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Synthesis of Mono and Difunctional Oligoisobutylenes

1. Synthesis of Mono and Dichlorooligoisobutylenes

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Summary

α-chloro et α,ω dichlorooligoisobutylenes ($\overline{Mn}$ in the range 1000-3000) have been prepared according to Kennedy's classical method. ^{13}C NMR spectra of these oligomers have been registered and analyzed.

INTRODUCTION

J.P. Kennedy et al. (J.P. Kennedy 1976, 1977, 1980 ; Feinberg 1976) studied the synthesis of α-chloro- and α,ω dichloropolyisobutylenes. They prepared polymers with relatively high molecular weights. In the present work we report the synthesis of low molecular weight ($\simeq$ 1000) polyisobutylenes with one or two chlorinated end-groups. The structure of the oligomers has been studied by ^{13}C NMR.

EXPERIMENTAL

1) General technics of polymerization - Synthesis of α-chloroisobutylene :

a- Isobutylene (Matheson Gas Products) is dried on sieve (4 Å) then on baryum oxide. After drying it is condensed in liquid nitrogen.

b- Methylene chloride is refluxed in presence of oleum then distilled and dried on sodium wire.

c- Methyl chloride (Matheson Gas Products) is dried on sieve then on baryum oxide. It is liquefied

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at - 50°C.

d- BCl_3 (Merck) is used without purification and is stored in a graduated tube.

e- Polymerizations : These are carried out in vacuo (0.1 torr). After the introduction of the solvent and of the water in the reactor the monomer is distilled in the solution which has been cooled at the required temperature. Then the initiator is introduced as rapidly as possible. After 10 minutes a small quantity of methanol is added.

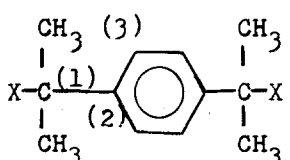
f- Extraction of the polymers : the solvent is distilled off and the polymer is dissolved in hexane. The solution is washed by water and after decantation and evaporation of the organic layer the polymer is dried at room temperature for 12 hours.

2) Synthesis of p di(2chloro-2-isopropyl) benzene (Bela and Kennedy)

Gaseous HCl is reacted at 0°C with p di-(2hydroxy-2-propyl)benzene in solution in methylene chloride. The p(2-chloro-2-propyl)benzene is purified by lyophilisation in benzene and recristallisation in petroleum ether.

M.P. ($\simeq$ 67°C, decomposition)

^{13}C NMR spectra ($CDCl_3$, δ (p.p.m.) relative to T.M.S.)



X = OH or Cl

$\delta C(methyl) = 34,1$; $\delta C(1) = 69.1$

$\delta C(2) = 145.4$; $\delta C(3) = 125.25$

p di(2-hydroxy-2-propyl benzene) is obtained by reacting methyl magnesium iodide with dimethyltere-phthalate in ether (Lutz et al. 1979). The resulting

product is recristallized in benzene.

M.P. ($\simeq$ 141°C)

^{13}C NMR δ(C methyl) = 32.2 ; $\delta(C_1)$ = 71.2

$\delta(C_2)$ = 148.1 ; $\delta(C_3)$ = 124.2

3) Synthesis of α,ω dichlorooligoisobutylene

This is carried out as the synthesis of p(α chloro oligoisobutylene).

RESULTS AND DISCUSSION

1) Synthesis of chlorooligoisobutylene

We used the same method as Kennedy (1976) and Feinberg (1976) which consists in an initiation of isobutylene by system BCl_3, H_2O in a polar solvent such as CH_2Cl_2 or CH_3Cl according to the following mechanism :

- Initiation

$$H_2O + BCl_3 \rightleftharpoons [H_2O, BCl_3] \rightleftharpoons H^{\oplus}, BCl_3OH^{\ominus}$$

$$CH_2=C(CH_3)_2 + H^{\oplus}, BCl_3OH^{\ominus} \rightleftharpoons CH_3-C^{\oplus}(CH_3)_2, BCl_3OH^{\ominus}$$

- Propagation

$$CH_3-C^{\oplus}(CH_3)_2, BCl_3OH^{\ominus} \xrightarrow{M} \sim C^{\oplus}(CH_3)_2, BCl_3OH^{\ominus}$$

- Terminaison

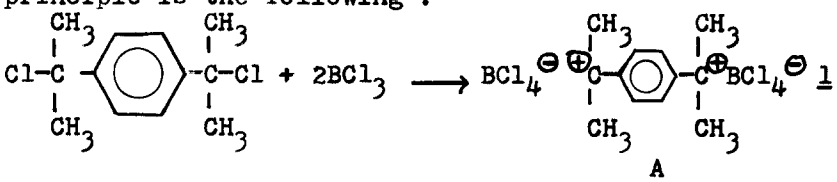
$$\sim C^{\oplus}(CH_3)_2, BCl_3OH^{\ominus} \longrightarrow \sim C(CH_3)_2-Cl + BCl_2OH$$

In order to obtain low molecular weight polymers, we studied the influence of the nature of the solvent, of the ratio $[H_2O]/[BCl_3]$, and of

[M], on the molecular weight of the polymer. These results are reported in table 1. The necessary amount of water was obtained either by using water saturated CH_2Cl_2 or by adding water to the polymerization solution. Water content has been obtained by ^1H NMR according to Marechal (1964).

II) Synthesis of α, ω dichloroisobutylenes

We used the "inifer method" (Kennedy, 1980) whose principle is the following :



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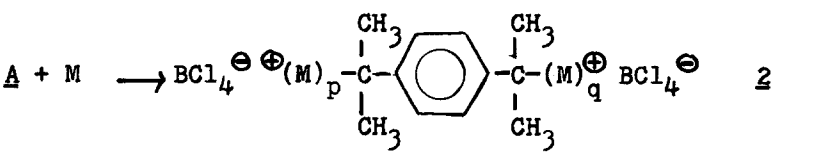
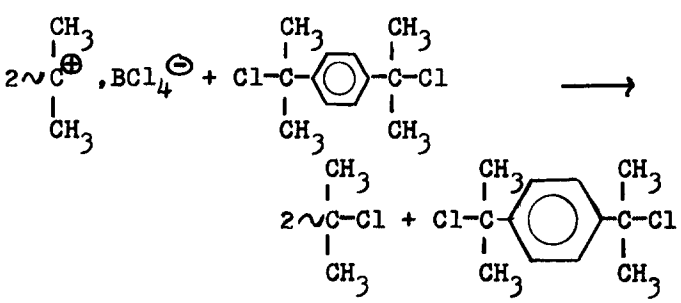




As for monochlorinated compounds, we studied the influence of various experimental parameters on molecular weight. The results are reported in table 2.

III) Analysis of α chloro and α, ω dichloro-oligoisobutylenes.

1) Total chlorine content :

Table 1

Synthesis of α chloropolyisobutylenes - Influence of experimental conditions on the molecular weight - Time of contact between initiator and monomer is 10 minutes.

Temperature °C	Solvent	Monomer (mole.l^{-1})	$[BCl_3]$ mole l^{-1}	$\frac{[H_2O]}{[BCl_3]}$	Yield %	$\overline{Mn}$
- 70	CH_2Cl_2	1.00	0.70	0.82	92	21 000 (a)
- 70	CH_2Cl_2	1.00	0.95$_5$	0.82	88	16 800 (a)
- 50	CH_2Cl_2	1.00	0.72	0.82	92	13 500 (a)
- 50	CH_2Cl_2	1.00	0.96	0.82	64	10 700 (a)
- 30	CH_2Cl_2	1.00	0.39	0.84$_5$	85	1 745 (b)
- 10	CH_2Cl_2	1.00	0.71	0.84	22	1 033 (b)
0	CH_2Cl_2	1.00	0.70	0.85	7	1 130 (b)
- 30	CH_2Cl_2	0.50	0.36	0.83	83	3 750 (b)
- 30	CH_2Cl_2	0.38	0.13	0.86	62	1 900 (b)
- 30	CH_2Cl_2	0.56	0.12	0.84	93	3 110 (b)
- 40	CH_3Cl	1.11	0.92	0.72	37	2 360 (b)
- 40	CH_3Cl	1.30	1.25	0.82	21	2 660 (b)

(a) obtained by viscosimetric measurements and use of Mark-Houwink's relation for polyisobutylene :

$$\overline{Mn} = ([\eta] / 3.6 \times 10^{-4})^{1/0.64}$$

(b) Tonometric determination

Table 2

Synthesis of α,ω dichloropolyisobutylenes - Influence of experimental conditions on molecular weight - The time of contact between initiator and monomer is 10 minutes - Solvent is CH_3Cl and temperature is - 70°C - Molecular weights were obtained by tonometry Inifer is p-di(2-chloro-2 isopropyl)benzene.

Isobutylene (Mole.l^{-1})	Inifer (mole.l^{-1} x 10^2)	$\frac{[BCl_3]}{[Inifer]}$	$\frac{[Inifer]}{[Isobutylene]} \times 10^2$	Yield %	$\overline{Mn}$
2.22	2.39	5.0	1.1	20	1085
2.14	3.04	4.05	1.4	29	1160
1.10	2.49	9.5	2.3	38	1030
0.81	1.18	16	1.45	40	1350
1.45	2.63	10.6	1.8	44	1480
1.94	3.04	9.5	1.6	51	1330
2.74	4.04	5.9	1.5	31	1260
1.16	1.93	11.6	1.7	37	1345
1.90	3.01	11.2	1.6	55	1630
0.87	2.06	7.3	2.4	48	1180
1.15	2.41	12.4	2.1	64	1750

Chlorine content was obtained by Schöniger's method. From chlorine content it was possible to calculate molecular weights. These values fit well with those obtained by tonometry as shown in table 3.

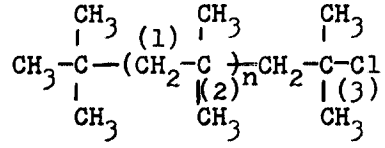
Table 3

Sample	chlorine content (weight %)	$\overline{Mn}$ (from chl. cont.)	$\overline{Mn}$ (from tonometry)
α monochloro-oligoisobutylene	1.3	2731	3110
α,ω dichloro-oligoisobutylene	7.6	934	1030
α,ω dichloro-oligoisobutylene	5.1	1440	1480
α,ω dichloro-oligoisobutylene	4.9	1440	1330

2) ^{13}C NMR Spectra

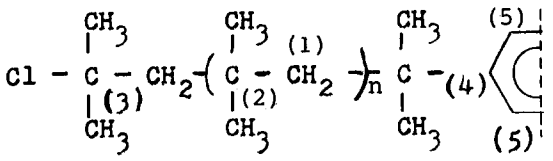
The spectrum was registered in deuterated chloroform. Chemical shifts (p.p.m.) are relative to tetramethyl silanes.

The results obtained for α-monochlorooligoisobutylenes correspond to the following structure :



$\delta C(1)$: 59.5 ; $\delta C(2)$: 38.1
$\delta C(methyl)$: 31.2 ; $\delta C(3)$: 71.6

Those obtained for α,ω dichloroisobutylenes are relative to the following structure :



δC(1) : 59.5 ; δC(2) : 38.1 ; δC(methyl) : 31.2
δC(3) : 71.6 ; δC(4) : 146.95 ; δC(5) : 125.4

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