A ^{13}C and ^{1}H n.m.r. study of the pyridine-initiated oligomerization of maleic anhydride and of the polymer structure

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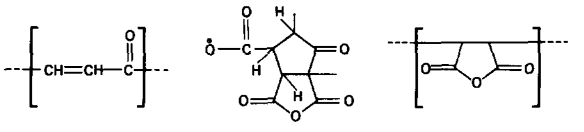
The polymerization of maleic anhydride with pyridine in acetone solution was carried out directly in a n.m.r. tube. The polymer conversion increases with increase in the concentration of initiator. The reaction gives a brown powdery soluble solid. The structure of the oligomer was investigated by ^{13}C n.m.r. and ^{1}H n.m.r. spectroscopy. The major peaks of the material were consistent with the presence of pyridine, succinic anhydride units and probably with a substituted cyclobutane ring.

(Keywords: maleic anhydride; pyridine; n.m.r. spectroscopy; oligomer)

INTRODUCTION

The polymerization of maleic anhydride (MA) initiated by pyridine (Py) has been investigated by several authors[1,2]. The polymerization was found to be initiated by a charge transfer complex formed from the initiator and maleic anhydride[3].

The reaction is exothermic and proceeds with carbon dioxide evolution. The simultaneous occurrence of two different mechanisms has been suggested[4] for the polymerization. On the basis of proposed mechanisms, maleic anhydride polymers consist of conjugated ketoolefins, cyclopentanone derivatives[5] and succinic anhydride units, shown below:



It may be observed that the absorption characteristics of the polymer obtained are defective and sometimes inconsistent with the proposed structures[6].

In this paper we report information concerning oligomerization carried out directly in the n.m.r. tube, and the probable structure of a polymer prepared in well defined conditions investigated mainly by ^{13}C and ^{1}H n.m.r. spectroscopy.

EXPERIMENTAL

Oligomerization was carried out in acetone solution at 25°C in a nitrogen atmosphere, and the reaction mixture was not stirred.

Using the reactants in the molar ratio MA/Py = 1.64 the reaction was practically complete after 40 h.

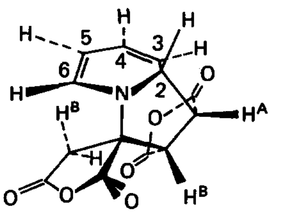
The carbon dioxide was measured by absorption in $Ba(OH)_2$ solution. The reaction was poured into toluene or benzene to precipitate the oligomer which was then separated by filtration. The oligomer was purified from the residual pyridine by repeated dissolution in acetone and precipitation in toluene. The oligomer dried at 50°C at reduced pressure is a brown powder, soluble in water and dimethylsulphoxide (DMSO), and insoluble in dichloromethane and chloroform. ^{13}C and ^{1}H n.m.r. spectra have been registered in DMSO-d_6 solution with a Varian XL 200 FT spectrometer. The i.r. spectrum has been registered in a KBr pellet with a Perkin–Elmer FT spectrometer.

RESULTS AND DISCUSSION

The MA–Py mixture with the initiator in excess is initially yellow and in about an hour turns dark brown or black. (The colour changes later as the MA/Py ratio increases.)

Figure 1 shows the time conversion curves for the oligomerization of MA dissolved in acetone with different concentrations of Py at room temperature. The conversion has been measured by the ratio of integral values of MA protons to Py protons. The conversion curves show that polymer formation increases appreciably with base concentration.

In the early stages of the reaction of MA with Py in the n.m.r. tube, the spectra exhibit the signals characteristic of the intermediate product described by Wurm, Regel and Hallensleben[3], shown below:



Afterwards all these signals disappear but for resonance peaks due to the geminal CH_2 system. The polymer used for spectroscopic investigations was prepared in conditions corresponding to curve B in *Figure 1*.

In the stated conditions the reaction is practically

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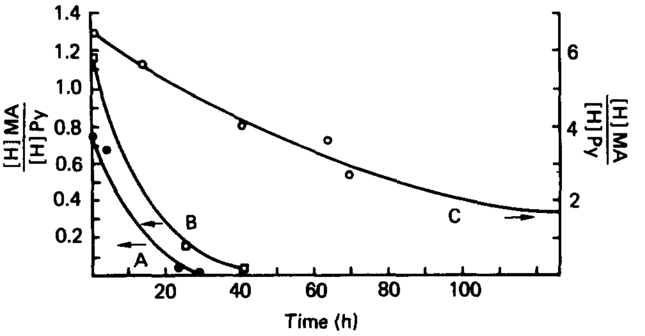


Figure 1 Time conversion curves for the polymerization of MA (2 g) with different molar ratios of MA/Py at room temperature in acetone (20 ml) solution. A, $r=0.81$; B, $r=1.63$; C, $r=7.9$

Table 1 Characteristics of the product used for spectroscopic investigation

Composition (%)	C 53.02 H 3.61 N 2.6
Empirical formula	$C_{24}H_{19}O_{14}N$
Molecular weight[a]	500
$\frac{\text{Oligomer (g)}}{\text{1 mol Py}}$	538.4

[a] Determined in acetone at 30°C with a Knauer osmotensiometer

complete in 40 h with 20 moles of CO_2 per 100 moles of MA being produced. The characteristics of the product are summarized in *Table 1*.

The i.r. spectrum of the polymer (*Figure 2*) shows bands at 1780 and 1849 cm^{-1} attributable to anhydride groups, and at 1730 cm^{-1} due to carboxylic functions. *Table 2* shows the data obtained from studying the ^{1}H and ^{13}C n.m.r. spectra. ^{13}C n.m.r. spectra show two resonance regions ranging from 180.0 to 165 ppm and from 60 to 30 ppm.

The signals at low field have been attributed to carbonyl groups in the anhydridic and carboxylic functions. The signals at high field are attributable to sp^3 carbons and DEPT experiments suggest these are due to: two quaternary carbons, six C–H groups and two CH_2 groups. The peaks at δ 148.3, 137.8 and 124.42 are characteristic of the pyridine molecule.

Attribution of the carbon atoms to the corresponding protons was obtained by experiment using ^{1}H single frequency selective decoupling. The ^{1}H spectrum shows one broad singlet signal at 12.6 ppm attributable to carboxylic protons (probably three protons). The signals at δ2.99 (d; J 6.5 Hz), δ3.42 (dd; J 9; 6.5 Hz), δ3.99 (dd; J 10; 9 Hz), δ4.21 (d; J 10 Hz) are attributable to the protons of the succinic anhydride units. The doublet at δ2.9 and 2.5 (J 17.5 Hz) are typical of an AB system (geminal protons). Signals at δ 3.55, 3.75 and 3.59 are due to protons reciprocally coupled, but not interacting with the other ^{1}H nuclei present in the molecule as shown by the correlation spectroscopy, COSY, experiment (*Figure 3*).

On the basis of all the available data we tentatively propose for this coupling system the structure of a substituted cyclobutane. The presence of the cyclobutane ring is emphasized by the value of 136 Hz found for the $^1J_{C\text{-}H}$ coupling constant of C-18 which is very close to the value of 134 Hz reported in the literature[7] for cyclobutane.

^{1}H and ^{13}C n.m.r. spectra show the absence of olefinic protons as well as of cyclopentanone derivatives, and suggest that the proposed structures (shown earlier) are not correct.

The spectroscopic data indicate that the simplest molecule is characterized by the presence of the following groups:

$6\ \text{—CH}\quad 2\ {>}\text{CH}_2\quad 2\ \text{—C—}\quad 9\ {>}\text{C=O}\quad 1\ \text{Py molecule}$

Moreover the percentage nitrogen content indicates that 1 mole of Py is contained in 538.5 g of the oligomer.

The molecular weight determined by the tensiometric method is 500.

On the basis of chemical and spectroscopic data we propose the following probable structure for the oligomer

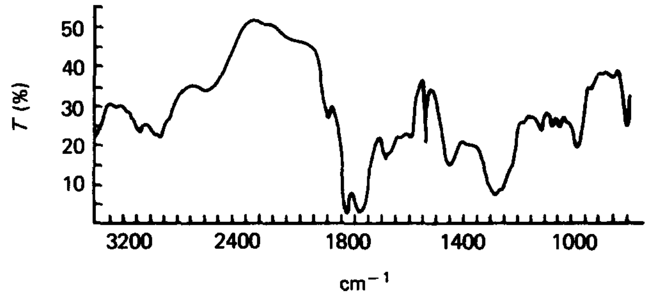
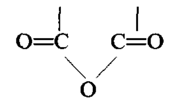


Figure 2 Infra-red spectrum of the oligomer

Table 2 ^{13}C and ^{1}H n.m.r. chemical shifts[a] and J_{H-H} coupling constant

^{13}C (ppm)[b]	Multiplicity[c]	Assignments	^{1}H (ppm)	J_{H-H} (Hz)	Ref.
176.41	s				
174.27	s	—C=O OH	12.6	–	
173.86	s				
172.66	s				
171.69	s				
171.49	s				
171.15	s				
170.92	s				
169.35	s				
148.30	d		8.60	(ddd 5; 1.5; 1)	
137.88	d	Py	7.88	(ddd 8; 8; 1.5)	
124.42	d		7.46	(ddd 8; 5; 1.5)	
54.31	s	4 —C—	–		
53.76	d	19 —C—H	3.55	(dd 6.5; 2)	(7)
53.02	s	16 —C—	–		
51.63	d	6 —C—H	2.99	(d 6.5)	
48.72	d	15 —C—H	4.21	(d 10)	
46.97	d	17 —C—H	3.75	(dd 6.5; 2)	(7)
46.78	d	10 —C—H	3.42	(dd 9; 6.5)	
46.32	d	11 —C—H	3.96	(dd 10; 9)	
35.71	t	3 —C H_A H_B	2.90–2.50	(d 17.5; d 17.5)	
33.76	t	18 ${>}CH_2$	3.59		(7)

[a] Chemical shifts in ppm (rel. TMS)

[b] ^{13}C n.m.r. spectra were analysed by ^{1}H noise decoupling, ^{1}H single frequency selective decoupling and DEPT experiments

[c] s (singlet), d (doublet), t (triplet)

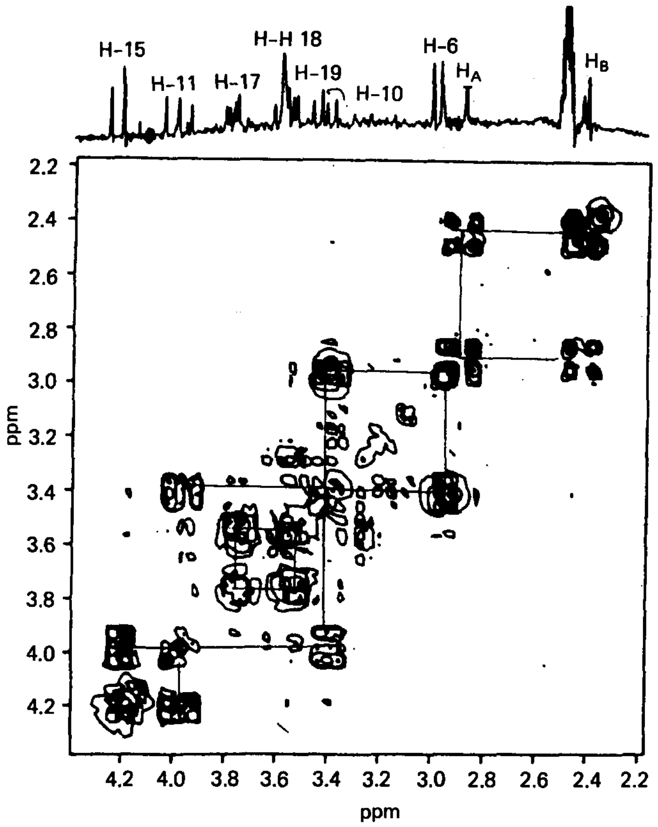
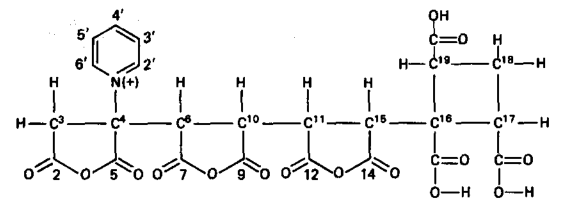


Figure 3 200 MHz spectrum in DMSO (absolute value contour plot after symmetrization). A resolution enhanced 1-D spectrum of the sample is shown (upper trace). Spectral window, 1700 Hz; acquisition time, 0.30 s; relaxation delay, 1 s; 100 scan for 256 traces

obtained from the stated conditions:



Details on the oligomerization reaction and on the analysis of the signals attributed to the substituted cyclobutane will be published separately.

CONCLUSIONS

According to other authors, the conversion of MA increases with the increase of pyridine concentration.

The product of the reaction in the adopted conditions is an oligomer (MW 500) and contains neither cyclopentanone derivatives nor carbonylvinylene units. Our results do not confirm the previous proposed structures. Every molecule of the oligomer formed contains 1 mole of Py, three succinic anhydride units and probably a cyclobutane substituted ring.

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