X-ray diffraction studies of some halatopolymers

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The crystal structure and degree of crystallinity of a number of melt-spinnable halatopolymers has been investigated. These materials can be characterized by a well defined 'ionic' peak at low diffraction angle. In general they have a tetragonal unit cell, although the more perfectly crystalline materials may well belong to a triclinic crystal system. Changes in crystallinity were investigated in terms of method and conditions of preparation, and of thermal treatment. Stannous dicarboxylates had the most widely variable crystallinity.

Keywords Crystal structure; degree of crystallinity

INTRODUCTION

Halatopolymers are a group of ionic materials which display some of the properties of both salts and polymers[1]. They have the general formula

$$HOOC[-(CH_2)_n-COO-M-OOC]_N(CH_2)_n-COOH$$
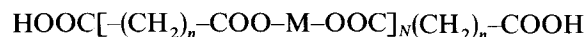
where M is a divalent metal ion, $n = 6$, 8 or 10, and N is the number of repeat units. When prepared by precipitation from aqueous solution, the halatopolymers are highly crystalline and salt-like, but on melting, they display polymer-like behaviour such as high melt viscosity and viscoelasticity. A less crystalline structure is obtained when halatopolymers are prepared by synthesis from a viscous melt using the melt polymerization method.

These unusual melt-spinnable polymers possess structures which can be formulated as linear chains containing both ionic and covalent bonds; for example, stannous sebacate with $n = 8$, has a repeat unit:
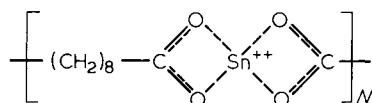
It is the presence of ionic bonded inorganic cations, in addition to the covalent bonds within the acid 'monomer', which constitute the basic characteristic feature by which the halatopolymers differ from other polymers.

There has been very little reported in the way of structural studies of halatopolymers, although Economy and Mason[2] have shown that barium sebacate has a tetragonal unit cell with $a = 0.864$ nm, and $c = 1.542$ nm. Here we report the crystal structure and relative crystallinities of a number of suberates and sebacates.

EXPERIMENTAL

Preparation

Halatopolymers are obtained by the 'halatopolymeric transition' of divalent metal salts of dicarboxylic acids, which are obtained either by precipitation from water or by melt polymerization. The former is very simple and produces a good yield, whereas the latter is limited to the divalent metal dicarboxylates which possess melting points below their decomposition temperatures. Detailed information about the preparation of halatopolymers will be provided elsewhere[3].

X-ray diffraction

X-ray diffraction photographs were taken using a flat-plate camera, with the specimens in 1.5 mm diameter glass capillaries. For quantitative work, powders were examined in the symmetrical reflection mode on a modified Hilger and Watts Y115 diffractometer mounted on a Hilger and Watts Y90 constant output X-ray generator utilizing CuKα radiation. Counting was normally carried out at 15 steps per degree, data being recorded on punched-paper tape via a scintillation counter, pulse-height analyser, and timer-scaler system. Correction and normalization of the data to electron units followed the method discussed in detail by Hindeleh, Johnson and Montague[4], with some additional modifications to deal with the heavy metal ions of the halatopolymers.

Assessment of absolute crystallinity based on peak-area measurement could not be considered because of the small proportion of total scatter in the crystalline peaks and the difficulties of separating them from the background and from each other. The only relevant method for crystallinity evaluation is that of the correlation crystallinity index; this was calculated for the various groups of specimens following a procedure described earlier[5,6].

A program was written to evaluate, draw, and index, the simulated diffraction rings expected from any set of unit-cell data, as an aid to indexing the diffraction traces. This later work was carried out on the University of Leeds Computing Service's Amdahl V/7 computer, the earlier work utilized an ICL 1906A computer.

RESULTS

Unit cell determination

The first and strongest peak found in the diffraction pattern of an halatopolymer, is in the region 5–8 degrees 2θ, where θ is the Bragg angle, and is due to the molecular repeat c corresponding to a periodicity of 1.1 to 1.7 nm. In the case of ionomers this peak is sometimes referred to as the 'ionic' peak[7]. A typical diffractometer trace from a halatopolymer is shown in *Figure 1* (zinc suberate). It should be noted that after correction and normalization to electron units, the ionic peak is considerably reduced in intensity. Higher orders of this peak are nearly always found without difficulty; fitting of the other peaks is not as straightforward and was best carried out by recourse to computer simulation. The best-fit tetragonal unit cells are given in *Table 1* for several suberates and sebacates. Typical densities based on these cells are 1.67 g cm^{-3} for magnesium sebacate, Mg OOC(CH$_2$)$_8$COO, and 1.95 g cm^{-3} for stannous sebacate, Sn OOC(CH$_2$)$_8$COO; experimental values were 1.71 and 2.10 g cm^{-3} respectively.

Values of crystallite size in the c direction can be evaluated from the 001 profile. They are all in the range 15–25 nm, giving values for the minimum number of repeats N between 11 and 22. Zinc suberate, for example, has a crystallite size in the c direction of 20.4 nm, and an N value of at least 19. In the case of polymers, the crystallite size in the chain direction can only give a minimum length to the molecule.

The X-ray diffraction trace of stannous sebacate is shown in *Figure 2*. There appear to be additional peaks which do not fit the tetragonal crystal system. This specimen was analysed in the Central Research and Development Department of E. I. duPont de Nemours, utilizing an auto indexing program by Visser[8]. Two possible solutions were found: (i) a triclinic (pseudotetragonal) unit cell with $a = 0.473$ nm, $b = 1.387$ nm, $c = 0.472$ nm, $\alpha = 95.5$, $\beta = 108.0$, and $\gamma = 108.0$ degrees; (ii) a monoclinic unit cell with $a = 1.387$ nm, $b = 0.765$ nm, $c = 0.555$ nm, and $\beta = 97.4$ degrees.

Correlation crystallinity index

In order to rank the halatopolymers in order of crystallinity, it is necessary to select arbitrarily one specimen with maximum crystallinity as the 100% specimen, and one specimen with minimum crystallinity as the 0% specimen. The cadmium dicarboxylates were chosen for maximum crystallinity and their zinc counterparts for minimum crystallinity, so that the data in *Table 2* could be evaluated. In fact, zinc dicarboxylates have a non-zero crystallinity, and a parallel evaluation was carried out with a stannous sebacate prepared by precipitation at 100°C as the least crystalline specimen (V3 = 0, *Table 2*).

Several series of stannous sebacates were prepared at different pH values, temperatures, and molar proportions
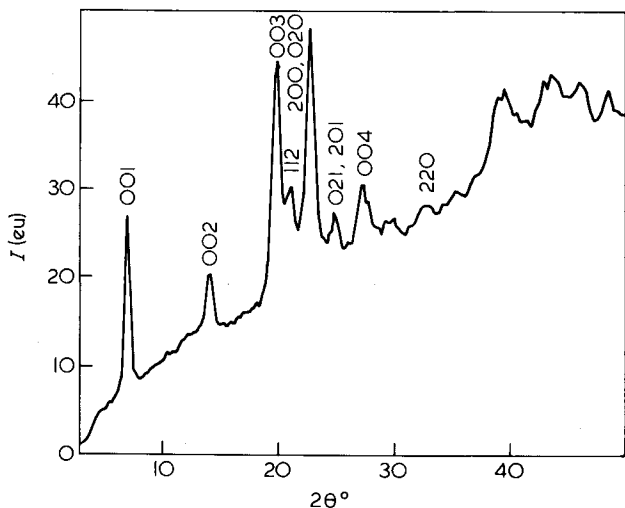

Figure 1 Corrected and normalized X-ray diffraction trace of zinc suberate. Peaks indexed in terms of a tetragonal unit cell
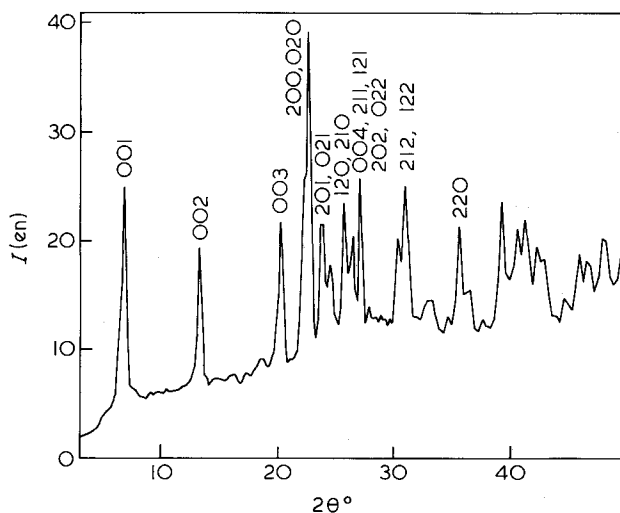

Figure 2 Corrected and normalized X-ray diffraction trace of stannous sebacate. Peaks indexed in terms of a tetragonal unit cell

Table 1 Unit cell dimensions (tetragonal crystal system) of divalent metal suberates and sebacates prepared by precipitation from water at 20°C and pH 8.0

Cation M(2+) for MOOC(CH$_2$)$_n$COO	Suberates n = 6			Sebacates n = 8		
	a (nm)	c (nm)	vol (nm^3)	a (nm)	c (nm)	vol (nm^3)
Cd	0.832	1.216	0.842	1.016	1.559	1.609
Sn	0.778	1.153	0.698	0.892	1.362	1.085
Ca	0.772	1.216	0.725	0.820	1.559	1.048
Pb	0.764	1.366	0.798	0.773	1.742	1.041
Ba	0.788	1.153	0.716	0.804	1.524	0.985
Mn	0.752	1.183	0.669	0.792	1.456	0.913
Mg	0.876	1.123	0.862	0.826	1.311	0.894
Zn	0.868	1.069	0.805	0.792	1.325	0.831

Table 2 Correlation crystallinity index of divalent metal suberates and sebacates prepared by precipitation from water at 20°C and pH 8.0

Cation M(2+) for MOOC(CH₂)ₙCOO	Correlation crystallinity index (%)		
	Suberates $n = 6$	Sebacates $n = 8$	V3 = 0 $n = 6$
Cd	100	100	100
Sn	73	46	76
Ca	65	44	64
Ba	63	34	56
Mn	60	30	50
Pb	57	40	58
Mg	41	4	20
Zn	0	0	18

V3 = 0 Stannous sebacate prepared by precipitation from water at 100°C as zero crystalline sample

Table 3 Correlation crystallinity index of stannous sebacates

Conditions of preparation			Molar proportion acid: metal salt	Correlation crystallinity (%)
pH	Temp. (°C)	Method		
6.4	20	P	1 : 1	22
6.4	50	P	1 : 1	15
6.4	100	P	1 : 1	8
8.0	20	P	1 : 1	100
8.0	50	P	1 : 1	21
8.0	100	P	1 : 1	19
11.6	20	P	1 : 1	94
11.6	50	P	1 : 1	42
11.6	50	MO	1 : 1	21
11.6	100	P	1 : 1	20
8.0	100	P	3 : 2	22
8.0	100	P	2 : 3	23
8.0	100	P	1 : 2	0
8.0	100	P	2 : 1	23
—	197	MP	1 : 1	27

P   Prepared by precipitation from aqueous solution
MO Prepared by precipitation from aqueous solution and then fused
MP Prepared by melt polymerization

of reactants. The correlation crystallinity indices were evaluated with the specimen prepared at pH 8.0, 20°C, and with acid/metal ratio 1:1, as the 100% crystalline standard (this is the specimen with a triclinic unit cell), and that prepared at pH 8.0, 100°C, and with acid/metal ratio 1:2, as the 0% crystalline standard. The results are given in *Table 3*.

Series of sebacates were prepared in a similar manner for all the other cations (Cd, Ca, Ba, Mn, Pb, Mg, Zn); in each case the crystallinity index did not change significantly from the value for the specimen prepared at pH 8.0 and 20°C (*Table 2*).

Generally, the metal dicarboxylates obtained by precipitation from aqueous solution are more crystalline than their counterparts obtained by melt synthesis; however, fusion leads to viscoelastic melts which, on cooling, are less crystalline than those materials prepared by melt synthesis. The correlation crystallinity indices as a function of method of preparation are illustrated in *Figure 3*. It must be noted that the stannous sebacates are ranked according to the scale of *Table 3*, and the other metal dicarboxylates according to *Table 2*.

DISCUSSION

The metal dicarboxylates can be characterized by the presence of a very well defined ionic peak at a relatively low angle of 2θ. This peak is also characteristic of the ionomers, which are a group of ionic polymers with the ionic bonds pendant to the covalent backbone structure rather than within it, as is the case with the halatopolymers. Further indication of the ionic nature of these highly crystalline materials is shown by the fact that they possess colours which are associated with the cations; for example, manganous dicarboxylates are pink, and stannous dicarboxylates are pale yellow. One important characteristic of stannous suberate is that it exhibits spherulitic growth on slow cooling of the melt.

Because it was not possible to grow single crystals of the halatopolymers, the crystal structure had to be determined from powder patterns. All the materials studied here could be indexed in terms of simple tetragonal unit cells with four repeat units. This agrees with the crystal system reported for barium sebacate by Economy and Mason[2], as does our c value (1.52 nm as compared to 1.542 nm), although the value of a found here is smaller (0.804 nm compared to 0.864). Reflections in the stannous and cadmium dicarboxylates which do not fit a tetragonal system, were found by autoindexing to belong to a triclinic system. It seems logical that if the other halatopolymers could have been crystallized more perfectly they too would have shown the reflections of triclinic systems.

Some of the halatopolymers have been found to contain water of crystallization[1,2]; when the density of magnesium sebacate is evaluated with one molecule of water per repeat unit, its value is 1.85 g cm⁻³; this is higher than the experimental value of 1.71 g cm⁻³ and more realistic than the density calculated without water.

One of the main objectives of this work was to prepare specimens with enhanced polymer properties, therefore a low correlation crystallinity was sought. No significant changes in crystallinity were achieved by varying the method of precipitation of any halatopolymer except the stannous dicarboxylates. Although fibres could be spun from all halatopolymers, only the stannous sebacates produced fibres with apparently different physical
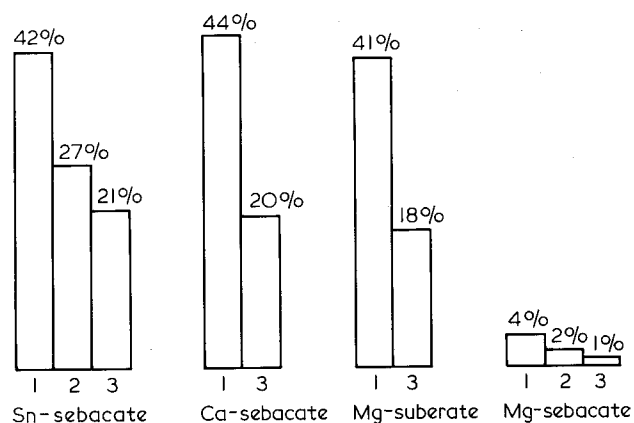
Figure 3 Correlation crystallinity indices of some metal dicarboxlates prepared by different methods. 1 = Prepared by precipitation from aqueous solution; 2 = prepared by melt synthesis; 3 = prepared as in (1) and then fused

properties. Unfortunately, the fibres were so weak and brittle that normal strength testing was impossible. The zero crystalline standard, stannous sebacate prepared at pH 8.0, 100°C, and acid/metal ratio 1:2, was the best material for fibre production and could be drawn at 90°C to a draw ratio of 1.5:1. There was no change in crystallinity after drawing. The 100% crystalline standard could be spun into a fibre which showed preferred orientation of the 001 reflections, but could not be drawn. No other fibres spun from halatopolymers showed any semblance of preferred orientation. The brittle nature of the fibres is attributed to a combination of factors, including a high degree of crystallinity and ionic crosslinking.

CONCLUSIONS

Halatopolymers are highly crystalline materials when prepared by precipitation, but, on melting, they become thermoplastic and less crystalline. The crystal structure can be considered tetragonal, to a first approximation, although the more perfect materials belong to a triclinic system. They are found to contain water of crystallization.

Of the many dicarboxylates prepared from different cations, only stannous dicarboxylates can be prepared with widely varied degrees of crystallinity. All the halatopolymers can be spun into fibres, of an extremely weak and brittle nature, and stannous dicarboxylates of low crystallinity can be spun into fibres which may be drawn. The only fibres with preferred orientation were spun from stannous sebacate of high crystallinity.

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