

Synthesis and Characterization of (3,4-Difuryl-2,5-dimethyl) Phenyl-Polyvinyl Silicon Oils

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SYNOPSIS

(3,4-Difuryl-2,5-dimethyl)phenyl-polyvinyl silicon oils (DDP-C-gum) were synthesized by Diels-Alder reaction of polyvinyl silicon oil (C-gum) with 3,4-difuryl-2,5-dimethylcyclopentadienone (DDCP) in diphenyl ether at reflux temperature under atmospheric pressure. Their structures were characterized by $^1\text{H-NMR}$, UV, and IR spectra. Properties such as viscosity, refractive index, color, and thermal stability of some DDP-C-gums were obtained.

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INTRODUCTION

Methyl-vinylpolysiloxane, also called polyvinyl silicon oil, has been used as a concentrated crosslinker¹ for silicone rubbers, which is why it is called C-gum. We can assume that if the C-gums containing furyl-phenyl groups possess better thermostability than C-gum, they will be more useful crosslinkers for vulcanization of heat-curable silicone rubbers (HCSR). This article will report the synthesis and characterization of (3,4-difuryl-2,5-dimethyl)phenyl-polyvinyl silicon oils (DDP-C-gums).

EXPERIMENTAL

Materials

Polyvinyl silicon oil was an industrial product obtained from the No. 4 Factory of Chemical Industry, Jinan, Shandong, China. We determined its viscosity, 90 cp, and vinyl group contents, 8.9 mol %. 3,4-Difuryl-2,5-dimethylcyclopentadienone was prepared according to the procedure outlined by Yamashita and Masumura.² Its melting point is 196–200°C (liter, 196–198°C)² and its structure was established by $^1\text{H-NMR}$, UV, IR, and elementary analysis.

Synthesis of DDP-C-gums consisted of 11.3 g (vinyl group 0.0133 mol) of C-gum, 0.4 g (0.00167

mol) of 3,4-difuryl-2,5-dimethylcyclopentadienone, and 10 mL of diphenyl ether introduced into a 125-mL round bottom 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 was refluxed with stirring under an atmosphere of dry nitrogen and its color changed from original violet to gold-yellow, and then heated for half an hour 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 1 torr pressure for 6 h. Finally, a yellow transparent liquid was obtained. The diphenyl ether layer should be a mixture. But so far we have not found a good way to separate and purify the components; therefore components remain to be identified. In similar manner, other reactions were conducted according to 4, 2, and 4/3 molar ratios of vinyl group in C-gum to DDCP, respectively. The products obtained were characterized by $^1\text{H-NMR}$, UV, and IR spectra and their viscosity, refractive index, and thermogravimetric analysis (TGA) were measured. At the same time, the control test (only C-gum was treated under the same reaction conditions) was performed to compare with the above.

ANALYSIS

$^1\text{H-NMR}$ spectra were recorded on an FX-90Q spectrometer in deuteriochloroform (CDCl_3). UV

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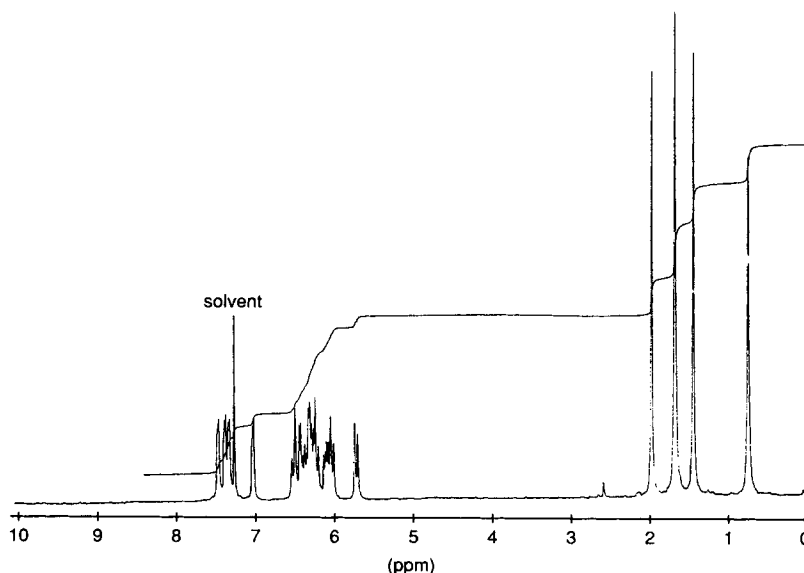


Figure 1 The $^1\text{H-NMR}$ spectrum of DDCP.

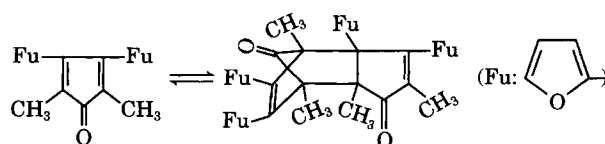
spectra were examined on a UV-240 spectrophotometer with 0.4% (v/v) product solution in chloroform. IR spectra were measured in the region of $400\text{--}4000\text{ cm}^{-1}$ by film coating with a Nicolet-5DX spectrometer. N_D^{20} were taken on a wzs-Abbe Refractometer.

The relative viscosity was acquired on an Ubbelohde viscosity meter with a bath temperature of $20.00 \pm 0.01^\circ\text{C}$ with a 0.1913 g dL^{-1} product solution in toluene.

TGA for DDP-C-gums was measured with a TGS-2-type under the following conditions: sample sizes 8–11 mg; N_2 40 mL/min; rate of heating $20^\circ\text{C}/\text{min}$ from room temperature to 550°C .

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 are shown in Figure 1. There are four peaks, 0.76, 1.42, 1.64, and 2.00 ppm, indicating the four different kinds of hydrogens in the four methyl groups in the dimer. And there are other peaks between 5.8 and 7.4 ppm in Figure 1 demonstrating the existence of the furyl groups in dimer. The integral of the hydrogens in all the methyl groups is the same as that of the hydrogens in all the furyl groups. The biggest absorption of the UV spectrum for the furyl groups in dimer is 310 nm. The IR spectrum (KBr) exhibits peaks due to two carbonyl groups: 1785 and 1675 cm^{-1} . The results of the elementary analysis were shown as follows. Found: C, 74.87%; H, 4.89%; N, 0.00%; Calc: C, 74.89%; H, 5.03%; N, 0.00%.

Table I Preparation Conditions, Yields, and Properties of DDP-C-Gums

No.	C-Gum (g)	DDCP (g)	V_i/DDCP (mol/mol)	Diphenyl Ether (mL)	Reaction Time (h)	Yields (%)	Color	N_D^{20}	Viscosity ^a (Time)
1	11.3	0		10	1.5	70.0	Pale yellow	1.4073	1'18"4
2	11.3	0.4	8 : 1	10	1.0	65.3	Yellow	1.4122	1'18"9
3	11.3	0.8	4 : 1	10	1.0	67.7	Pale orange	1.4168	1'20"0
4	11.3	1.6	2 : 1	10	1.5	64.8	Orange	1.4219	1'21"0
5	11.3	2.4	4 : 3	10	1.5	67.8	Red	1.4267	1'24"6

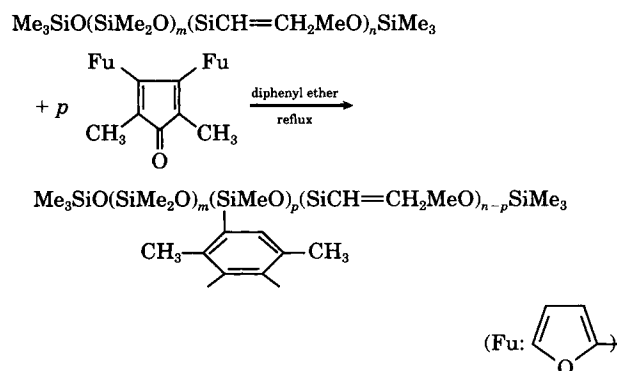
^a The viscosity of toluene at 20°C is 1'14"7.

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

No.	t^a (s)	η_{sp}	η_{sp}/c (g dL ⁻¹)
1	78.4	0.0495	0.259
2	78.9	0.0562	0.294
3	80.0	0.0710	0.371
4	81.0	0.0843	0.441
5	84.6	0.1325	0.695

^a $t_0 = 74.7$ s; $c = 0.1913$ g dL⁻¹.

Polyvinyl silicon oils containing tetraphenyl phenyl groups and condensed rings³⁻⁷ were previously prepared via the Diels-Alder reaction of polyvinyl silicon oil with tetraphenylcyclopentadienone, phencyclone, and acencyclone, respectively. However, the synthesis of DDP-C-gums have not been reported in the literature. We have prepared them according to the following scheme:



In the references, the reactions used in the synthesis are either in a sealed tube at high temperature, or in α -chloronaphthalene (b.p. 259–260°C) in reflux temperature. However, we replaced α -chloronaphthalene with diphenyl ether (b.p. 258°C) as the solvent in the open vessel and obtained fairly good results. Diphenyl ether is cheaper and less toxic than the α -chloronaphthalene. Before those experiments we tried to accomplish the reaction using tetrahydro-

naphthalene (b.p. 206°C) as a solvent at the reflux temperature, but the reaction failed. We suspected that the furyl groups in DDCP might react with C-gum although we did not get this kind of product. We used furil to react with C-gum to resolve the problem. The test demonstrated that the furyl groups in furil did not react with C-gum because the reaction mass did not change. So we now presume that the furyl groups in DDCP do not react with C-gum. This result is the same as in the literatures.^{8,9}

The conditions of the reactions of C-gum with DDCP and some relative data of products measured are outlined in Table I. In this table, we can see that the viscosity, refractive index, and color are all increased in turn with the increasing content of the (3,4-difuryl-2,5-dimethyl)phenyl group.

According to the values in Table I we calculated the η_{sp} and η_{sp}/c and put the values in Table II.

The ¹H-NMR spectra of DDP-C-gums were determined in DCCl₃ and with CHCl₃ as internal standard. The chemical shifts of typical protons are shown in Table III.

We attempted to measure the contents of the vinyl group in the C-gum and DDP-C-gums with the IBr method, but the colors of the systems were too dark to observe the endpoint of titration. Later, we examined the integral of various hydrogens in the ¹H-NMR spectra to estimate the contents of the vinyl group. The values of the vinyl group are shown in Table IV. In this table, we find that the contents of the vinyl group from the integral are always lower than those of the theoretical calculation. Obviously, it is because of the vinyl group's being damaged, partly when the C-gum reacted with DDCP in the process of heating (see TGA).

The UV spectra of C-gum and DDP-C-gums were shown in Figure 2. Figure 2 indicates that in the UV region C-gum has no absorption but all the DDP-C-gums have absorption. On the other hand, in this figure, the heights of the peaks are increased with increasing the contents of the (3,4-difuryl-2,5-dimethyl)phenyl group. In order to compare with them, the UV spectra of furil, 3,4-difuryl-2,5-di-

Table III ¹H-NMR Data for DDP-C-Gum in CDCl₃

Proton Type	SiCH ₃				—SiCH=CH ₂
Chemical shift (ppm)	0.02 (s)	5.76–6.6 (m) 7.0–7.4 (m)	2.1–2.3 (m)	7.1–7.4 (s)	5.84–5.92 (m)

Table IV Contents of Vinyl Group for DDP-C-Gums

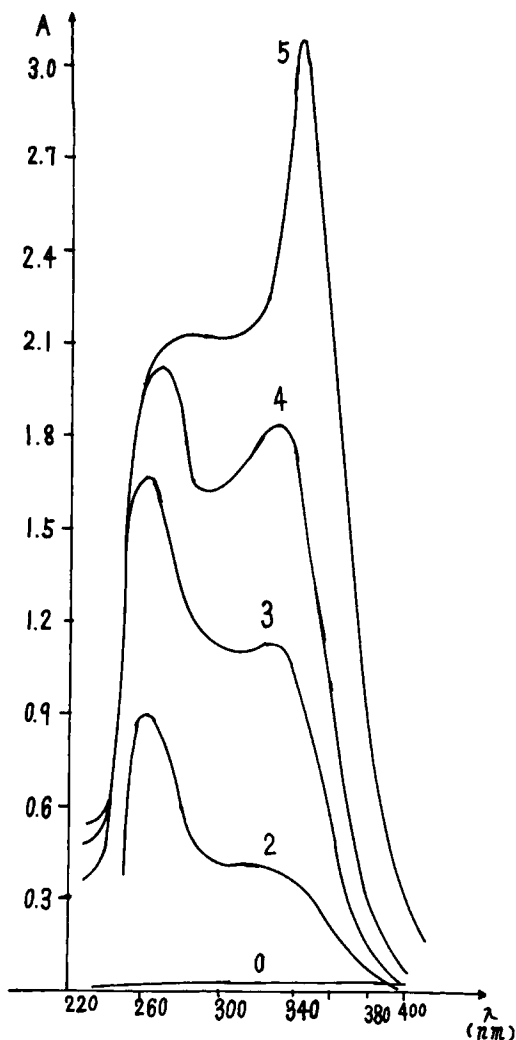
	No.					
	0	1	2	3	4	5
Vi/DDCP (mol/mol)	C-Gum	Control test	8 : 1	4 : 1	2 : 1	4 : 3
Calculated (%)	8.90	8.90	7.78	6.67	4.45	2.22
Found (%)	8.90	7.45	6.29	5.42	4.07	2.05

methylcyclopentadienone, and diphenyl ether were also made and presented in Table V. Obviously, the data in the left column in Table V are the absorptive peaks of the furan ring and the data in right column are those of the benzene ring. At the same time, the

heights of peaks are relatively increased with the increasing contents of (3,4-difuryl-2,5-dimethyl)-phenyl.

Figure 3 is the IR spectra of C-gum and DDP-C-gums. In Figure 3, we can find that C-gum does not have the absorptive peaks at 3115, 1706, 1541, 1495, and 600 cm^{-1} ; but all of the DDP-C-gums have absorptive peaks at those positions. The absorptive peaks at 3115 and 1706 cm^{-1} should be attributed to stretching vibration for Ar-H; the absorptive peaks at 1541 and 1495 cm^{-1} to stretching vibration for the aromatic ring-skeleton; and at 600 cm^{-1} to deformation vibration for the furyl-skeleton. The same as UV spectra, the heights of these peaks are increased with increasing contents of the (3,4-difuryl-2,5-dimethyl)phenyl group. This is good evidence that DDP-C-gums have the aromatic rings, i.e., phenyl and furyl rings.

TGA curves have been done at the rate of 40 mL/min of N_2 and the heating rate of 20°C/min. However, only four are shown in Figure 4 for clarity. We can see that on raising the temperature to 90°C under nitrogen atmosphere, the material C-gum (No. 0) begins to reduce weight, and to 119°C the control test's C-gum (No. 1) begins to reduce the weight.

**Figure 2** The UV spectra of C-Gum and DDP-C-gums.**Table V** UV Data of Products and Materials in CHCl_3

Sample	UV (nm)	
Diphenyl ether		276
Furil	302	
DDCP	310	
No. of DDP-C-gums		
0	None	None
2	328	257
3	332	260
4	338	266
5	345	274

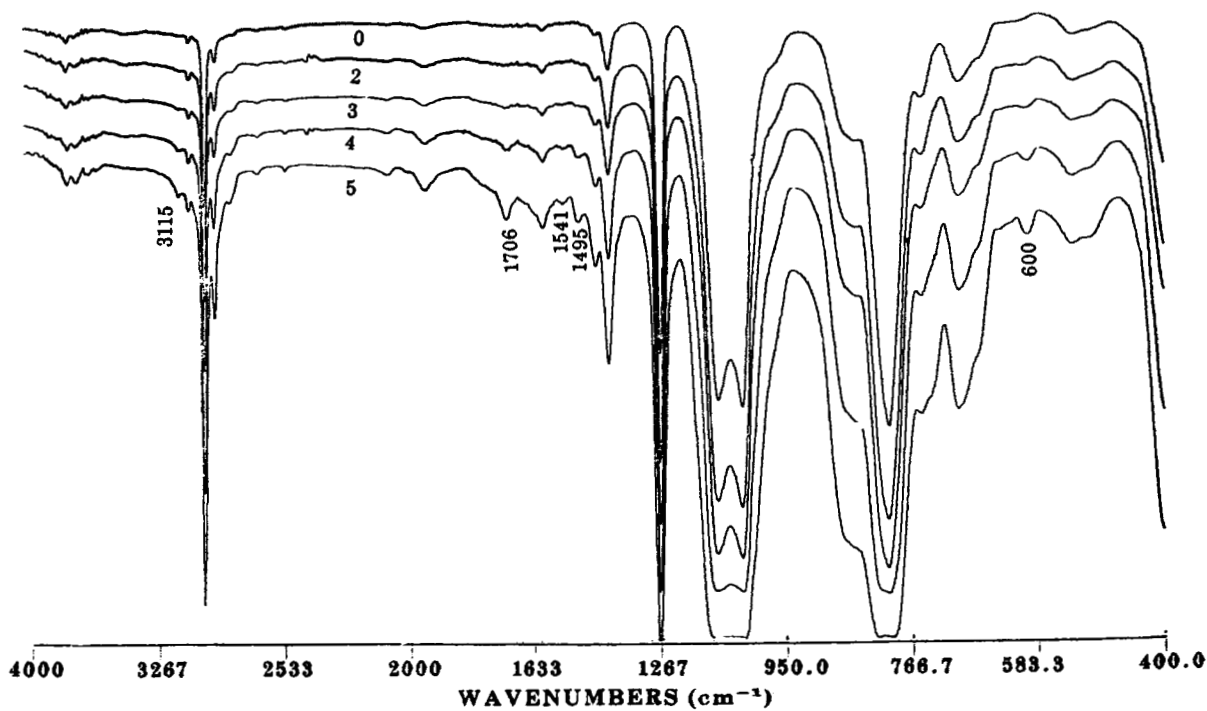


Figure 3 The IR spectra of C-Gum and DDP-C-gums.

On the other hand, the temperatures of the beginning of weight loss for various DDP-C-gums are obviously different. The more the contents of the

(3,4-difuryl-2,5-dimethyl)phenyl group in the DDP-C-gums, the higher are their temperatures of the beginning weight loss (see Table VI).

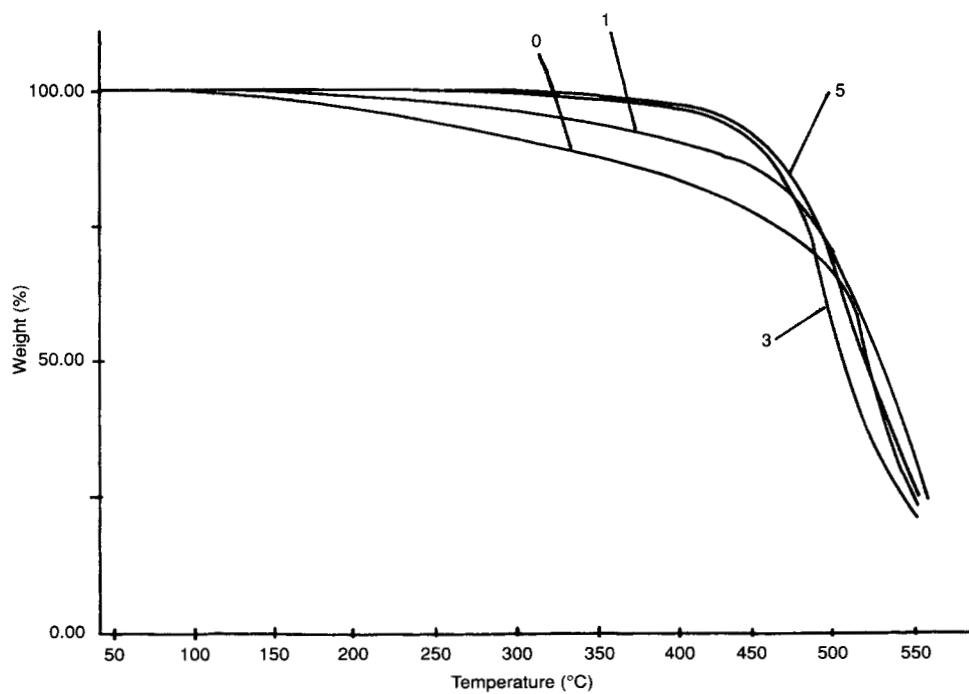


Figure 4 The TGA curves of C-Gum and DDP-C-gums.

Table VI TGA Data for DDP-C-Gums

No.	Vi/DDCP (mol/mol)	Temp. of Beginning Wt Loss (°C)	Wt loss (%) at 399.2°C	Color of Product at 550°C
0	C-Gum	90.5	12.5	Pale yellow
1	Control test	119.0	9.93	Yellow
2	8 : 1	265.7	4.51	Red
3	4 : 1	273.8	4.23	Purple
4	4 : 2	281.9	3.90	Purplish black
5	4 : 3	300.0	3.84	Black

The effects of the contents of the (3,4-difuryl-2,5-dimethyl)phenyl groups in the samples on the viscosity and TGA agree with the literature.^{5,6} We had done some reproducibility experiments of TGA. For the same sample under the same conditions, the difference of the temperatures between the two determinations was not more than 5°C when the weight loss reached 5%.

CONCLUSION

The C-gum contained in the (3,4-difuryl-2,5-dimethyl)phenyl group was obtained using diphenyl ether as solvent by the Diels-Alder reaction of C-gum with 3,4-difuryl-2,5-dimethylcyclopentadienone. This is a convenient method. The DDP-C-gums possess better heat endurance than C-gum. Therefore, the series of organosilicon compounds could be a good prospect for the application of the vulcanization of the HCSR.

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