G.c./m.s. investigations on living oligo(ethylene) species functionalized by oxygen

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Living oligomers of ethylene obtained using sec-butyl-lithium complexed with tetramethylethylenediamine (TMEDA) were deactivated by oxygen. Mass spectrometry coupled with gas chromatography of the resulting product allowed the determination of the molecular mass distribution of the alcohols, the coupled products as well as the non-oxidized products formed.

(Keywords: living oligo(ethylene); functionalization; oxygen; gas chromatography; mass spectrometry)

INTRODUCTION

The reaction of molecular oxygen with organometallic products is generally fast. The speed of the reaction as well as the yields of oxidation products depend on the structure of the organic radical and the nature of the cation[1-5]. In all proposed mechanisms, metal peroxides appear as intermediate products, and consequently to the formation of alcohols or hydroperoxides depending on their structure and the experimental conditions of the reaction.

The deactivation of different carbanionic copolymers by oxygen in order to obtain either alcohols or macromolecular hydroperoxides has been studied previously. Brossas and Clouet[6] have synthesized dimeric dialcohols of isoprene by bubbling oxygen directly in a tetrahydrofuran solution of the dilithiated dimer. α,ω-Dihydroxylated polystyrenes and poly(α-methylstyrenes) have been obtained following the same process[7,8]. In these studies, the formation of hydroperoxides was avoided by introducing oxygen slowly into the solution containing the carbanionic species. Catala[9] deactivated poly(styryllithium) by inverse oxidation in tetrahydrofuran at −65°C, to obtain the macromolecular hydroperoxide.

The inverse oxidation method consists of a slow addition of a solution of the living polymer to a solvent saturated with oxygen. According to this method, the oxidation gives three main products: the alcohol, the hydroperoxide and the coupled product.

Reeb, Catala *et al.*[9-11] have studied the peroxidation of the dicarbanionic dimer of 1,1-diphenylethylene and 1,1-diphenyl 3-methylpentyllithium in tetrahydrofuran at −40°C. The products obtained together with an e.s.r. study, confirmed the radical character of the reaction.

Monocarbanionic oligomers of ethylene, obtained by initiation with tert-BuLi TMEDA in hexane have been oxidized at −65°C by inverse and direct oxidations[12].

More recently, Schué *et al.*[13] deactivated living oligomers of ethylene obtained by sec-butyllithium complexed tetramethylethylenediamine (TMEDA). Alcohols, coupled products as well as non-oxidized products, were characterized by both n.m.r. and mass spectrometry, coupled with gas chromatography.

In order to obtain more precise results on the molecular mass distribution of these products, we used more sophisticated mass spectrometry coupled with gas chromatography. For this purpose, we prepared living oligomers of ethylene using sec-butyllithium complexed with TMEDA and deactivated the oligomers by bubbling oxygen slowly through the solution. At the end of the reaction, acidified water was added.

EXPERIMENTAL

All the techniques used to oligomerize ethylene and oxidize the corresponding living species have been described elsewhere[13]. The living oligomers of ethylene were obtained in hexane, using sec-butyllithium (0.2 M) complexed with tetramethylethylene diamine (TMEDA) in the ratio [TMEDA]/[Sec-BuLi] = 1.5. Oxygen was introduced slowly into the solution containing the carbanionic species.

The investigations have been carried out with a combination gas chromatograph model 2700, mass spectro-

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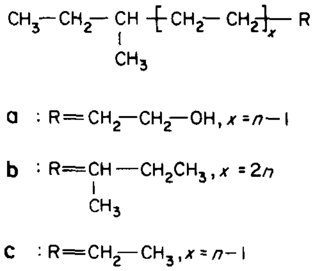
meter CH5 and computer spectrosystem 100 MS (Varian MAT, Bremen, FRG). As interface between gas chromatograph and mass spectrometer a direct coupling over a platinum capillary (30 cm x 0.1 mm i.d.) was used. The ion source of the mass spectromer was equipped with a high performance oil diffusion pump (600 l.s^{-1}) in order to introduce the total flow of the g.c.-column into the ion source.

The recording of the mass spectra was done by the repetitive recording method recording every 7 s a mass spectrum over the mass range m/e 15–450 at a scan speed of the seconds per decade. The total ion current was registered by a second ion source (reference ion source). All mass spectra were tape recorded. The experimental conditions of the g.c./m.s. analysis are summarized in *Table 1*.

RESULTS

The mass spectrometry coupled with gas chromatography allowed the characterization of three products (**a**–**c**) (*Figure 1*):



$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-[CH_2-CH_2]_x-R$$

$$\text{a}\ :\ R=CH_2-CH_2-OH,\ x=n-1$$

$$\text{b}\ :\ R=\underset{\underset{CH_3}{|}}{CH}-CH_2CH_3,\ x=2n$$

$$\text{c}\ :\ R=CH_2-CH_3,\ x=n-1$$

In order to explain the presence of 'a', we use the concerted type mechanism, proposed by Walling and Buckler[14]

$$\underset{A}{\text{Sec-Bu}+CH_2-CH_2)_n\,CH_2-CH_2Li-\text{TMEDA}} \xrightarrow{O_2} \underset{B}{\text{Sec-Bu}+CH_2-CH_2)_n\,CH_2CH_2-OOLi\text{-TMEDA}}$$

$$A+B \longrightarrow 2\ \text{Sec-Bu}+CH_2-CH_2)_n\,CH_2CH_2OLi\ :\ \text{TMDEA}$$

The presence of 'b', due to a coupling reaction, can be explained by a radical mechanism proposed by Russel[15]. This mechanism, based on an electron transfer from the anion to the oxygen, allows the formation of an alkyl radical which can recombine by the coupling reactions:

$$A+O_2 \longrightarrow \underset{C}{\text{Sec-Bu}+CH_2-CH_2)_n\,CH_2-CH_2^{\bullet}}+\text{TMEDALiOO}^-$$

$$2C \longrightarrow \text{Sec-Bu}+CH_2-CH_2)_n+CH_2-CH_2)_n\,\text{Sec}-\text{Bu}$$

Table 1 Experimental conditions for mass spectrometric analysis coupled with gas chromatography

Parameter	Value
G.c.-column	Glas capillary 8.5 m with SE52
Oven temperature	70°C–230°C, temperature-programmed with 4°C/min helium (4 ml/mn)
Volume of sample	0.2 μ
Temperature of injection block	250°C
Electron energy of ion source	70 eV
Electron energy of reference ion source	20 eV
Acceleration voltage	3 KV
SEV-voltage	2.75 KV
Emission	100 μA
Temperature of ion source	220°C
Temperature of interface	220°C
Resolution	700

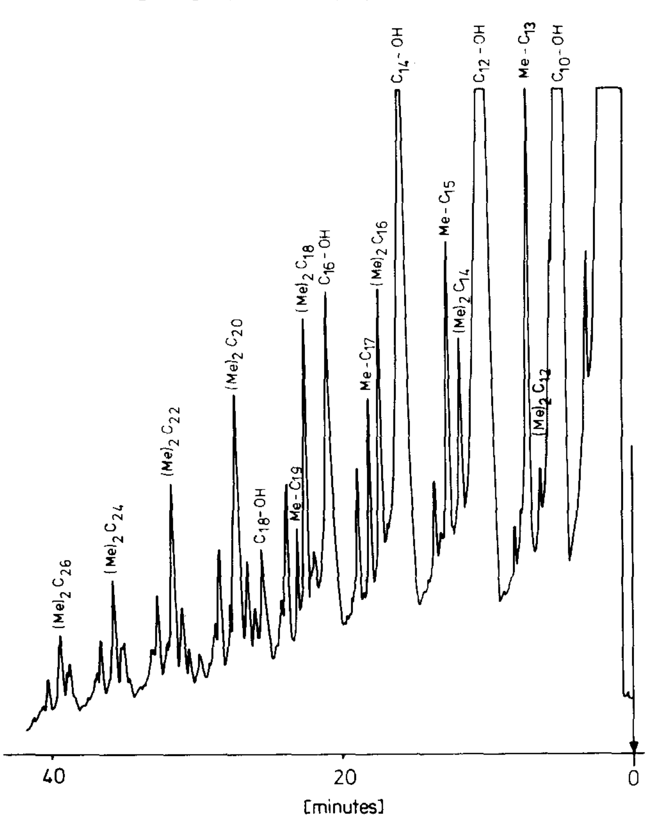


Figure 1 Gas chromatographic separation of the reaction mixture recording of the total ion current. Conditions of the separation are summarized in *Table 1*

Table 2 Distribution of the different hydrocarbons (in %)

$(Me)_2C_{12}$	2.2	MeC_{13}	18.8
$(Me)_2C_{14}$	7.2	MeC_{15}	11.7
$(Me)_2C_{16}$	10.7	MeC_{17}	7.5
$(Me)_2C_{18}$	11.3	MeC_{19}	3.8
$(Me)_2C_{20}$	10.0	MeC_{21}	1.8
$(Me)_2C_{22}$	7.6	MeC_{23}	0.4
$(Me)_2C_{24}$	4.3	MeC_{25}	0.1
$(Me)_2C_{26}$	2.6	MeC_{27}	0
	55.9		44.1

Produce 'C' results from the living oligomers which have not been oxidized due to too short a time of reaction and which have been deactivated by the acidified water.

The concentration of the alcohols decreases rapidly with increasing number of C-atoms. The alcohols up to C_{18} have been positively characterized. The hydrocarbons of the reaction mixture consist of methyl and dimethyl alkanes. The content of methyl alkanes decreases with increasing number of C-atoms whereas the dimethyl alkanes reach their maximal concentration at dimethyl C_{18}. The first have been characterized up to 3-methyl nonadecane, the latter up to 3,24-dimethylhexacosane.

The two series can be differentiated from the alkanes by mass spectroscopy, the difference is mainly based on the proportion of intensity of M–C_2H_5 and M–2CH_3. The cleavage of C_2H_5 from the symmetrically structured dimethyl alkanes is more favoured because of the twofold possibility of fragmentation compared with that from the methyl alkanes. The latter exhibit a preference for the elimination of two methyl groups.

The mass spectra of 3-methyl pentadecane and 3,12-dimethyltetradecane, obtained from the reaction mixture and the gas chromatographic retention time and the fragmentation of the methyl alkane in the characteristic range M–C_2H_5 and M–2CH_3, are in accordance with the corresponding data for 3-methyl pentadecane which served as a reference. Differences, mainly in the range of low molecular masses, result from an overlapping substance in the reaction mixture. The isomeric dimethyl alkane was not available as a reference standard. Therefore, we have investigated the two isomers 3-methyl nonane and 3,6-dimethyl octane as references in order to draw an inference by analogy. Both compounds were not detected in the reaction mixture. In this case it was also shown that the ratio of fragmentation of M–C_2H_5 and M–2CH_3 for the 3,6-dimethyl octane is changed in favour of M–C_2H_5.

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