate is not very dense.

CONCLUSION

The polymerization of 4-vinylpyridine initiated by AIBN and HTEMPO is a controlled living free-radical polymerization. The synthesized P4VPs have a narrow polydispersity and hydroxyl end group. The molecular weight of P4VP increases with polymerization time. With the increase of the molar ratios of [HTEMPO]/[AIBN], the molecular weight decreases and the distribution of molecular weight becomes narrower. Thus, the molecular weight and molecular weight distribution can be controlled through changing polymerization time and concentration of HTEMPO. XPS results show that the synthesized P4VP can be tethered on the surface of silicon wafer through the reaction between the hydroxyl end of P4VP and the native silicon oxide layer on the wafer surface.

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