

Synthesis and Characterization of (3,4-diphenyl-2,5-dimethyl)phenyl-Poly(vinyl silicon) Oils

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SYNOPSIS

(3,4-Diphenyl-2,5-dimethyl)phenyl-poly(vinyl silicon) oils (DPDMP-C-gums) have been synthesized by Diels-Alder reaction of polyvinyl silicon oil (C-gum) with 3,4-diphenyl-2,5-dimethylcyclopentadienone (DDCP) in diphenyl ether at reflux temperature under normal pressure. The structures of the prepared compounds were characterized by $^1\text{H-NMR}$, IR, and UV spectra, and some of their properties, such as color, viscosity, refractive index, and thermooxidative stability of the DPDMP-C-gums, were obtained. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The liquid methyl-vinylpolysiloxane [poly(vinyl silicon) oil] has been used as a concentrated cross-linker for silicone rubbers; therefore we prefer to call it C-gum. The C-gums containing polyphenylphenyl have been used for vulcanization of heat-curable silicone rubber.¹ While another kind of C-gums containing (3,4-difuryl-2,5-dimethyl)phenyl (DFDMP) has been synthesized, it has found that all are characteristic of good heat resistance.² Although some organosilicon compounds containing (3,4-diphenyl-2,5-dimethyl)phenyl (DPDMP) have also been synthesized,³ until now high molecular compounds of this kind have not been reported. For this article, the C-gums containing DPDMP have been prepared and characterized. The resulting polysiloxanes possess better heat-oxidative endurance than C-gum as a material.

EXPERIMENTAL

Materials

C-gum was prepared according to the procedure outlined by Wu and coworkers⁴ and we determined

its vinyl group content to be 8.7 mol %. 3,4-diphenyl-2,5-dimethylcyclopentadienone (DDCP) was prepared according to Japp and Meldrum.⁵

Synthesis of DPDMP-C-Gum

8.63 g (vinyl group 0.010 mol) C-gum, 0.325 g (0.00125 mol) DDCP (mole ratio of vinyl to DDCP, 8 : 1), and 10 mL diphenyl ether were introduced into a 125-mL flask equipped with a mechanical stirrer, a reflux condenser connected to a drying tube of calcium chloride, a nitrogen inlet tube, and a thermometer. The reaction mixture appeared pale yellow. Heated in the flask with stirring under a atmosphere of dry nitrogen, the mixture turned into red when the temperature rose to 70°C. When the temperature reached 220°C, the mixture began to emit gases. We continued raising the temperature until it was 250°C, then refluxed the mixture and kept this temperature for 30 min to end the reaction.

After cooling, the supernatant liquid was separated from the solvent and washed with methanol. Then the liquid was dried in a vacuum dryer at 80°C under 5 Torr pressure for 5 h. Finally, a transparent liquid was obtained. The other products were prepared similarly according to 4, 2, and $\frac{4}{3}$ molar ratios of vinyl group in C-gum to DDCP, respectively. The above obtained products were all characterized by $^1\text{H-NMR}$, IR, and UV spectra, and their viscosity, refractive index, and thermooxidative stability were

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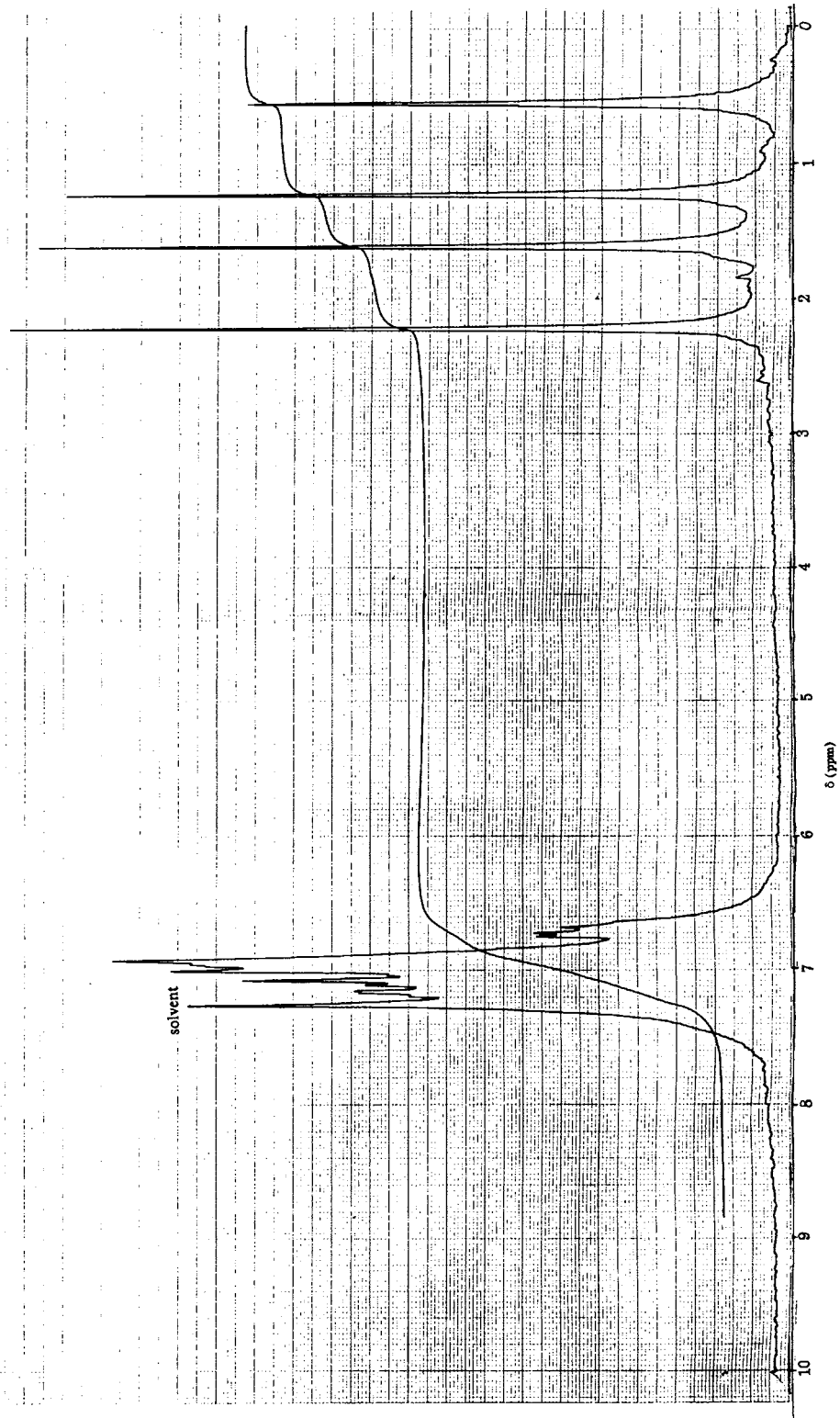


Figure 1 The ¹H-NMR spectrum of DDCP.

measured. At the same time, the control test (only the material C-gum was treated under the same reaction conditions) was performed for comparison.

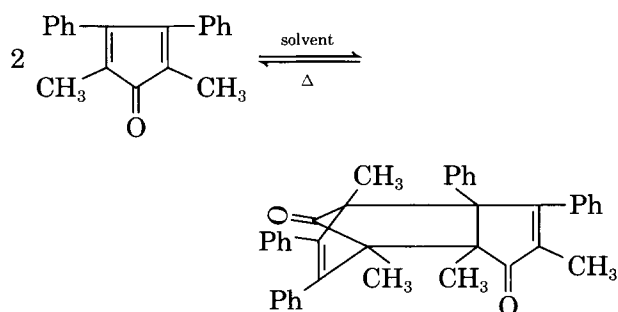
Analysis

$^1\text{H-NMR}$ spectra were recorded on an FX-90Q spectrometer in deuteriochloroform (CDCl_3). IR spectra were measured in the region of $400\text{--}4,000\text{ cm}^{-1}$ by film coating with a Nicolet-5DX spectrometer. UV spectra were examined on a UV-240 spectrometer with $20\text{ mg}/25\text{ mL}$ product solution in chloroform, which was also used as a reference. N_D^{20} were taken on a WZS-Abbe refractometer. The relative viscosity was measured on a Ubbelohde viscosity meter with bath temperature $25 \pm 0.01^\circ\text{C}$ with 0.4980 g dL^{-1} product solution in toluene. The thermooxidative stability was measured by a box oven under the following conditions: after every sample ($500 \pm 5\text{ mg}$) was put in an oven, the temperature of the oven began to rise at the rate of $20^\circ\text{C}/\text{min}$. When the temperature reached 250°C it was main-

tained for 24 h. Then the samples were weighed at room temperature.

RESULTS AND DISCUSSION

DDCP exists as a dimer at room temperature and becomes monomeric upon heating. The structure of DDCP can be expressed as follows:



The $^1\text{H-NMR}$ spectrum of DDCP is shown in Figure 1. There are four peaks—0.56, 1.24, 1.62 and 2.22

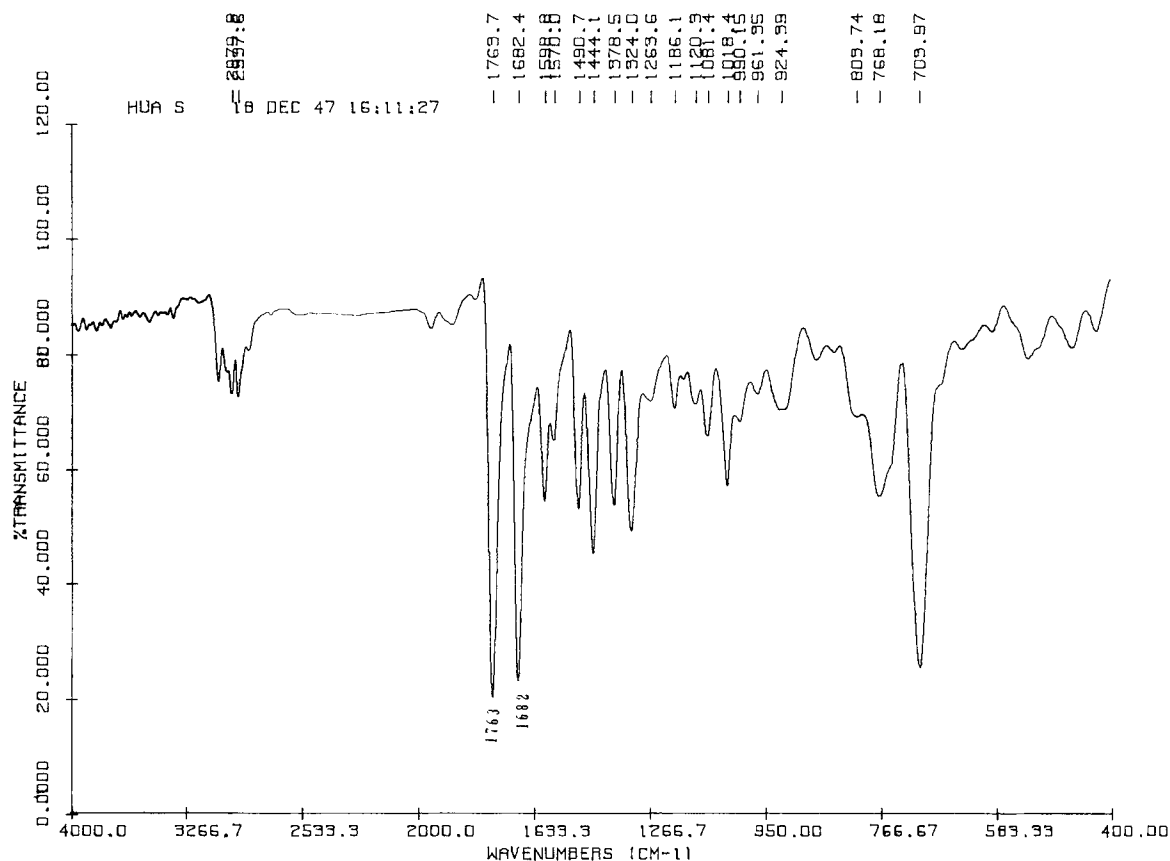


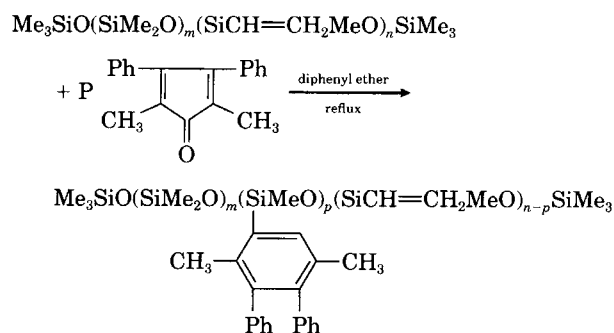
Figure 2 The IR spectrum of DDCP.

Table I Preparation Conditions and Yields for DPDMP-C-Gums

No.	C-Gum (g)	DDCP (g)	Vi/DDCP (mol/mol)	Diphenyl Ether (ml)	Reflux Time (min)	Yield (%)
1	8.6	0	—	10	30	69.3
2	8.6	0.325	8 : 1	10	30	72.3
3	8.6	0.650	4 : 1	10	30	57.7
4	8.6	1.30	2 : 1	10	30	64.8
5	8.6	1.95	4 : 3	10	30	57.8

ppm—indicating the four different kinds of hydrogens in the four methyl groups in the dimer. Other peaks between 6.44 and 7.68 in that figure demonstrate the existence of the phenyl groups in the dimer. The ratio of the integral of the hydrogens in all the methyl groups to that of the hydrogens in all the phenyl groups is 3 : 5. The IR spectrum (KBr) exhibits peaks due to two carbonyl groups: 1763 and 1682 cm^{-1} (see Fig. 2).

DPDMP were synthesized according to the following scheme:



The synthesis mechanism of DPDMP-C-gum should be the same as Liu and colleagues.³ In ref-

erences, the similar reactions⁶ used in the synthesis are either in a seal tube at high temperature or in α -chloronaphthalene at reflux temperature. However, we have replaced α -chloronaphthalene with diphenyl ether, which is cheaper and less toxic. As mentioned above, DDCP exists as a dimer at room temperature; therefore the solution of DDCP in diphenyl ether was almost colorless before heating. When the temperature rose to 70°C the dimer began to depolymerize, turning into the red monomer. When the temperature reached 200°C the reaction mixture began to fade and emit gases, demonstrating the Diels-Alder reaction. When the mixture was refluxed at 250°C for 0.5 h, the red color of the mixture was completely lost, which showed that the DDCP was used up. Obviously, the phenomenon mentioned above is due to the decrease of red DDCP (monomer) while the Diels-Alder reaction is carried out; then the Diels-Alder product gives out CO and H₂, resulting in the DPDMP-C-gum. The results are shown in Table I.

In Table I we find that all the yields are comparatively low because it is difficult to separate the products from diphenyl ether layer, and because the several washings of the products with methanol cause losses. We have studied the methanol layer

Table II Some Properties of DPDMP-C-Gums

No.	Vi/DDCP (mol/mol)	Color	N_D^{20}	Viscosity* (time)	Weight Loss at 250°C (%)
0	C-GUM	Colorless	1.4069	1'21"9	12.25
1	Control	Pale yellow	1.4135	1'22"4	7.84
2	8 : 1	Orange	1.4244	1'23"1	7.52
3	4 : 1	Red	1.4320	1'23"7	7.21
4	2 : 1	Dark red	1.4380	1'24"3	6.55
5	4 : 3	Purple	1.4391	1'25"4	5.83

* The viscosity of toluene at 25°C is 1'19"8.

Table III Values of η_{sp} and η_{sp}/c for Products

No.	Time (t)* (s)	η_{sp}	η_{sp}/c (dL g ⁻¹)
0	81"9	0.0263	0.0528
1	82"4	0.0326	0.0655
2	83"1	0.0414	0.0831
3	83"7	0.0489	0.0982
4	84"3	0.0564	0.1133
5	85"4	0.0702	0.1410

* $t_0 = 79.8$ s, $c = 0.4980$ g dL⁻¹.

and diphenyl ether layer to clarify the cause of such losses and found that diphenyl ether and a small quantity of DPDMP-C-gum exist in the layers of methanol. Since the diphenyl ether layer is a more complex mixture, more study is needed to solve it.

The color, N_D^{20} , relative viscosity, and thermooxidative weight loss of the products are shown in Table II; here we see that the viscosity, refractive index, and color are all increased while the thermooxidative weight loss is decreased in turn with the increasing content of the DPDMP. We also noticed that every sample heated became a solid, its color was deeper than the original, and its elasticities increased in

turn, reading Table II from top to bottom. According to the viscosity values in Table II, we calculated the η_{sp} and η_{sp}/c of the products; these values appear in Table III.

The ¹H-NMR spectra of DPDMP-C-gums were determined in CDCl₃ and with CHCl₃ as an internal standard. The chemical shifts of typical protons appear in Table IV.

The contents of the vinyl groups in C-gum and DPDMP-C-gums were examined by the integral of various hydrogens in ¹H-NMR spectra. The values of the vinyl groups are collected in Table V, which shows that the contents of vinyl groups are always lower than those of theoretical calculations. Obviously, this is because of the vinyl group's being partly damaged when the C-gum reacted with DDCP in the process of heating (see Table V, Nos. 0 and 1).

The IR spectra (see Fig. 3) told us that C-gum does not have the absorptive peaks at 3080, 1706, and 1486 cm⁻¹ that all of the DPDMP-C-gums have. The peak at 3080 cm⁻¹ should be attributed to stretching vibration for Ar-H; at 1706 to the bending vibration for Ar-H; and at 1486 cm⁻¹ to the stretching vibration for ring-skeleton.

The UV spectra of the DPDMP-C-gums are recorded in Figure 4. The mainly absorptive peaks of the benzene rings in DPDMP-C-gums are listed in

Table IV ¹H-NMR Data for DPDMP-C-Gum in CDCl₃

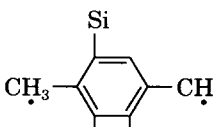
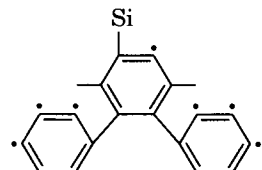
Proton Type	SiCH ₃			SiCH=CH ₃
Chemical Shift (ppm)	0.03 (s)	2.0 ~ 2.2 (m)	6.98 ~ 7.42 (m)	5.82 ~ 5.88 (m)

Table V Contents of Vinyl Groups for DPDMP-C-Gums

No.	0	1	2	3	4	5
Vi/DDCP (mol/mol)	C-Gum	Control Test	8 : 1	4 : 1	2 : 1	4 : 3
Calcd. (%)	8.7	8.7	7.61	6.52	4.35	2.17
Found (%)	8.7	8.2	7.21	5.83	3.85	1.97

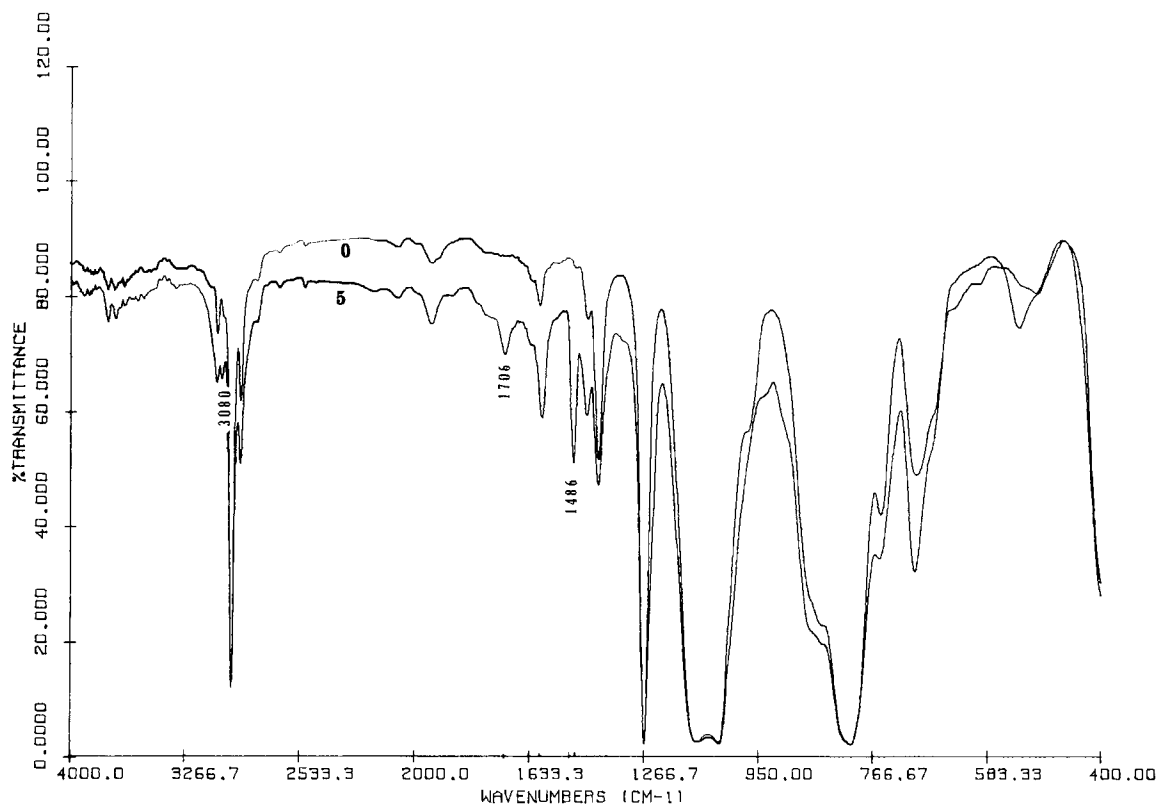


Figure 3 The IR spectra of C-gum and DPDMP-C-gum.

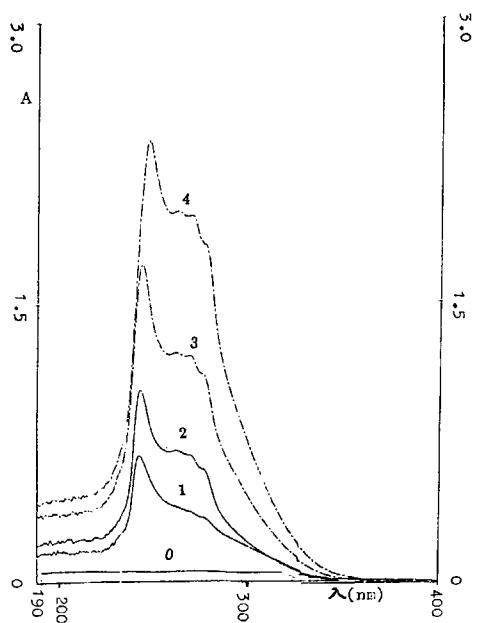


Figure 4 UV spectra of C-gum and DPDMP-C-gums.

Table VI. Here we see that the maximum absorptive peaks of the products' UV spectra are increased in turn with the increasing of contents of DPDMP, which is due to the increased effect among phenyl groups with the increasing phenyl group contents in molecules.

CONCLUSION

Polyvinyl silicon oil containing DPDMP groups was acquired using diphenyl ether as the solvent in a Diels-Alder reaction of polyvinyl silicon oil with DDCP. The DPDMP-C-gums possess better heat-oxidative endurance than does C-gum as a material and thus should have good prospects in the vulcanization of heat-curable silicone rubbers. At the same time, the series of organosilicon compounds containing vinyl phenyl, which contain two phenyl groups and two methyl groups, could be important in organic silicon macromolecular chemistry.

Table VI The Maximum Absorptive Peaks of the UV Spectra for Products

No.	0	1	2	3	4
Vi/DDCP (mol/mol)	Control	8 : 1	4 : 1	4 : 2	4 : 3
UV (nm)	None	244	245	251	252

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