Tetramer formation from methacrylic acid metal salts in solid state

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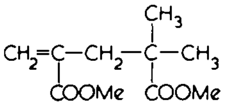
We have investigated the formation of tetramers of methacrylic acid *via* the thermal reaction of metallic salts of methacrylic acid salts in the solid state in the temperature range 300°–350°C. N.m.r. and mass spectra and gas chromatography were used in the characterization of the tetramers formed.

Keywords Reaction; thermal; methacrylic acid; metal salts; tetramer; solid state

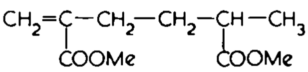
INTRODUCTION

Albisetti *et al.*[1] have reported the formation of dimethyl 1-hexene2,5-dicarboxylate (II) and trimethyl 1-nonene-2,5,8-tricarboxylate (IV) by heating methyl methacrylate (MMA) in the presence of inhibitors under pressure in a steel vessel. Stickler, Lingnau and co-workers[2,3] studied the spontaneous polymerization of MMA and obtained dimer II and trimer IV. They also identified two dimers, dimethyl 4-methyl-1-petene-2,4-dicarboxylate (I), dimethyl 1,2-dimethylcyclobutane-1,2-dicarboxylate and two trimers, trimethyl 4-methyl-1-octene-2,4,7-tricarboxylate (III), trimethyl 4-nonene-2,5,8-tricarboxylate, as products of the side reactions.

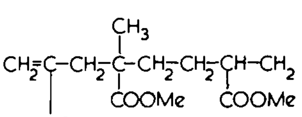
We have already reported[4-8] thermal oligomerizations of metallic salts of methacrylic acid (MA) in the solid state in the range 150°–240°C. In this temperature range, (initially) non-esterified forms of the dimers I and II and trimers III and IV were formed as the main products with good yields.


$CH_2{=}C(COOMe){-}CH_2{-}C(CH_3)(COOMe){-}CH_3$

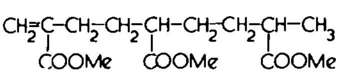
I


$CH_2{=}C(COOMe){-}CH_2{-}CH_2{-}CH(COOMe){-}CH_3$

II


$CH_2{=}C(COOMe){-}CH_2{-}C(CH_3)(COOMe){-}CH_2{-}CH_2{-}CH(COOMe){-}CH_2$

III


$CH_2{=}C(COOMe){-}CH_2{-}CH_2{-}CH(COOMe){-}CH_2{-}CH_2{-}CH(COOMe){-}CH_3$

IV

Here, we wish to report on the formation of the tetramers of MA by the thermal reaction of the metallic salts at 300°–350°C in the solid state.

EXPERIMENTAL

CaMA and BaMA were prepared according to a previous report[8]. The monomer salts were heated at 350°C for 2 h. Resulting oligomers were then converted to methyl esters by treatment with diazomethane, which were fractionated under reduced pressure to give a dimer fraction (bp 88°–92°C/3mmHg), a trimer fraction (bp 147°–148°C/2mmHg) and a tetramer fraction (bp 183°–188°C/2mmHg). Oxidation of the tetramer fraction was conducted in aqueous solution with potassium permanganate in the presence of potassium hydroxide[9]. After the reaction was completed the solution was acidified with sulphuric acid and extracted with ether. The ether extract was treated with diazomethane to convert the acids into their esters. Fractional distillation under reduced pressure of the product yielded 21 fractions in bp range 93°C/23mmHg to 167°C/4mmHg. By preparative gas chromatography of the fractions, samples for analyses were isolated.

The n.m.r. and mass spectra of the seven components obtained from the oxidative fragments were taken.

Structure V: $\delta_H(CCl_4)$ 3.60(s,6H), 2.93–2.13(m,3H), 1.12(d,3H). m/e 129.0558(m^+-OCH_3), Calculated for $C_6H_9O_3$: 129.0551;

Structure VI: δ_H (CCl_4) 3.60(s,6H), 2.60–2.18(m,3H), 2.02–1.58(m,1H), 1.12(d,3H). m/e 143.0707(M^+-OCH_3), Calculated for $C_7H_{11}O_3$: 143.0707;

Structure VII: δ_H (CCl_4) 3.60(s,9H), 2.78–2.12(m,4H), 1.72–1.28(m,4H), 1.12(d,3H). m/e 229.1095(M^+-OCH_3), Calculated for $C_{11}H_{17}O_3$: 229.1075;

Structure VIII: δ_H (CCl_4) 3.58(s,9H), 2.40–2.08(m,4H), 1.94–1.34(m,6H), 1.12(d,3H). m/e 243.1198(M^+-OCH_3), Calculated $C_{12}H_{19}O_5$: 243.1203;

Structure IX: δ_H (CCl_4) 3.36(s,9H), 2.76–2.10(m,5H), 1.70–1.26(m,8H), 1.14(d,3H). m/e 329.1587(M^+-OCH_3), Calculated for $C_{16}H_{25}O_7$: 329.1598;

Structure XIII: $\delta_H(CCl_4)$ 3.58–3.76(m,9H), 2.12–2.84(m,3H), 1.44–1.95 (m,2H), 1.10–1.35(m,6H). m/e 229.1097(M^+-OCH_3), Calculated for $C_{11}H_{16}O_5$: 229.1075;

Structure XIV: $\delta_H(CCl_4)$ 3.56–3.72(m,9H), 2.16–2.70(m,3H), 1.40–1.64(m,4H), 1.08–1.25(m,6H). m/e 243.1249(M^+-OCH_3), Calculated for $C_{12}H_{19}O_5$: 243.1231;

Structure XV: $\delta_H(CCl_4)$ 3.62(s,12H), 2.10–2.90(m,5H), 1.30–1.78(m,6H), 1.04–1.24(m,6H). m/e 329.1588(M^+-OCH_3), Calculated for $C_{16}H_{25}O_7$: 329.1597.

The n.m.r. spectra were obtained with Nippon Denshi Model MH 100 apparatus. The mass spectra were taken on Hitachi RMU-7H type mass spectrometer. For the gas chromatography measurements a Yanagimoto Model G-80 apparatus was employed under the following conditions: column packing, silicone SE-30; column temperature, 280°C; carrier gas, He 25 ml min^{-1}.

RESULTS AND DISCUSSION

Thermal reaction of calcium methacrylate (CaMA) and barium methacrylate (BaMA) in the solid state at a temperature above 300°C under reduced pressure gave tetramers in addition to the dimers and the trimers. These oligomer formations were followed by gas chromatography of the product esterified with diazomethane. The tetramers obtained from BaMA consisted of six components, whose gas chromatographic peaks could be separated in two groups, namely group A and B, as shown in *Figure 1*. However, CaMA did not give group A, but only group B under the same conditions.

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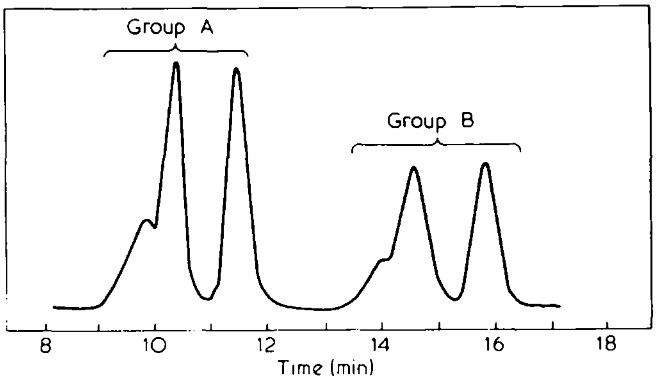
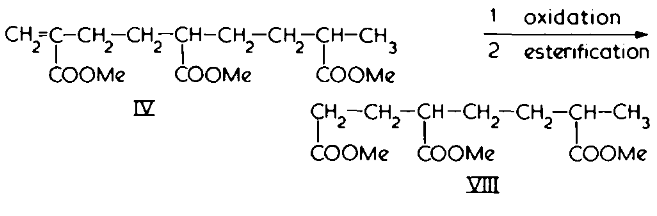


Figure 1 Gas chromatogram of tetramer from barium methacrylate at 350°C

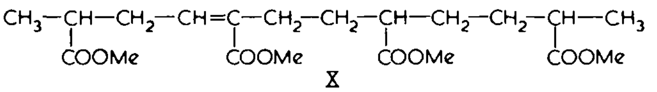
Conversion curves for BaMA and CaMA to oligomers at 350°C are shown in *Figures 2* and 3. Tetramer fractions containing both groups A and B were obtained by fractional distillation of oligomer esters. By hydrogenation of these fractions, triplet gas chromatographic peaks due to group A and group B are altered to singlet peaks. This fact indicates that each of group A and B consists of three components of the same carbon skeleton with a double bond in a different position.

In order to determine the positions of double donds in the tetramers, oxidative scissions of the double bond were carried out with potassium permanganate in aqueous solution. The methyl esters of the oxidative fragments were identified as follows: dimethyl propane-1,2-dicarboxylate(V), dimethyl butane-1,3-dicarboxylate(VI), trimethyl hexane-1,2,5-tricarboxylate(VII), trimethyl heptane-1,3,6-tricarboxylate(VIII) and tetramethyl nonane-1,2,5,8-tetracarboxylate(IX). The oxidative scission of the double bond having a methoxycarbonyl group on the carbon of the double bond was considered to occur with elimination of the methoxycarbonyl group. This fact was confirmed by the oxidation of IV with potassium permanganate followed by esterification with diazomethane giving only VIII.



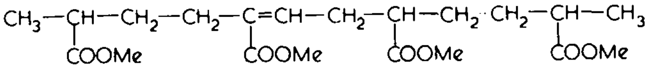
$$\underset{\text{IV}}{CH_2{=}\underset{COOMe}{C}-CH_2-CH_2-\underset{COOMe}{CH}-CH_2-CH_2-\underset{COOMe}{CH}-CH_3} \xrightarrow[\text{2 esterification}]{\text{1 oxidation}} \underset{\text{VIII}}{\underset{COOMe}{CH_2}-CH_2-\underset{COOMe}{CH}-CH_2-CH_2-\underset{COOMe}{CH}-CH_3}$$

The most probable combinations of oxidative fragments are as follows, V–VIII, VI–VII and IX–methyl acetate. Methyl acetate which should be formed as an oxidative fragment, could not be isolated from the oxidative products probably because this compound was lost in the evaporation procedure due to its low boiling point. Therefore, the probable structures of the tetramers are as follows:



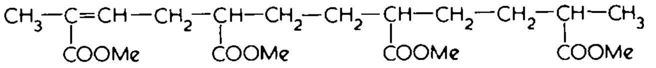
$$CH_3-\underset{COOMe}{CH}-CH_2-CH{=}\underset{COOMe}{C}-CH_2-CH_2-\underset{COOMe}{CH}-CH_2-CH_2-\underset{COOMe}{CH}-CH_3$$

X



$$CH_3-\underset{COOMe}{CH}-CH_2-CH_2-\underset{COOMe}{C}{=}CH-CH_2-\underset{COOMe}{CH}-CH_2\cdot CH_2-\underset{COOMe}{CH}-CH_3$$

XI



$$CH_3-\underset{COOMe}{C}{=}CH-CH_2-\underset{COOMe}{CH}-CH_2-CH_2-\underset{COOMe}{CH}-CH_2-CH_2-\underset{COOMe}{CH}-CH_3$$

XII

Using the same experiment on the fraction of group A gave V, VI, trimethyl 2-methylpentane-1,2,4-tricarboxylate(XIII), trimethyl 3-methylhexane-1,3,5-tricarboxylate(XIV) and tetramethyl 5-methyloctane-1,2,5,7-tetracarboxylate(XV). From these results, the probable structures of the tetramers of group A are as follows:

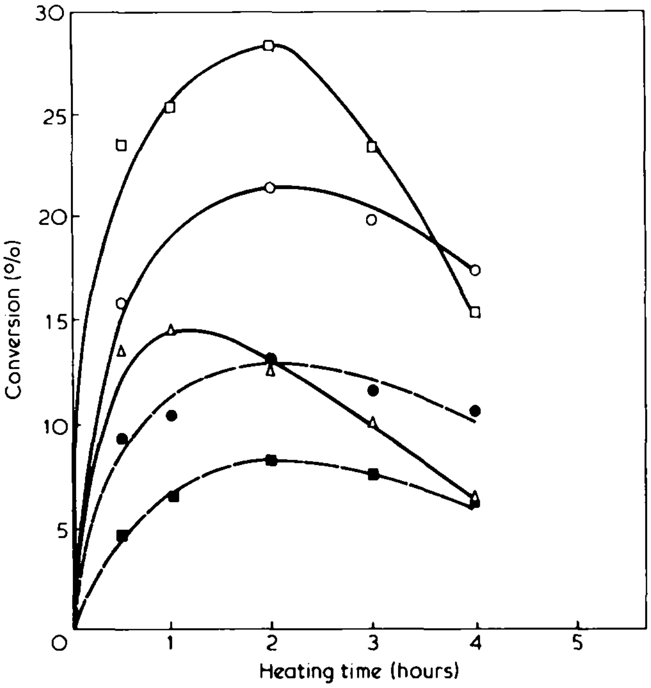


Figure 2 Conversion of barium methacrylate to oligomer at 350°C. □, Trimer; ○, tetramer; ●, tetramer of group A; △, dimer; ■, tetramer of group B

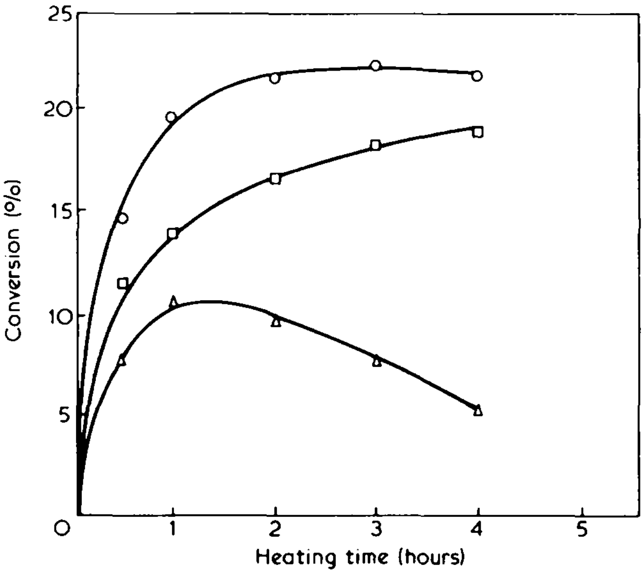
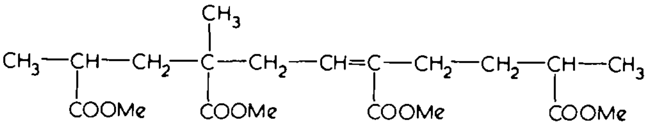
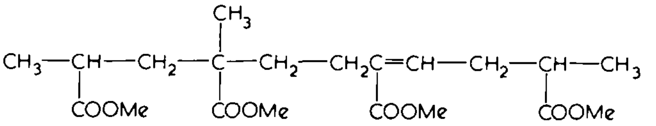


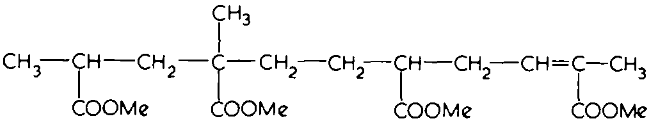
Figure 3 Conversion of calcium methacrylate to oligomer at 350°C. ○, Tetramer (group B); □, trimer; △, dimer


$CH_3-\underset{COOMe}{CH}-CH_2-\overset{CH_3}{\underset{COOMe}{C}}-CH_2-CH=\underset{COOMe}{C}-CH_2-CH_2-\underset{COOMe}{CH}-CH_3$

XVI


$CH_3-\underset{COOMe}{CH}-CH_2-\overset{CH_3}{\underset{COOMe}{C}}-CH_2-CH_2\underset{COOMe}{C}=CH-CH_2-\underset{COOMe}{CH}-CH_3$

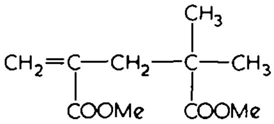
XVII


$CH_3-\underset{COOMe}{CH}-CH_2-\overset{CH_3}{\underset{COOMe}{C}}-CH_2-CH_2-\underset{COOMe}{CH}-CH_2-CH=\underset{COOMe}{C}-CH_3$

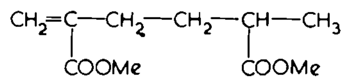
XVIII

The exact individual yields of the six isomers could not be determined, because the oxidative fragmentation reaction was not a quantitative one.

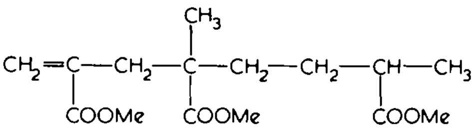
The thermal oligomerization of BaMA at 190°-240°C gave two dimers (I, II) and two trimers (III, IV). However, CaMA gave one dimer (II) and one trimer (IV) as follows[5,6]:


$CH_2=\underset{COOMe}{C}-CH_2-\overset{CH_3}{\underset{COOMe}{C}}-CH_3$

I


$CH_2=\underset{COOMe}{C}-CH_2-CH_2-\underset{COOMe}{CH}-CH_3$

II


$CH_2=\underset{COOMe}{C}-CH_2-\overset{CH_3}{\underset{COOMe}{C}}-CH_2-CH_2-\underset{COOMe}{CH}-CH_3$

III

If the tetramers are formed by the addition of trimer biradicals to the monomer, CaMA gives tetramers which belong to the group A, and BaMA tetramers which belong to both group A and group B. The formation of three isomers having a double bond at different positions may be explained by proton migration. In the solid state, different molecular microenvironments can exist in contrast to the liquid state in which the microenvironment may be considered to be uniform these difference in microenvironment may cause differences in proton migration to give the three isomers. Details on the mechanism of these tetramer formations will be reported in the near future.

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Thermal degradation of a series of phosphorylated resins of polyethylene

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The copper ore solutions, particularly those from Chuquicamata deposits (Chile), contain up to 15 ppm of Uranium which is covered by using ion-exchange Amberlite IRA-400. We have prepared specific resins for uranium from polyethylene phosphorylated. The recovery can be made by using the direct combustion of charged resin. This method is less expensive than the elution with acid and U_3O_8 is obtained directly.

Keywords Degradation; thermal; polyethylene; resins; thermogravimetric analysis; uranium

INTRODUCTION

Thermogravimetric analysis (t.g.a.) data provide information about the temperature at which major fragmentation occurs and is therefore an indication of the inherent stability of the polymer structure[1].

The resins used were prepared from polyethylene (DOW PE-515) phosphorylated with PCl_3 and O_2[2] and then crosslinked with ethylenediamine, ethyleneglycol, diethyleneglycol and triethyleneglycol respectively. These resins are specific for uranium, cheap and have greater maximum capacities than commercial Amberlite IRA-400[3]. In actual fact, the more often used resin for the recovery of uranium from copper solution is the Amberlite IRA-400[4]. When the resins are charged, the elution of uranium is made by such salts and acids such as: HCl, H_2SO_4 or Na_2CO_3,[5,6]; but another possibility for a rapid recovery of the metal is the direct combustion of the resin. For this reason it is important to know the thermal stability of the resins and the composition of the resulting residue.

RESULTS AND DISCUSSION

In this report the thermogravimetric data were obtained using a Thermobalance TGS-1, Perkin-Elmer Model

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