

SHORT COMMUNICATION

LIQUID STATE ^1H AND ^{13}C -NMR STUDIES ON POLYMERISATION REACTION OF 2,2'-DIFURFURYOXY-2- SILAPROPANE

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RINGKASAN: Pengkajian ini adalah bertujuan untuk menyediakan kopolimer 2,2'-difurfuryloxy-2-silapropane (DFS) dan 1,1'-(methylenedi-4,1-phenylene) bismaleimide (BM). DFS telah disediakan pada 0°C melalui tindakbalas 2 mol furfuryl alcohol (FA) dengan 1 mol dichlorodimethylsilane (DCMS) dengan kehadiran pyridine dan chloroform sebagai pelarut. Pembentukan sebatian ini telah dicirikan oleh spektroskopi ^1H dan ^{13}C -NMR dan spektrometer massa. DFS berkebolehan menjalani tindakbalas Diels-Alder. Kumpulan-kumpulan hujung furan DFS boleh bertindak dengan kumpulan-kumpulan dienophile bahan-bahan lain. Kopolimer DFS-BM telah disediakan melalui tindakbalas DFS dengan BM pada suhu bilik (18°C) dalam chloroform (CDCl_3). Pencirian telah dilakukan melalui pengkajian spektrum-spektrum ^1H dan ^{13}C -NMR kopolimer tersebut.

ABSTRACT: The purpose of this study was to prepare the copolymer of 2,2'-difurfuryloxy-2-silapropane (DFS) and 1,1'-(methylenedi-4,1-phenylene) bismaleimide (BM). DFS was prepared at 0°C through the reaction of 2 moles of furfuryl alcohol (FA) with 1 mole of dichlorodimethylsilane (DCMS) in the presence of pyridine and chloroform as a solvent. The formation of this compound was characterized by the ^1H and ^{13}C -NMR spectroscopy and mass spectrometry. DFS has the ability to undergo the Diels-Alder reaction. The furan end groups of DFS could react with dienophile groups of other materials. The adduct of DFS-BM was prepared by the reaction of DFS with BM at room temperature (18°C) in chloroform (CDCl_3). Characterization of the adduct was carried out through a study of the ^1H and ^{13}C -NMR spectra of the adduct.

KEYWORDS: Furfuryl alcohol (FA), dichlorodimethylsilane (DCMS), 2,2'-difurfuryloxy-2-silapropane (DFS), 1,1'-(methylenedi-4,1-phenylene) bismaleimide (BM), condensation reaction, Diels-Alder reaction.

INTRODUCTION

At present, most of the plastic materials are prepared from derivatives of crude oil. The aim of this study is to find alternative starting materials to produce a new polymer. Furfuryl alcohol (FA) is one of the starting materials which may produce a new polymer. FA is prepared commercially from agricultural wastes containing pentosans (Degering, 1969), such as xylose, which are then dehydrated to yield furfural (Figure 1). Aldehyde furfural is the starting material for the preparation of FA. FA can be manufactured commercially by both liquid and vapour phase hydrogenation of furfural. It can also be prepared by the Cannizzaro reaction (Vogel, 1968) of aldehyde furfural (Figure 1).

2,2'-difurfuryloxy-2-silapropene (DFS) was prepared by condensation reaction between FA and dichlorodimethylsilane (DCMS) in a chloroform solution to yield DFS (Figure 1). Pyridine was added to the reactants in order to neutralise the hydrogen chloride evolved.

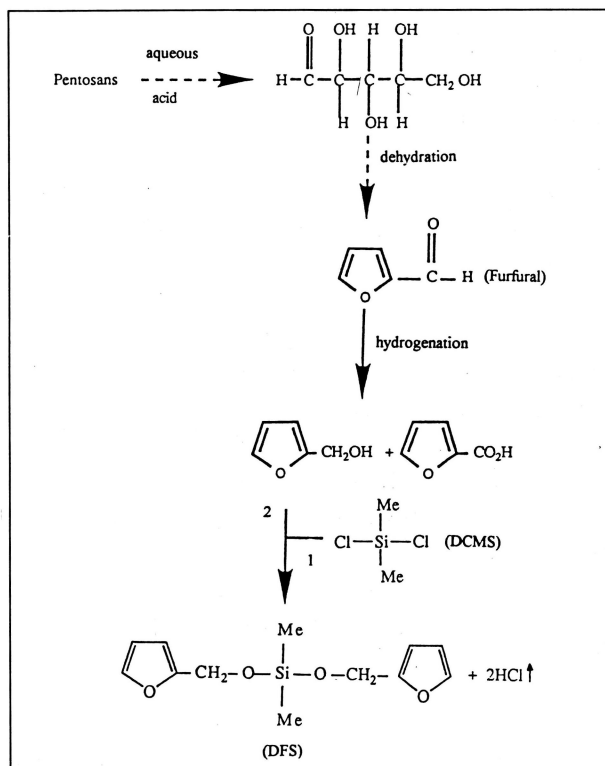


Figure 1. The preparation of DFS

Diels and Alder discovered 1,4-cyclo-addition of dienes that was named after them (Fieser and Fieser, 1963). The reaction proved to be one with great versatility and synthetic utility. The Diels-Alder reaction in its simplest form is represented in Figure 2. In general terms, the reaction is one between a conjugated diene (a 4π -electron system) and a monoene (a 2π -electron system), called a dienophile, which is substituted by electron withdrawing groups. The product of the Diels-Alder reaction is often called an adduct (Carruthers, 1971).

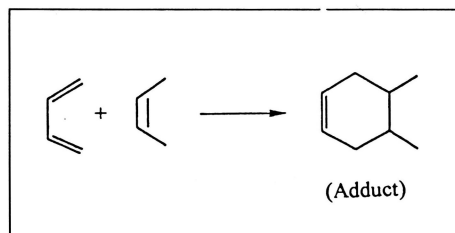


Figure 2. The general form of Diels-Alder reaction

It was reported that, when furan and maleimide undergo a Diels-Alder reaction at 25°C (Figure 3), the major product is the endo-adduct. When the reaction is carried out at 90°C , however, the major product is the exo-isomer. The endo-product is formed under kinetic control at low temperatures whereas, the exo-product is formed under thermodynamic control (Fieser and Fieser, 1963) at high temperatures.

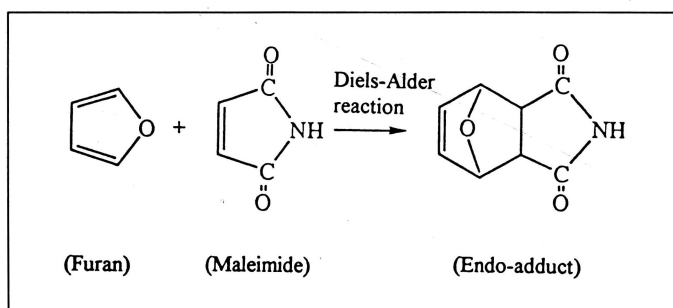


Figure 3. Diels-Alder reaction of furan and maleimide to form endo- and exo-adduct

DFS has the ability to undergo the Diels-Alder reaction. The furan end groups of DFS can react with dienophile groups of other materials. Diels-Alder reaction could occur when DFS is treated with 1,1'-(methylenedi-4,1-phenylene) bismaleimide (BM) (Figure 4). Since BM possesses two reactive centres and DFS also has two reactive furan centres, reaction between them will produce a linear polymer (Young, 1991).

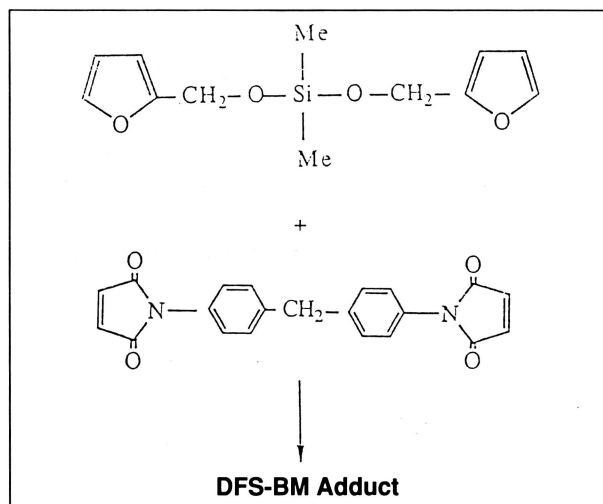


Figure 4. The preparation of DFS-BM adduct from DFS and BM

MATERIALS AND METHODS

Material purification

DCMS, BM, pyridine and ether were used in, as received conditions without any further treatment. Chloroform was washed with plenty of water, dried over sodium sulphate (Na_2SO_4) anhydride and was distilled at 61°C before being used. FA was also distilled under reduced pressure to remove condensed products.

Methods

Preparation of DFS

FA (16.73 g, 0.171 mole) was dissolved in 300 ml chloroform contained in a 1-litre flask fitted with a stirrer and cooled to 0°C . Pyridine (13.39g, 0.169 mole) was then added. DCMS (10 g, 0.078 mole) was added dropwise into the flask for the first 30 min under dried conditions. The solution was further stirred for 2 h at room temperature (18°C). A clear colourless solution was obtained. Addition of ether (x5 the volume of solution) caused the formation of a white precipitate which was removed by filtration. The filtrate was washed with water and dried over anhydrous sodium sulphate. After filtration, the solvent was removed under reduced pressure at 60°C to leave a yellow viscous residue which was subsequently confirmed to be DFS.

Diels-Alder Reaction of DFS

The reaction between DFS and BM is as shown in Figure 4. The experimental procedure is described. DFS (1 ml, 1.07g) was dissolved in 4 ml chloroform. One-fifth of the solution

containing DFS (0.214 g, 8.492×10^{-4} mole) was placed in an NMR tube and BM (0.305 g, 8.492×10^{-4} mole) was added to the tube. The tube was then kept at room temperature (18°C) for the liquid state NMR measurement. ^1H and ^{13}C -NMR spectra were obtained, primarily at intervals of two hours then at intervals of one day until the completion of the reaction.

Characterization

^1H and ^{13}C -NMR spectra of DFS and DFS-BM adduct were recorded on a General Electric Q300 NMR Spectrometer using tetramethylsilane (TMS) as a reference for ^1H -spectra and chloroform as a reference for ^{13}C -spectra (Williams, 1973). Formula weight analysis was performed on an VG AutoSpec Mass Spectrometer (Bark and Allen, 1982).

RESULTS AND DISCUSSION

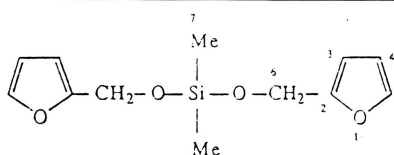
Synthesis of DFS

DFS was prepared by condensation DCMS and FA in the presence of pyridine to neutralise the hydrochloric acid formed. The molecular structure of the product was confirmed as DFS by ^1H and ^{13}C -NMR spectroscopy. A list of peak assignments is given in Table 1.

Table 1. The chemical shift of protons and carbons

Position	Chemical shift		
	^1H -NMR		^{13}C -NMR
	δ/ppm	*RAP	δ/ppm
1	-	-	-
2	-	-	153.4
3	6.31	1H	107.77
4	6.25	1H	110.13
5	7.37	1H	142.25
6	4.66	2H	56.79
7	0.16	3H	-1.19

*RAP : Relative amount of protons.



The mass spectrum of DFS was found to be consistent with its structure (Figure 5). The formula mass of DFS is 252 and the expected fragmentation pattern could be as shown in Figure 6.

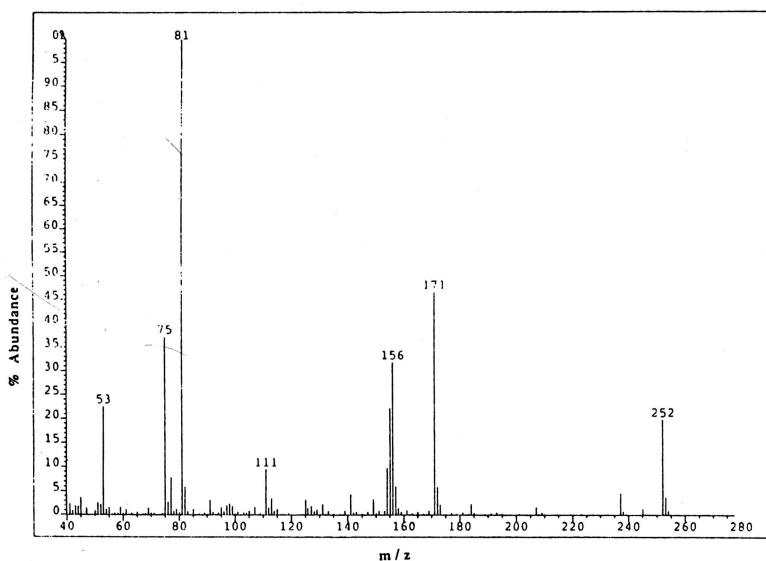


Figure 5. Mass spectrum of 2,2'-Difurfuryloxy-2-Silapropane

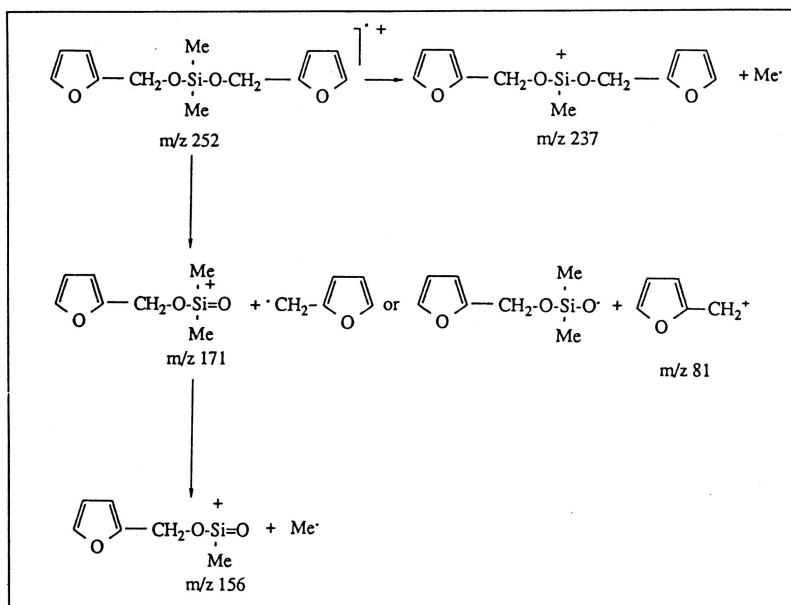


Figure 6. Mass spectral fragmentation of DFS

NMR studies of DFS-BM adduct

^1H -NMR

DFS was reacted with BM in a 1:1 molar ratio at room temperature (18°C). The solvent used was chloroform. The expected molecular structure of the adduct is shown in Figure 7. After two days the adduct became a gel. This is probably because each monomer unit possesses two functional groups which take part in the polymer formation. The system therefore gave rise to a linear polymer formation. Gelation was observed to proceed with increase in the molecular weight of the polymer (Billmeyer, 1984).

In order to determine the molecular structure of the adduct, the peaks of protons in ^1H -NMR spectrum of Figure 8 were assigned and the results are as listed in Table 2. The endo- and exo-adduct of DFS-BM was calculated. The peaks of **g'+f'** (endo+exo) and **c',d'** (endo+exo) were taken as references to estimate the amount of adduct in the adduct mixture (using the formula shown below). The results are listed in Table 3.

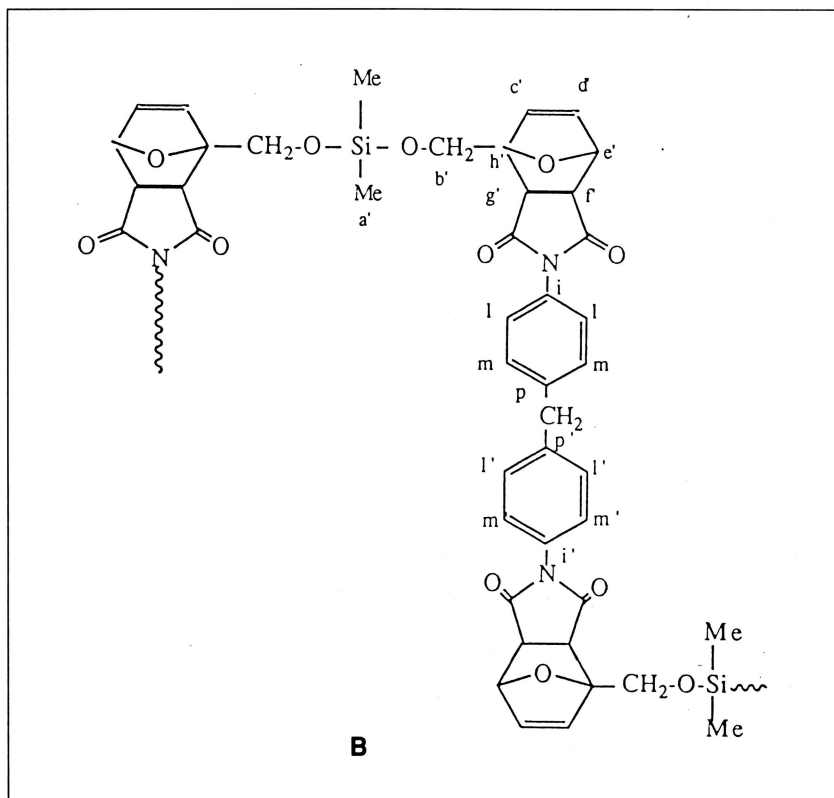


Figure 7. The molecular structure of DFS-BM adduct

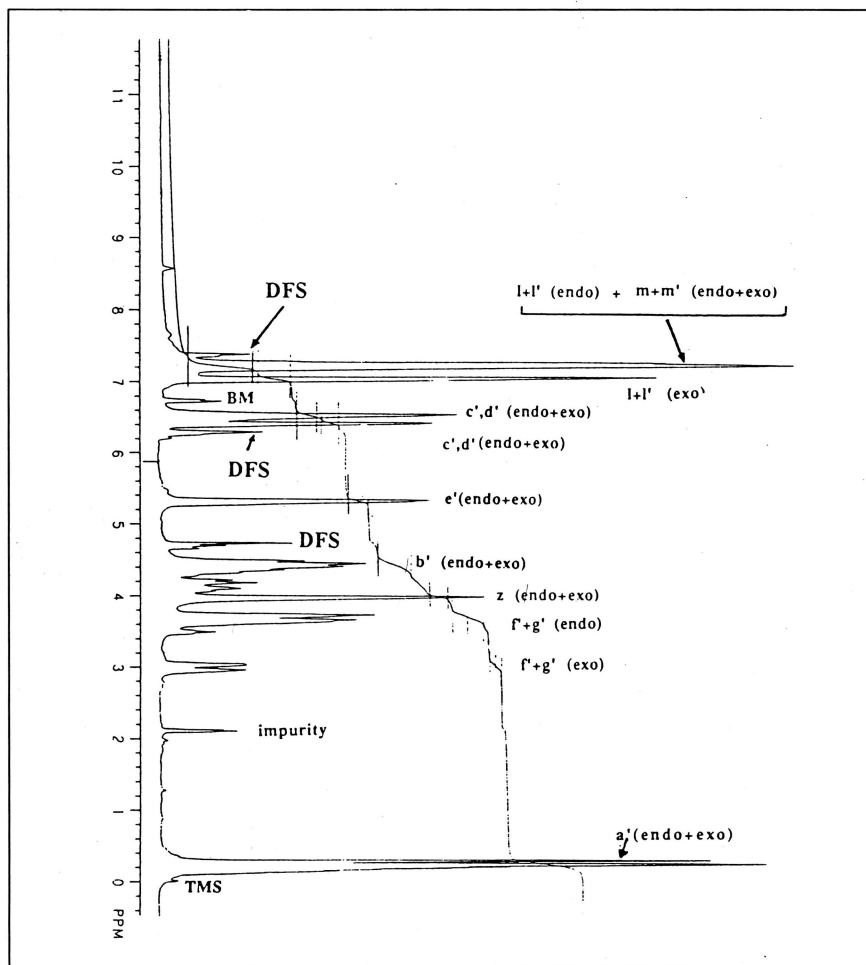


Figure 8. ¹H-NMR spectrum of DFS-BM adduct

$$\text{The fractional amount of endo-adduct} = \frac{\text{Integration of endo-peaks}}{\text{Total integration of endo- and exo-peaks}}$$

The amount of endo-product was much higher than that of exo-product in the first stage of reaction. However, the exo-product is stable at room temperature (18°C) and it may be seen that the amount of exo-adduct increased from day one through three days after the polymer had been exposed to room temperature (18°C).

The degree of adduct formation was determined by choosing the integration of peaks **b** (4.71 ppm) of DFS and **b'** (4.43 ppm) of the adduct. The results are summarised in Table 4. The formation of the adduct was very fast for the first few hours and appeared to have reached a limit of approximately 83% after two days.

Table 2. Proton peaks from ^1H -NMR of DFS-BM adduct

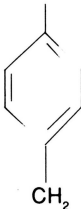
Position	Chemical shift δ/ppm	Amount of proton		
		Integration	Relative	Actual
a' endo+exo	0.17-0.27	26	3H	CH_3
b' endo+exo	4.34-4.43	16	2H	CH_2
c',d' endo+exo	6.51	16	2H	CH
c',d' endo+exo	6.4			CH
e' endo+exo	5.30-5.31	8	1H	CH
g'+f' endo	3.62-3.64	16	2H	CH
g'+f' exo	2.95-3.03			CH
l+l' exo	7.02			
l+l' endo	7.18-7.22	40	8H	2 x 
m+m' endo+exo				
z endo+exo	3.95	14	2H	CH_2

Table 3. The amount of endo- and exo-adduct

Time (day)	Peak	Integration height (mm)	Amount of adduct (%)	
			Endo	Exo
1	g'+f' endo	11.5	79	21
	g'+f' exo	3		
2	g'+f' endo	12	75	25
	g'+f' exo	4		
3	g'+f' endo	19	73	27
	g'+f' exo	7		

Table 4. Adduct formation with time

Time	Conversion to adduct (%)
2 h	53
1 day	76
2 days	83
3 days	85

¹³C-NMR

The ¹³C-NMR spectrum of DFS-BM adduct (Figure 9) were analysed and the assignment of carbon peaks are listed in Table 5 to characterize the structure of the adduct. From this study, the molecular structure of the adduct was found to be that of **B** (Figure 7).

Table 5. Carbon peaks of DFS-BM adduct

Position	Chemical shift δ/ppm	Assignment
a'	-3.57-0.65	endo+exo
z	40.58	endo+exo
f'+g'	44.73-49.82	endo+exo
b'	60.07-60.45	endo+exo
e'	79.37-81.03	endo+exo
h'	91.49-92.13	endo+exo
l	125.98-126.17	endo+exo
m	129.22	endo+exo
p	133.72	endo+exo
d'+c'	134.55-136.67	endo+exo
i	140.6	endo+exo
C=O	173-173.64	endo+exo

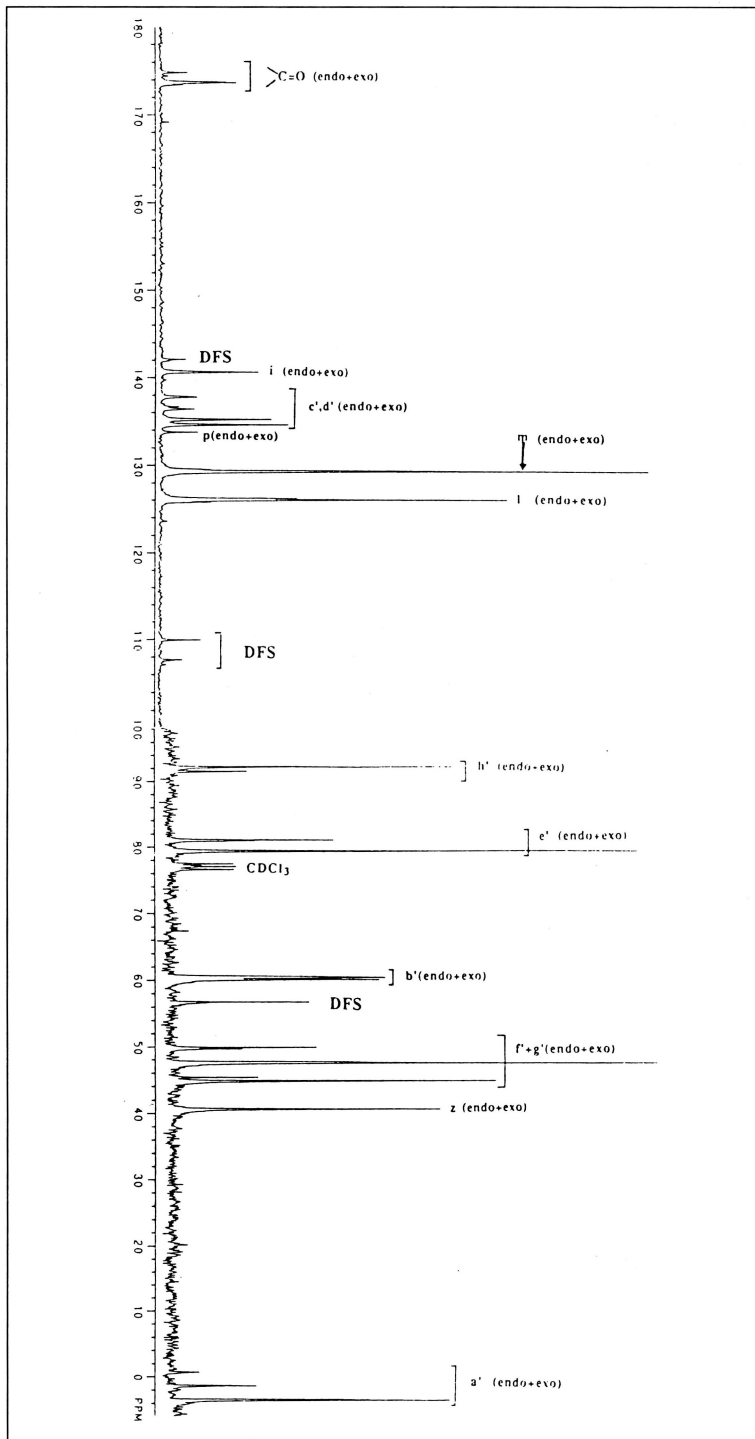


Figure 9. ^{13}C -NMR spectrum of DFS-BM adduct

CONCLUSION

It has been shown that the copolymer of DFS-BM can be successfully prepared by Diels-Alder reaction. Evidence of the presence of DFS-BM adduct of the structure shown was identified by the ^1H and ^{13}C -NMR spectra.

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