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Novel polyester by inverse electron demand Diels-Alder polyaddition of bispyrone with divinyl ether

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SUMMARY

The inverse Diels-Alder reaction of bispyrone **4** with divinyl ether **5** leads to the polymer **6**; with the number-average molecular weight M_n=4000 (gel permeation chromatography). The chemical structure of the polymer is determined by ^{1}H NMR spectroscopy and model reaction. Moreover, the stereochemistry of the model compound was investigated by means of 2D COSY spectroscopy.

INTRODUCTION

2-Pyrones with electron-attracting substituents undergo inverse electron-demand Diels-Alder cycloaddition with electron-rich dienophiles [1-3]. The conversion of 5-methoxycarbonyl- pyran-2-on and ethyl vinyl ether to a 1:2-adduct has been described in the literature [4]. To our knowledge, the reaction of bispyrone with electron-demand substituents has not been discussed in the literature yet. Previously, we reported that the bispyrones with electron-releasing underwent Diels-Alder reaction with bismaleimides to give linear polymers with coronand structures [5,6]. In the present paper we want to show, that it is possible to obtain a linear polymer with ester structure from electron-poor bispyrone and divinyl ether. The application of 2D NMR techniques allowed to distinguish between the both isomers **3A** and **3B**.

EXPERIMENTAL

Preparation of syn-8-ethoxy-3-oxo-2-oxabicyclo[2.2.2.]oct-5-en-6-carbon acid methylester 3

(1.18g,7.66.10^{-3}mol) cumalic acid methyl ester and (1.1g, 0.015mol) ethyl vinyl ether were dissolved in 30ml ethyl alcohol. The mixture was stirred 20h at room temperature. The ethyl alcohol was evaporated and the residue recrystallized from diethyl ether : petrolether 3:1 to obtain colourless needles. (yield 1.58g, 91% m.p = 52 °C).

$C_{11}H_{14}O_5$ (226.23)	Calc.	C 58.40	H 6.24
	Found	C 58.62	H 6.69

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Preparation of cumalic acid chloride

(50g,0.37mol) cumalic acid was suspended in 150ml thionyl chloride and refluxed for 3h. To accelerate the reaction two drops dimethylformamide were added. The thionyl chloride was evaporated and the residue was distilled in vacuum. (yield 29.4g, 52% , b.p$_{1.5}$= 104°C).

$C_6H_3O_3Cl$ (158.54)	Calc.	C 45.45	H 1.91	Cl 22.36
	Found	C 45.83	H 1.75	Cl 21.62

Preparation of 1,8-bis[5-carboxy-pyron-2-yl]octane 4

A mixture of (26g, 0.168mol) cumalic acid chloride and (12.01g, 0.082mol) 1,8-octandiole was heated at 70°C. After 6h the brown oil was dissolved in ethyl acetate and extracted with a 25% solution of potassium bicarbonate. Then the solution was washed with water three times. The ethyl acetate was evaporated and the residue was purificated with silica gel (eluent toluene:ethyl acetate 9:1). A colourless product was obtained. (yield 15.3g, 48%, m.p : 124°C).

$C_{20}H_{22}O_8$ (390.39)	Calc.	C 61.53	H 5.68
	Found	C 61.89	H 5.48

Preparation of Polymer 6

A mixture of (1.5g, 3.84.10^{-3}mol) bispyrone **4** and (0.56g, 3.84.10^{-3}mol) 1,4-butandiol divinyl ether **5** in 7ml dichloroethane was stirred at 80°C. After 84h the mixture was cooled and the solution was added in drops to 200ml n-hexane at 5°C. The dichloroethane was decanted and the polymer isolated. This process was repeated two times. The obtained polymer was dried in vacuum. (yield 1g, 50%)

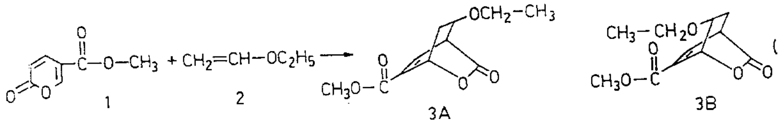
M_n=4000 (GPC).

$(C_{28}H_{36}O_9)_n$ (516.59)$_n$	Calc.	C 65.10	H 7.02
	Found	C 64.36	H 7.89

RESULTS AND DISCUSSION

model reaction

To explain the chemical structure and the stereochemistry of the polymer a model reaction was carried out (eq.1). 5-Methoxycarbonyl-pyran-2-on **1** also reacted with ethyl vinyl ether. Two isomers (**3A** and **3B**) were expected in this reaction. The 2D NMR spectra (fig.1) are in agreement with the structure of the isomer **3A**. It shwoes the coupling of the two protons 2H-5 with H-6 and H-4.



(1)

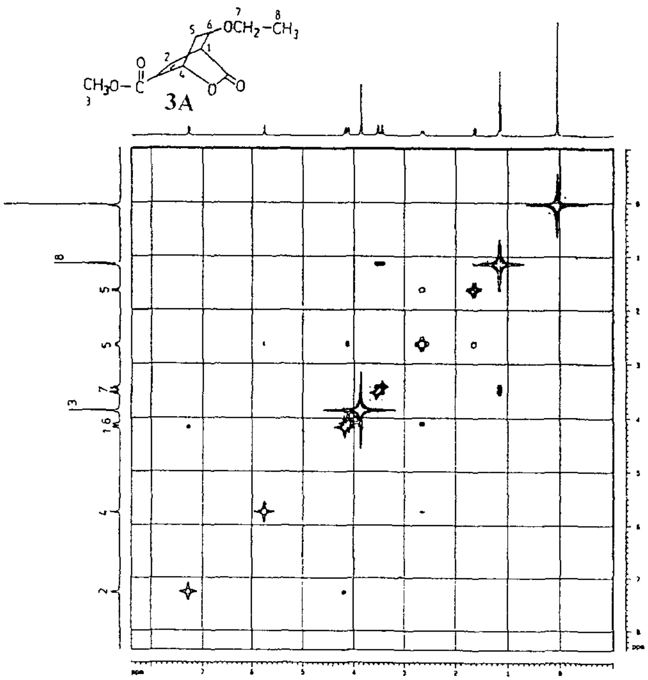
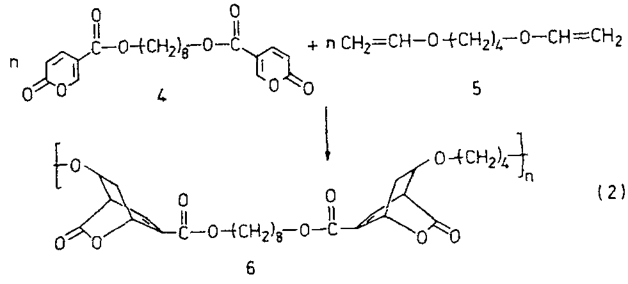


Fig.1 2D ^{1}H NMR spectra (400MHz, $CDCl_3$) of model compound **3**

The coupling of H-6 with H-4 is not established. It can be assumed that the two H-5 protons are not equivalent. Their coupling appears in δ= 2.61 and δ=1.58 ppm.

Polyaddition reaction

The Diels-Alder reaction of bispyrone **4** with 1,4-butandiol divinyl ether in mol ratio 1:1 leads to the polymer **6** (eq.2) with the number average molecular weight M_n=4000 (GPC). The ^{1}H NMR spectra of the polymer, bispyrone and the model compound are represented in the figure 2. The assignment of the characteristic peaks of the polymer structure (δ= 7.24;H-2, 5.66;H-4, 4.12;H-1, 4.06;H-6) is comparable with characteristic peaks of the model compound. The two protons in position 5 are also unequivalent in the polymer. The signals, which designated by E belong to the end-groups.



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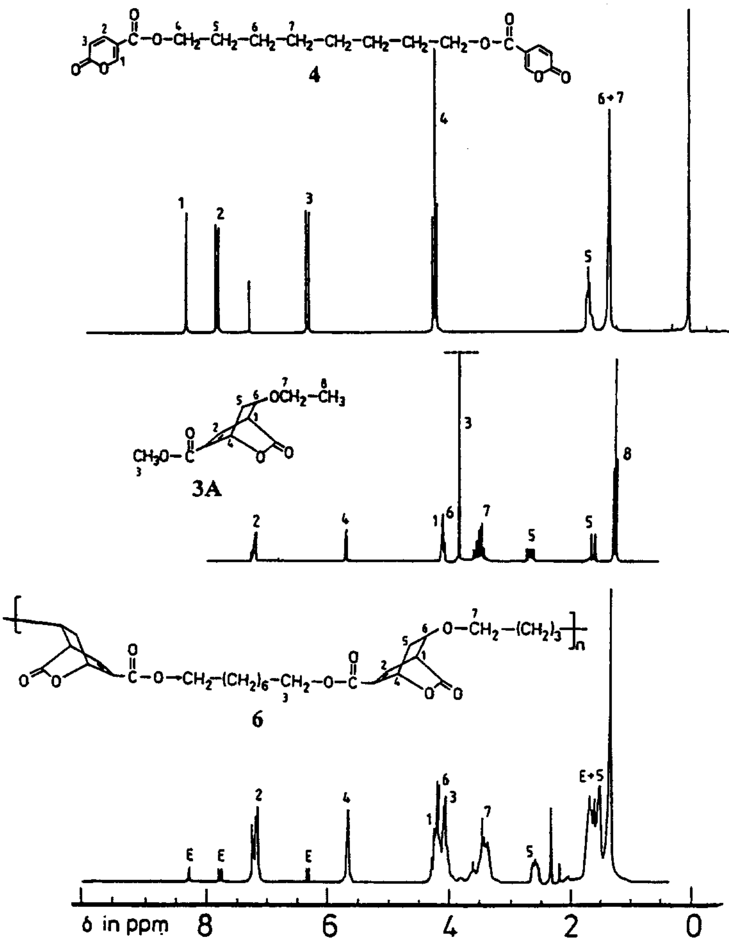

Fig.2 ^{1}H NMR spectra (200 MHz, $CDCl_3$) (a) of bispyrone 4, (b) of model compound 3A, (c) of polymer 6

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