Synthesis and Characterization of (3,4-Diphenyl–2,5-Diethyl)Phenyl–Polyvinyl Silicon Oils

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ABSTRACT: (3,4-Diphenyl–2,5-diethyl)phenyl–polyvinyl silicon oils (DPDEP-*C*-Gums) have been synthesized by the Diels–Alder reaction of polyvinyl silicon oil (*C*-Gum) with 3,4-diphenyl–2,5-diethylcyclopentadienone (DDCP) in diphenyl ether at reflux temperature under normal pressure. The structures of the prepared compounds were characterized by ^{1}HNMR, infrared, and ultraviolet spectra, and some of their properties, such as color, viscosity, refractive index, and thermal–oxidative stability were obtained.
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Key words: (3,4-diphenyl–2,5-diethyl)phenyl–polyvinyl silicon oil; methyl-polyvinyl silicon oil; 3,4-diphenyl–2,5-diethylcyclopentadienone; diphenyl ether; Diels–Alder reaction

INTRODUCTION

The liquid methyl–vinylpolysiloxane, named polyvinyl silicon oil, has been used as a concentrated cross linker for silicone rubbers. This is the reason it is named *C*-Gum.[1,2] The *C*-Gums containing polyphenylphenyl have been synthesized and used for vulcanization of heat-curable silicone rubbers (HCSR).[3] Although some organosilicon compounds containing (difuryl–dimethyl)phenyl or (dimethyl–diphenyl)phenyl have also been synthesized,[4–6] the organosilicon compounds containing (diphenyl–diethyl)phenyl have not been reported. This article will report the synthesis and characterization and some of properties of (3,4-diphenyl–2,5-diethyl)phenyl–polyvinyl silicon oils (DPDEP–*C*-Gums).

EXPERIMENTAL

Materials

Polyvinyl silicon oil was prepared according to the procedure outlined in Wu et al.[7] and we determined its vinyl group contents to be 11.0 mol % by ^{1}HNMR. 3,4-diphenyl–2,5-diethylcyclopentadienone was prepared according to the procedure outlined in Japp and Meldrum.[8]

Synthesis of (3,4-Diphenyl–2,5-Diethyl)Phenyl–Polyvinyl Silicon Oils

6.82 g (0.010 mol vinyl group) of *C*-Gum, 0.36 g (0.00125 mol) of 3,4-diphenyl–2,5-diethylcyclopentadienone (the mole ratio of vinyl to DDCP is 8 : 1), and 10 mL diphenyl ether were introduced into 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 reddish orange. Heating the mixture in the flask with stirring under an atmosphere of dry nitrogen, the mixture turned red when the temperature rose to 70°C. At 220°C, gas evolved. Temperature was raised to 250–260°C for 2 h to end the reaction. After cooling, supernatant liquid was separated from solvent and washed with methanol. The liquid was dried in a vacuum dryer at 80°C under 5 torr pressure for 5 h, yielding a

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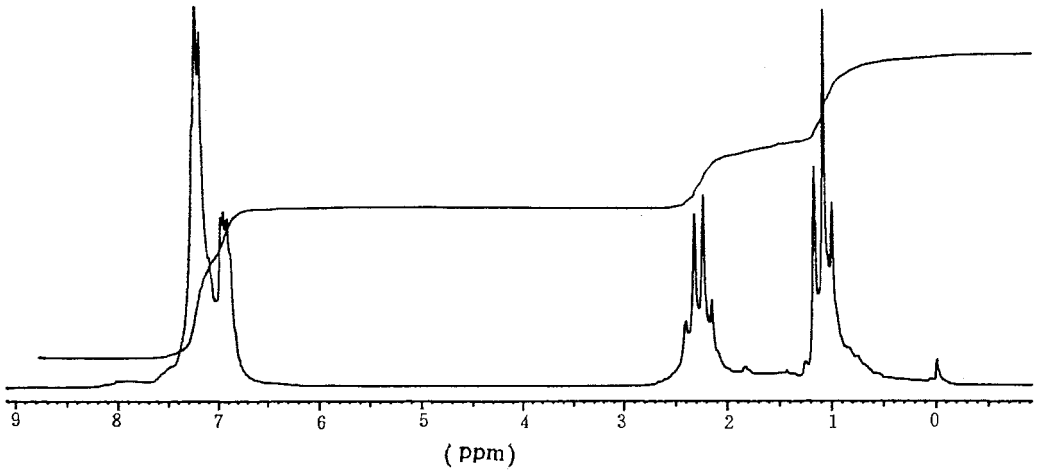


Figure 1 The ^{1}H-NMR spectrum of DDCP.

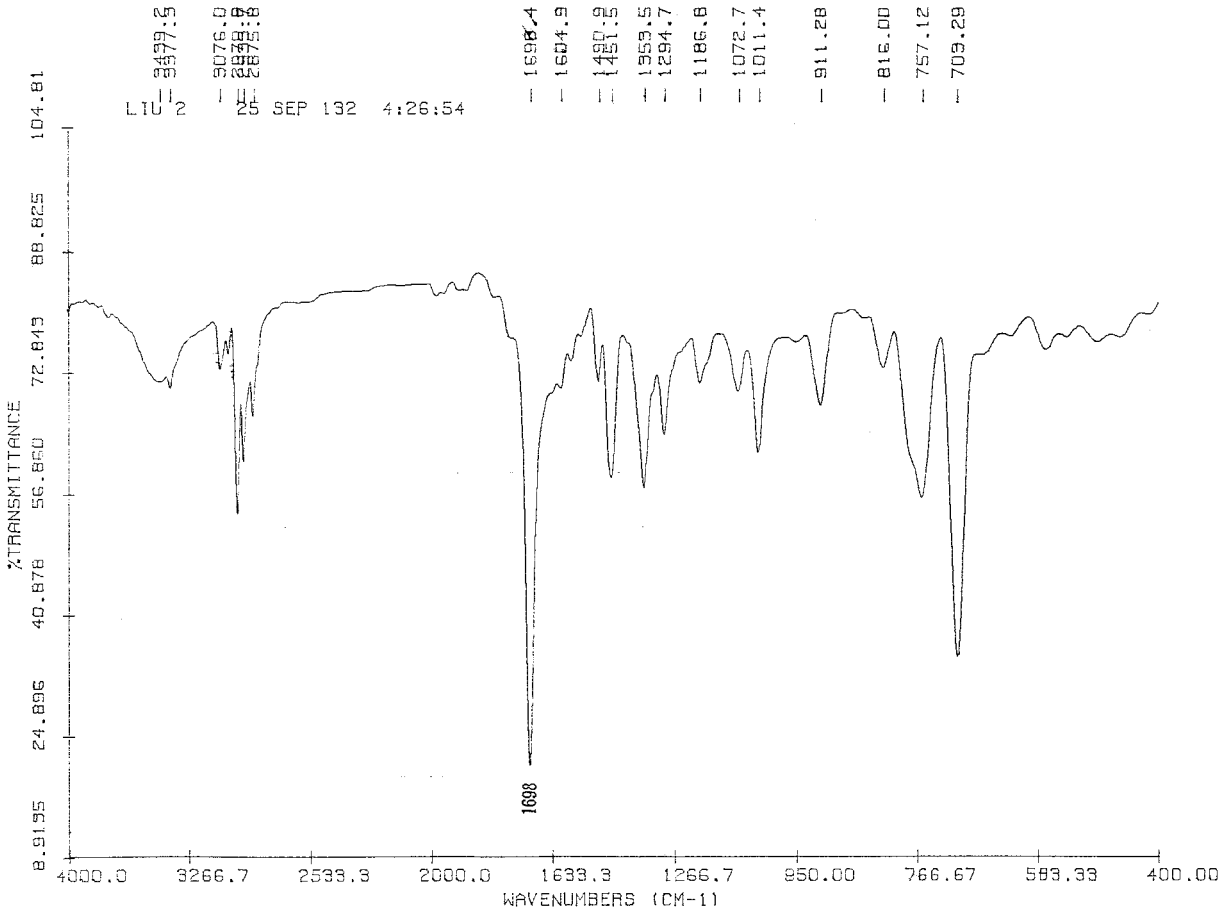


Figure 2 The IR spectrum of DDCP.

Table I The Preparation Conditions and Yields for DPDEP-*C*-Gums

No.	*C*-Gum (g)	DDCP (g)	Vi/DDCP (mol/mol)	Diphenyl Ether (mL)	Reflux Time (h)	Yield[a] (%)
1	6.82	0	—	10	2.0	62.6
2	6.82	0.36	8 : 1	10	2.0	57.4
3	6.82	0.72	4 : 1	10	2.0	55.5
4	6.82	1.44	2 : 1	10	2.0	50.5
5	6.82	2.16	4 : 3	10	2.0	56.8

[a] The low yields are due to the loss during purification.

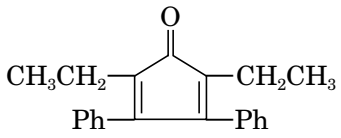
transparent liquid. The other products were prepared similarly according to 4, 2, and 4 : 3 molar ratios of vinyl group in *C*-Gum to DDCP, respectively. The above obtained products were all characterized by ^{1}HNMR, infrared (IR), and ultraviolet (UV) spectra; and their viscosity, refractive index, and thermal–oxidative stability were measured. At the same time, the control test (only material *C*-Gum was treated under the same reaction conditions) was performed to compare with the above.

Analysis

^{1}HNMR spectra were recorded on a FX-90Q spectrometer in deuterochloroform ($CDCl_3$). IR spectra were measured in the region of 400–4000 cm^{-1} by film coating with Nicolet-5DX spectrometer. UV spectra were examined on a UV-240 spectrometer with 20 mg : 25 mL product solution in chloroform, which was also used as a reference. N_D^{20} were taken on WZS-Abbe refractometer. The relative viscosity was acquired on Ubbelohde viscosity meter with a bath temperature of 25.00 ± 0.01°C, with 0.5000 ± 0.0020 g dL^{-1} product solution in toluene. The thermal–oxidative stability was measured by a box oven under the following conditions: after every sample (500 ± 5 mg) was put in an oven, the temperature of the oven began to rise at the rate of 20°C/min. When the temperature rose to 250°C, we kept it for 24 h. Then the samples were weighed at room temperature.

Results and Discussion

The structure of DDCP can be expressed as follows



The ^{1}HNMR of DDCP is shown in Figure 1. The two multiplets (δ, ppm), 0.99–1.21 (t) and 4.08–4.22 (q), indicate the ethyl groups. Other peaks between 6.80–7.50 in Figure 1 arise from the phenyl groups in DDCP. The IR of DDCP, shown in

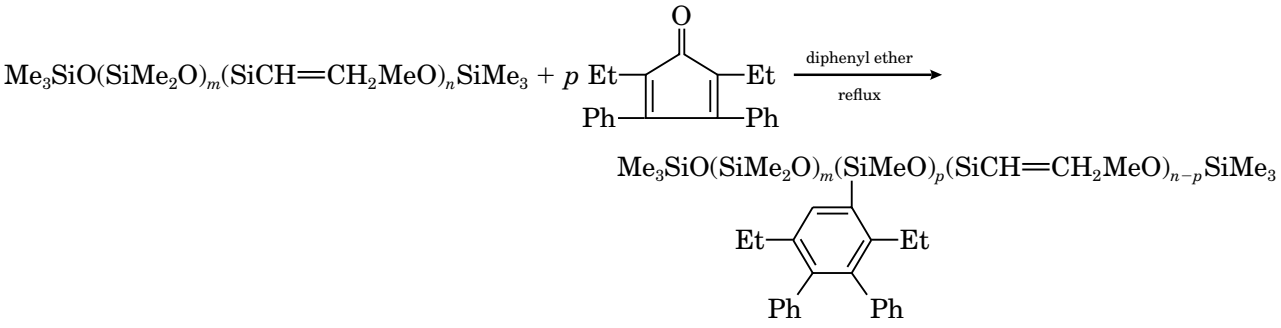
Table II Some Properties for DPDEP-*C*-Gums

No.	Vi/DDCP (mol/mol)	Color	N_D^{20}	η_{sp}/c (dL g^{-1})	Weight Loss (%) at 250°C
0	*C*-Gum	colorless	1.4089	0.04251	16.52
1	control	pale yellow	1.4105	0.06502	12.8
2	8 : 1	orange	1.4145	0.07752	11.91
3	4 : 1	red	1.4172	0.09253	11.32
4	2 : 1	dark red	1.4220	0.1012	10.10
5	4 : 3	purple	1.4272	0.1150	9.55

Table III ^{1}HNMR Data for DPDEP-*C*-Gum in $CDCl_3$

Proton Type	$SiCH_3$ (s)	CH_3CH_2– –CH_2CH_3 (m)	$-CH_2CH_3$ (m)	Si (m)	$SiCH{=}CH_2$ (m)
Chemical shift (ppm)	0.03	2.30–2.76	0.70–0.85	6.98–7.42	5.82–5.88

Figure 2, exhibits a peak due to the carbonyl group, at 1698 cm^{-1}. (3,4-Diphenyl–2,5-diethyl)phenyl–polyvinyl silicon oils were synthesized according to the following scheme:



Similar reactions[9] have been performed either in sealed tubes at high temperature or in α-chloronaphthalene at reflux temperature. However, we replaced α-chloronaphthalene with diphenyl ether, which is cheaper and less toxic; the results are summarized in Table I.

The color, N_D^{20}, the value of η_{sp}/c and thermal–oxidative weight loss of the products are shown in Table II.

From Table II, we can see that the color, N_D^{20}, and the value of η_{sp}/c all increased, while the thermooxidative weight loss decreased in turn with the increasing content of the (3,4-diphenyl–2,5-diethyl)phenyl. We also noticed that every sample heated became a solid; in addition, its color was deeper than original, and its elasticity increased in turn from top to bottom.

The ^{1}HNMR spectra of DPDEP-*C*-Gums were determined in $CDCl_3$ with $CHCl_3$ as an internal standard. The chemical shifts of typical protons are listed in Table III.

The contents of the vinyl groups in *C*-Gum

Table IV Contents of Vinyl Groups for DPDEP-*C*-Gums

	Sample No.					
Contents	0	1	2	3	4	5
Vi/DDCP (mol/mol)	*C*-Gum	control test	8 : 1	4 : 1	2 : 1	4 : 3
Calcd (%)	11.0	11.0	9.6	8.2	5.5	2.8
Found (%)	11.0	10.1	8.3	7.2	5.5	3.2

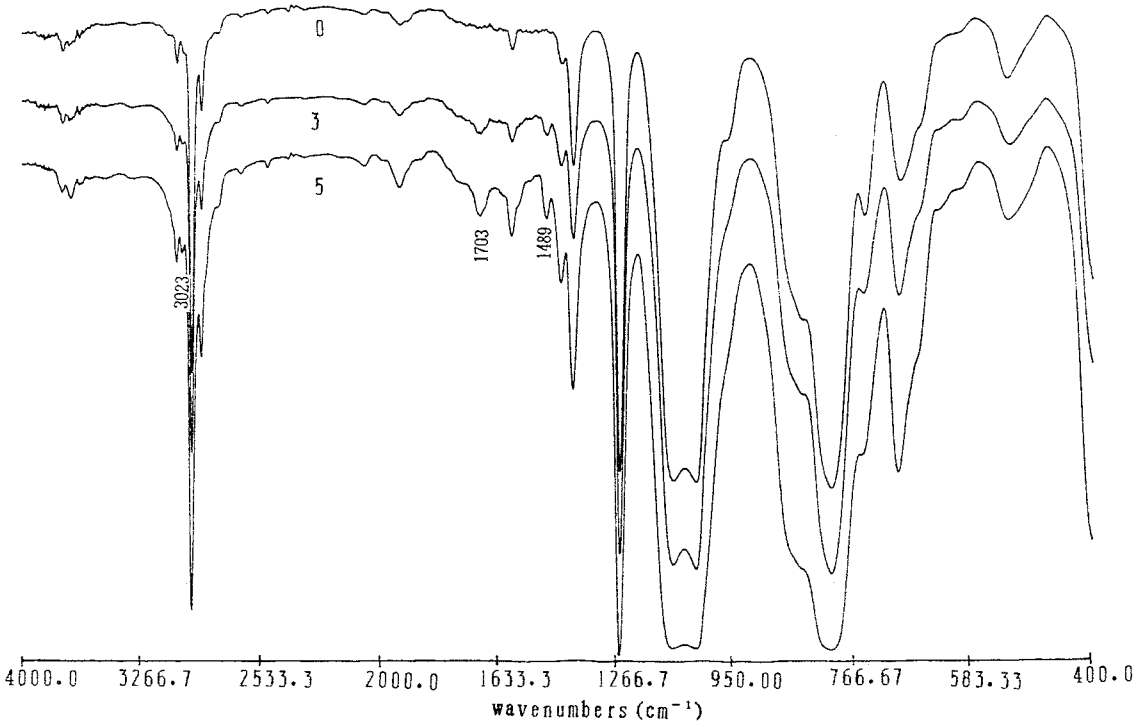


Figure 3 The IR spectra of *C*-gum and DPDEP-*C*-gums.

and DPDEP-*C*-Gums were examined by the integral of various hydrogens in ^{1}HNMR spectra. The analysis results are collected in Table IV. In Table IV, we find that samples 1 to 3 have less vinyl groups than those of 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 Table IV, nos. 0 and 1). However, samples 4 and 5 show the theoretical concentration of vinyl groups. This may be due to incomplete reaction.

The IR spectra (see Fig. 3) indicate that *C*-Gum has no peaks at 3023, 1703, and 1489 cm^{-1}, where the DPDEP-*C*-Gums have peaks attributed to the stretching vibration for Ar—H (3023 cm^{-1}), the bending vibration for Ar—H (1703 cm^{-1}), and the stretching vibration for ring skeleton (1489 cm^{-1}).

The UV spectra of the DPDEP-*C*-Gums show absorption peaks due to the benzene rings (Table V and Fig. 4).

CONCLUSION

Polyvinyl silicon oil containing the (3,4-diphenyl–2,5-diethyl)phenyl group was prepared using di-

Table V The Absorptive Peaks of the UV Spectrum for Products

	Sample No.				
Contents	1	2	3	4	5
Vi/DDCP (mol/mol)	control	8 : 1	4 : 1	4 : 2	4 : 3
UV (nm)[a]	none	242	244	246	248

[a] DDCP is at 260.

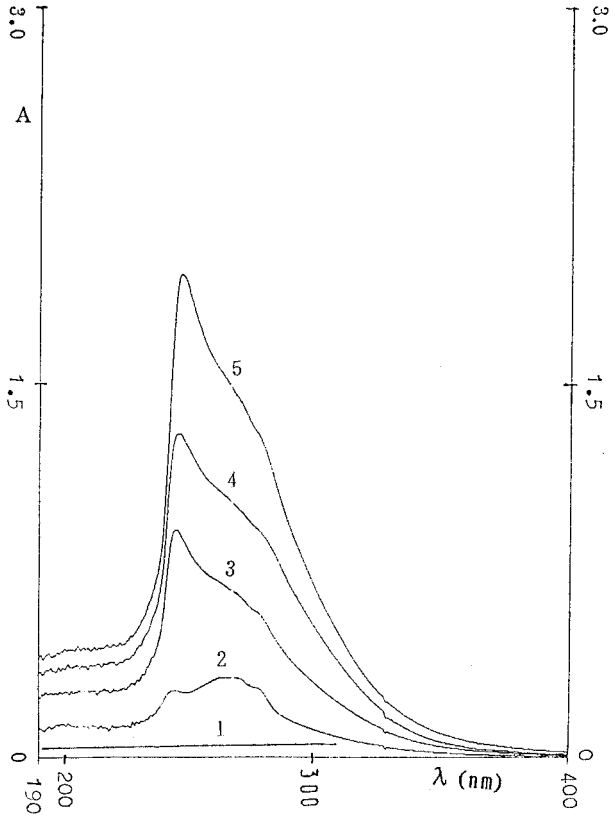


Figure 4 The UV spectra of *C*-gum and DPDEP-*C*-gums.

phenyl ether as the solvent by the Diels–Alder reaction of polyvinyl silicon oil with 3,4-diphenyl–2,5-diethyl–cyclopentadienone. This series of organosilicon compounds could be of interest in synthetic organic chemistry and organic silicon macromolecular chemistry.

REFERENCES

1. Z. Du and J. Yu, *China Synth. Rubber Ind.,* **9,** 388 (1987).
2. S. Feng and Z. Du, *J. Appl. Polym. Sci.,* **43,** 1323 (1991).
3. S. Feng, J. Chen, and Z. Du, *Acta Polym. Sinico,* **6,** 471 (1987).
4. Z. Liu, H. Lu, Y. Gao, and Z. Du, *Phosphorus, Sulfur, and Silicon,* **86,** 193 (1994).
5. Z. Liu, H. Lu, S. Hao, X. Wen, and Z. Du, *J. Appl. Polym. Sci.,* **55,** 1733 (1995).
6. Z. Liu, S. Hao, P. Zheng, and Y. Ding, *J. Appl. Polym. Sci.,* **60,** 1089 (1996).
7. G. Wu, D. Wang, and Y. Jiang, *Polym. Commun.,* **1,** 41 (1979).
8. F. R. Japp and A. N. Meldrum, *J. Chem. Soc.,* **79,** 1036 (1901).
9. Z. Du, *Chem. Res. Appl.,* **2,** 2 (1990).