Solid state properties of crystalline ionenes*

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The solid state properties of poly[(dialkylimino)alkylene] salts ('ionenes')

$$-[-(CH_2)_m-N(R)_2-]_n\ q.n.X$$

where $m=6$ or 10, $R=-CH_3$ or $-CH_2CH_3$ and X = monovalent ($q=1$) or bivalent ($q=0.5$) counterions, are discussed with respect to their thermal behaviour and crystal structure. The melting of ionenes strongly depends on the type of counterion X and with the same counterion decreases with increasing m and size of R. The melting enthalpies are surprisingly low, despite the relatively high melting transitions. Thus, the entropy of melting must be small, which indicates a relatively high disorder in the crystals. Due to an extraordinary crystallization behaviour, macroscopic polymer single crystals have been obtained from ionenes, the crystal structure of which has been analysed. In general, highly symmetrical lattice geometries have been found, with the type of unit cell depending on m and the type of X: (1) ionenes with spacer length $m=6$ in combination with monovalent spherical anions X give rise to hexagonal unit cells; (2) ionenes with spacer length $m=6$ in combination with divalent spherical anions X give rise to pseudocubic tetragonal unit cells; (3) ionenes with spacer length $m=10$ give rise to hexagonal unit cells if combined with spherical monovalent anions X. The details of the crystal structures turned out to be very unusual. The ionic sites (X^-, $-N^+R_2-$) form a regular lattice of high symmetry. The arrangement of chains connecting the ammonium groups can at present best be interpreted as 'random walk'.

(Keywords: ionenes; polyelectrolytes; crystal; lattice; thermal properties)

INTRODUCTION

Poly[(dialkylimino)alkylene] salts (ionenes)[1], cover a broad range of states from single crystalline to glassy solid[2]. Their tendency to crystallize depends on the length of the spacer between the ammonium groups, as well as the regularity of the distribution of the ionic sites along the polymer chain[3–5]. The crystallization behaviour of aliphatic ionenes has been discussed qualitatively by Tsutsui *et al.*[5], but no detailed studies on the crystal structure of these polyelectrolytes have yet been reported. Apart from two recent publications[2,6], little information is available about the melting behaviour of aliphatic ionenes. This is mainly because the ionenes undergo Hoffmann degradation[7], the extent of which depends on the basicity of the counterions.

In this paper the solid state properties of ionenes

$$-[-(CH_2)_m-N(R)_2-]_n\ q.n.X \qquad (1)$$

where $m=6$ or 10, $R=-CH_3$ or $-CH_2CH_3$ and X = monovalent ($q=1$) or bivalent ($q=0.5$) counterions, concerning their crystal structure and thermal behaviour are discussed. Ionenes in which the ionic species are regularly spaced along the main chain (symmetric ionenes) have been synthesized for this purpose, and by counterion exchange polymers with different solid state properties were obtained. In the following the nomenclature I-m-R-X will be used to describe the various combinations of the counterions with the main and side chain elements of the ionenes; I stands for the general structure (1) with m, R and X defined as the number of methylene groups in the alkylene spacer, the type of substituent ($-CH_3$, $-C_2H_5$) at the positively charged nitrogen of the ammonium groups and the counterion, respectively. Low molecular weight oligomers, 'trimers', were synthesized as well to serve as model compounds for the X-ray analysis of the crystal structure. Surprisingly, macroscopic single crystals, not only from the trimers but also from some polymeric ionenes, could be grown. This is one of the few cases in which macroscopic single crystals of polymers are obtainable[8], although the structure analysis reveals that they combine long range order and disorder in a very peculiar way.

EXPERIMENTAL

Aliphatic ionenes with six or ten methylene groups between the ionic sites were synthesized by reacting α,ω-dibromoalkanes with the corresponding N,N,N',N'-tetraalkyl-α,ω-diaminoalkanes using the method reported by Rembaum *et al.*[1,9,10]. The procedure for the synthesis of the ionenes and the corresponding trimers as well as for the counterion exchange has been reported elsewhere[2]. The molecular weights of the ionene bromides were determined by viscosimetry using Rembaum's method. The samples studied in this paper had molecular weights $20\times10^3 < M_w < 40\times10^3$.

The thermal properties were characterized using a Reichert Thermovar microscope equipped with a hot stage, a Mettler DSC-30 and a Perkin–Elmer DSC-7 analyser. The heating rate was kept constant at $20\ K\ min^{-1}$ for all of the differential scanning calorimetry (d.s.c.) measurements. Micrographs were taken with a

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* Dedicated to Professor E. W. Fischer on the occasion of his 60th birthday

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Table 1 Thermal properties of ionenes (1) for different alkylene spacer lengths and types of counterion

Polymer	Melting temp. (°C)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	Onset of decomposition temp. (°C)	Morphology of the crystalline material
I–6–Me–TOS[a]	250	24.7	43.3	280	Spherulites
I–6–Me–CF$_3$SO$_3$	207	6.1	12.7	308	Mosaic-like structure
I–6–Me–BF$_4$	276	6.5	11.8	335	Grainy structure
I–6–Me–PF$_6$[b]	233	–	–	233–300	Needles
I–6–Me–SbF$_6$[b]	235	–	–	235–262	Needles
I–6–Me–FeCl$_4$[b]	215–220	–	–	220	Polyhedric
I–6–Me–ZnCl$_4$[b]	–	–	–	260–280	Polyhedric
I–6–Me–ZnBr$_4$[b]	–	–	–	280	Polyhedric
I–6–Me–ZnI$_4$	233	–	–	233–250	Microcrystalline
I–6–Me–CdI$_4$	261	8.8	16.5	270	Microcrystalline
I–6–Me–HgI$_4$	242	11.1	21.5	260	Microcrystalline
I–10–Me–TOS[a]	99	14.8	39.7	280	Spherulites
I–10–Me–CF$_3$SO$_3$	118	2.5	6.5	260	Spherulites
I–10–Me–BF$_4$	128	8.3	20.7	300	Spherulites
I–10–Me–PF$_6$	226	12.2	24.5	250	Needles
I–10–Me–SbF$_6$	274	–	–	290	Needles
I–10–Me–FeCl$_4$	187	9.1	19.9	290	Polyhedric

[a] TOS, tosylate
[b] Obtained as single crystals

Zeiss Photomicroscope III equipped with polarizing optics.

The X-ray data were obtained using a Siemens D-500 θ, θ-Diffractometer with Ni-filtered Cu–Kα radiation. The X-ray analysis of the single crystals was carried out by Weissenberg and Burger cameras with Ni-filtered Cu–Kα radiation; intensity data were collected on a Enraf–Nonius CAD four circle diffractometer. Single crystals of polymeric ionenes as well as of their corresponding trimers were obtained from solution in DMF or water by slow evaporation of the solvent.

The electron micrographs were taken from platinum–carbon replicas of the microcrystalline polymer by a Zeiss-EM-902.

THERMAL PROPERTIES OF CRYSTALLINE IONENES

The thermal behaviour of ionenes with respect to their melting point and stability in the melt depends on the length of the alkylene spacer between the ionic sites and the type of counterion[2,6]. Concerning the counterion, two types of behaviour have been observed, as shown in *Table 1*. Of the ionene group I–6–Me–X, the polymers with PF$_6$, SbF$_6$, FeCl$_4$ and ZnBr$_4$ as counterions decompose before they melt or melt with strong decomposition. In contrast, ionenes with tetrafluoroborate, triflate and tosylate as counterions melt and recrystallize from the melt. The I–6–Me–triflate was particularly stable in the melt and did not show any signs of degradation even after several heating cycles, as shown in *Table 2*. The trimers

$$(R)_3N\text{–}[\text{–}(CH_2)_m\text{–}N(R)_2\text{–}]_3\text{–}R\ 4.q.X \qquad (2)$$

where R, m, q and X have the same meaning as in (1), showed similar thermal properties to their polymeric counterparts, as seen by comparison of the results compiled in *Tables 1* and *3*. T–m–R–X is used as an abbreviation for the trimers.

The melting temperature shows a dependency on the type of counterion and decreases for a given counterion with increasing length of the alkyl chain between the ammonium groups. The decomposition temperature seems to depend to some extent on the nucleophilicity of the counterion[7]. Ionenes with counterions like PF$_6$, which tend to hydrolyse or react with formation of fluoride ions, undergo fast decomposition.

In general, low melting enthalpies per polymer repeat unit were observed in comparison with other polymers such as polyamides and polyesters[11]. Melting enthalpies of 6.1 and 6.5 kJ mol^{-1} for I–6–Me–X with triflate and tetrafluoroborate as counterions were observed. The only exception was I–6–Me–tosylate, which showed a melting enthalpy of 24.7 kJ mol^{-1}, comparable to that of polyamides. To account for the low melting enthalpy despite the relatively high melting points, the entropy of melting ΔS must be relatively small. This points toward a certain disorder in the crystals, which will be revealed by the results of the crystal structure analysis in the next section.

Apart from the melting, other endothermic peaks due to solid–solid transitions were observed in some of the compounds. For example, the first d.s.c. scan of I–6–Me–triflate as recrystallized from a mixture of diethylether and acetone (1:1) showed an endothermic peak at 80°C that was not observed in subsequent scans (*Figure 1*, *Table 2*). This transition can be associated with the formation of a new crystal modification (β-modification), as evidenced by the X-ray diffractograms shown in *Figure 2*. Recrystallization from the melt gives rise to the β-modification only.

Similar behaviour was observed for I–6–Me–BF$_4$ crystallized from solution: a solid–solid transition was observed at 190°C, as shown in *Table 2*. The X-ray diffractogram recorded above this temperature showed differences to that measured at room temperature (see *Figure 3*) for I–6–Me–BF$_4$ recrystallized from the melt. The I–6–Me–BF$_4$ exhibites a crystal structure isomorphous with that of melt crystallized I–6–Me–triflate, as seen by comparing *Figures 2b* and *3c*. The trimer T–6–Me–BF$_4$ behaves analogously on thermal treatment (see *Table 3*). Annealing of the solid trimer at a temperature above 220°C gives rise to a structure isomorphous with the room temperature structure of the corresponding polymer after it has been quenched from the melt (see *Figure 3d*).

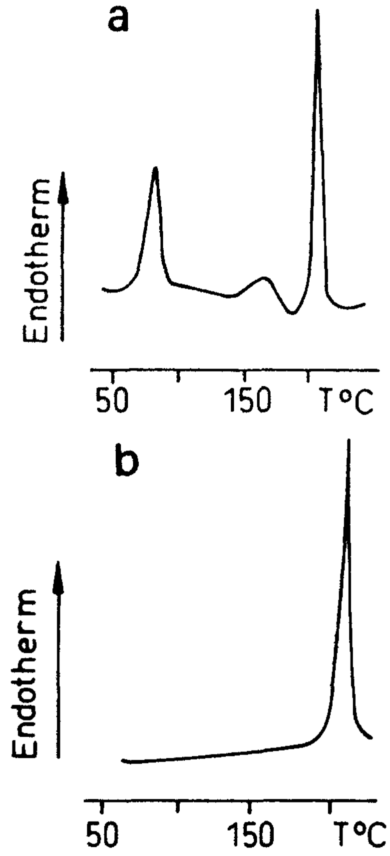


Figure 1 D.s.c. traces of I-6-Me-triflate: (a) first heating of solution crystallized material; (b) melt crystallized material

Table 2 D.s.c. characterization of I-6-Me-X, with X = BF_4 and triflate

Counterion	Scan	T_1[a] (°C)	ΔH_1[a] (kJ mol^{-1})	T_2[b] (°C)	ΔH_2[b] (kJ mol^{-1})
Triflate	1	80	2.9	207	6.1
	2	–	–	206	5.7
BF_4	1	190	5.7	276	6.5
	2	–	–	269	4.9

[a] Temperature/enthalpy of solid–solid transition in the first d.s.c. scan
[b] Melting transition temperature/enthalpy

The influence of the size of the divalent counterion MY_4^{2-}, with M = Zn, Cd, Hg and Y = Cl, Br, I, on the melting behaviour of ionenes was also studied. The melting point decreases with increasing atomic radius of the metal in the following order: $ZnI_4^{2-} > CdI_4^{2-} > HgI_4^{2-}$. I-6-Me-$ZnI_4$ melts under decomposition, while the ionenes with CdI_4^{2-} and HgI_4^{2-} as counterions melt and recrystallize from the melt.

CRYSTAL STRUCTURE OF THE IONENES

Ionenes of the general structure (1) crystallize readily under normal circumstances, their crystallization kinetics being controlled by the counterion and the length and flexibility of the spacer between the ionic groups in the polymer chain.

Compared with other polymers, the ionenes with $-(CH_2)_6-$ and $-(CH_2)_{10}-$ spacers exhibit extraordinary crystallization behaviour. Macroscopic single crystals can be obtained by crystallization through evaporation of the solvent at room temperature. The crystals of the polymers are isomorphous with the crystals obtained from the equivalent trimers (2). The same unit cell is observed if the end groups of the trimers are changed from methyl to n-butyl. To illustrate this behaviour, the X-ray diffractograms of the trimers T-10-Me-PF_6 with methyl and butyl end groups and of the corresponding polymer are compared in *Figure 4*. The intensities of the different Bragg peaks, however, vary with the nature of the materials. Most of the trimers did not exhibit an X-ray small angle reflection that could be correlated with the total length of the molecule. This means that the trimers do not form the layered structures typical of oligomers used as models for the corresponding polymers (n-alkanes are the best known examples of models for polyethylene). Consequently, the end groups must be randomly placed in the lattice.

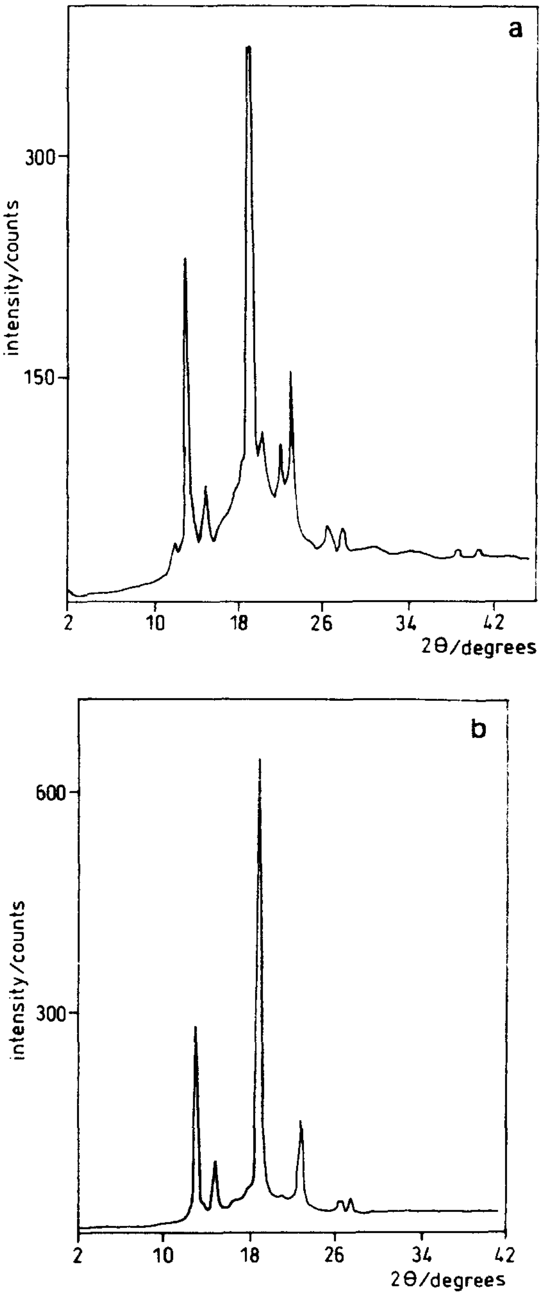


Figure 2 X-ray powder diffractograms of I-6-Me-triflate at (a) room temperature and (b) 100°C

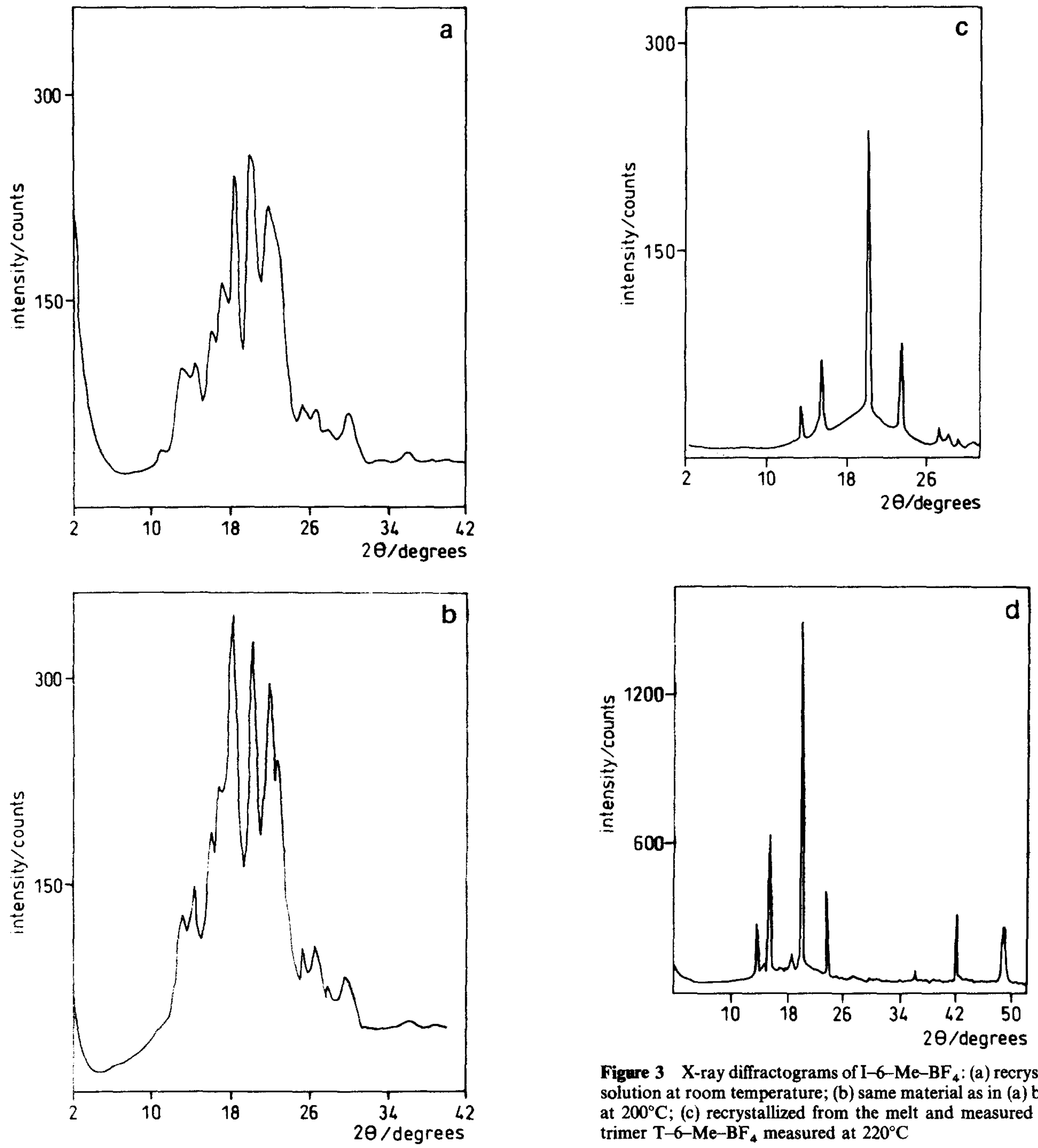


Figure 3 X-ray diffractograms of I–6–Me–BF_4: (a) recrystallized from solution at room temperature; (b) same material as in (a) but measured at 200°C; (c) recrystallized from the melt and measured at 22°C; (d) trimer T–6–Me–BF_4 measured at 220°C

The analyses of the diffractograms and of the single crystal X-ray patterns showed that all ionenes and trimers could be indexed in terms of unit cells of high symmetry. Depending on the type of counterion and spacer, three different families of structure were observed.

(1) materials (1) with a $-(CH_2)_6-$ spacer in combination with a monovalent spherical anion X give rise to a hexagonal unit cell;

(2) materials (1) with a $-(CH_2)_6-$ spacer in combination with a divalent counterion X give rise to a body centred tetragonal (pseudocubic) unit cell;

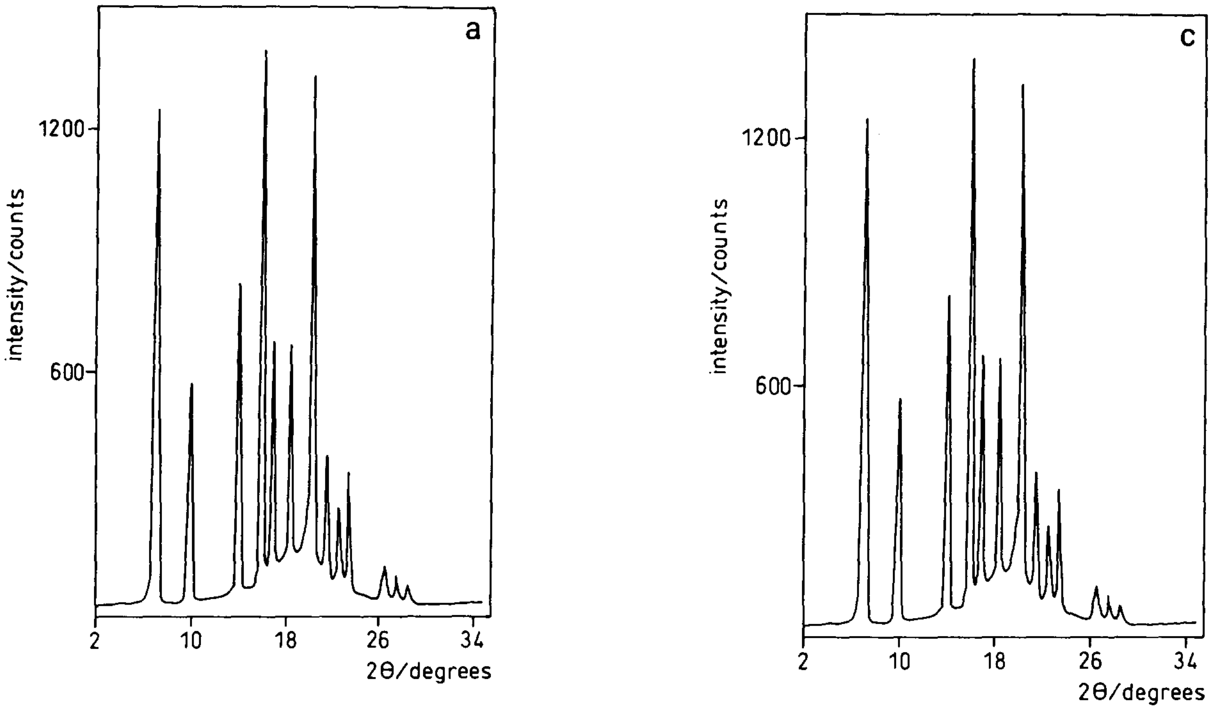
(3) materials (1) with a $-(CH_2)_{10}-$ spacer give rise to a hexagonal unit cell if combined with a spherical monovalent anion X.

The crystallographic data for these unit cells are given in *Tables 4* and *5*. The ionenes I–6–Me–X with $X = PF_6$, SbF_6 and $FeCl_4$ showed very sharp reflections with an

Table 3 Thermal properties of trimers (2) for different lengths of alkylene spacer and the types of counterions

Trimer	Melting temp. (°C)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
T–6–Me–TOS[a,b]	244	27.4	52.9
T–6–Me–BF_4[a]	257	5.4	10.2
T–6–Me–$FeCl_4$[a,c]	256	13.3	25.1
T–10–Me–TOS	95	15.8	42.9
T–10–Me–PF_6[a,c]	191	5.0	10.8
T–10–Me–PF_6[c,d]	236	13.6	26.7
T–10–Me–SbF_6[a,c]	232	16.5	32.7
T–10–Me–$FeCl_4$[a,c]	136	7.6	18.6

[a] Trimers with methyl end groups
[b] TOS, tosylate
[c] Single crystals were obtained
[d] Trimer with n-butyl end groups



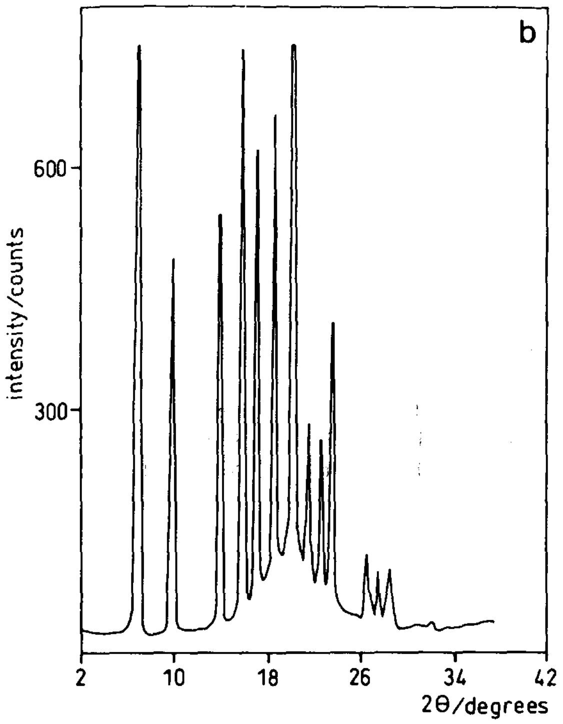


Figure 4 X-ray powder diffractograms of I–10–Me–PF_6 and model compounds (2) (trimers): (a) trimer I–10–Me–PF_6 with methyl end groups; (b) trimer T–10–Me–PF_6 with n-butyl end groups; (c) polymer I–10–Me–PF_6–trimer. All compounds were crystallized from solution[2]

almost complete lack of amorphous halo. These polymers and their trimers crystallize readily as needle-like or polyhedric single crystals. On the other hand, ionenes with tosylate as counterion exhibit a broad background in addition to a number of Bragg reflections and crystallize only in the form of spherulites. Increasing the length of the spacer between the ionic centres (ammonium groups) of the ionenes from hexamethylene to decamethylene reduces the tendency of the materials to form large single crystals readily from solution. In addition, a broad background is seen in the diffractograms, giving evidence of increasing disorder in the solid materials. We hesitate to call this background an 'amorphous halo', a term commonly used in the polymer literature to denote the fact that only a fraction of the material undergoes

Table 4 Parameters of the tetragonal unit cell of solution crystallized I–6–Me–X, with X a divalent counterion of type MeY_4

Polymer or trimer	Unit cell parameters		ρ_{calc}
	a (Å)	c (Å)	(g cm^{-3})
I–6–Me–$ZnCl_4$	9.36	13.07	1.343
I–6–Me–$ZnBr_4$	9.52[a]	13.46[a]	1.745[a]
T–6–Me–$ZnBr_4$	9.38[a]	13.27[a]	
I–6–Et–$ZnBr_4$	9.81	13.88	1.733
I–6–Me–ZnI_4	9.64	13.89	2.133
I–6–Me–CdI_4	9.78	13.75	2.121
I–6–Me–HgI_4	9.82	13.54	2.178

[a] Calculated from the single crystal X-ray diffraction data

Table 5 Parameters of the hexagonal unit cell of solution crystallized ionenes (1) or corresponding trimers (2), with X a monovalent counterion

Polymer or trimer	Unit cell parameters		ρ_{calc}
	a (Å)	c (Å)	(g cm^{-3})
I–6–Me–PF_6	7.75[a]	11.96[a]	1.457[a]
T–6–Me–PF_6	7.71	11.94	
I–6–Me–BF_4[b]	7.54	11.95	1.216
T–6–Me–BF_4[b]	7.47	11.95	
I–6–Me–CF_3SO_3[b]	7.90	13.06	1.303
I–6–Me–SbF_6	7.90	12.58	1.814
T–6–Me–SbF_6	7.82	12.57	
I–6–Me–$FeCl_4$	8.04	13.10	1.497
T–10–Me–$FeCl_4$	8.00	13.04	
I–10–Me–SbF_6	9.71	11.04	1.543
T–10–Me–SbF_6	9.74	10.86	
	9.86	10.85	
I–10–Me–$FeCl_4$	10.00	11.42	1.310
T–10–Me–$FeCl_4$	9.94	11.31	

[a] Calculated from the single crystal X-ray diffraction data
[b] Crystallized from the melt

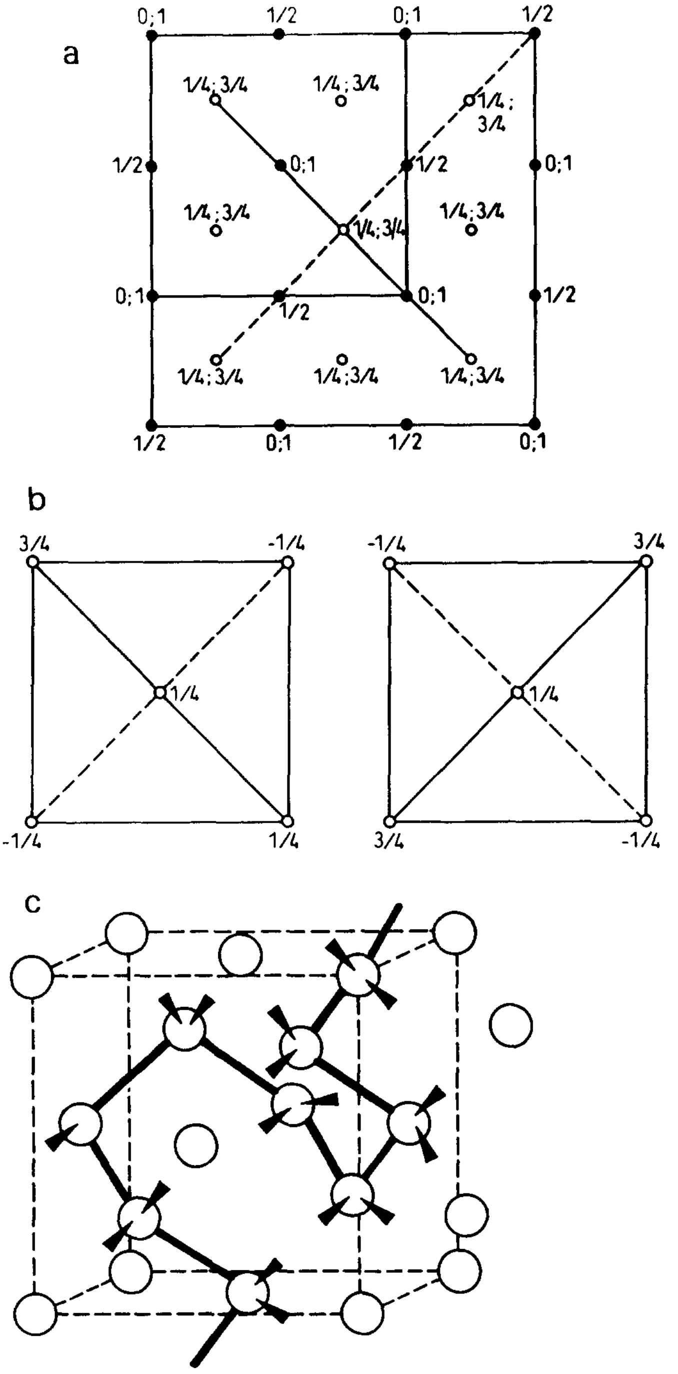


Figure 5 Unit cell of I–6–Me–X, with X a bivalent counterion of type MY_4. (a), (b) Projection of the structural model. ●, Counterion X; ○, N atoms. The numbers give the *z*-parameter. The N atom at ($\frac{3}{4}$, $\frac{3}{4}$, $\frac{1}{4}$) has eight neighbours at ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{3}{4}$) forming a cube. Two tetrahedra can be placed in this cube (*Figure 5b*). (c) Scheme of the 'random walk' of a polymer chain meeting cation lattice sites

crystallization, the remainder staying in an amorphous melt-like state. The origin of the broad background scattering may rather be linked to a special kind of disorder observed in these unusual materials, as will become obvious in the following section.

Structural model

A structural model should explain the following unusual features: crystallization of macroscopic polymer single crystals; the identical crystal structures of polymers and trimers; and crystallization in space groups of unusually high symmetry (hexagonal, cubic). The key to understanding the crystallization behaviour of the substances investigated is the fact that, unlike 'normal' polymers where van der Waals forces or hydrogen bonds govern the crystallization behaviour, here the ionic forces between cations on the chain and counterions dominate the crystal structure. This balance of ionic forces leads to crystal structures with the unusual feature that the polymer chains are not aligned in one distinct crystallographic direction. If the length of the spacer is increased to $m \approx 20$, however, lamellar structures are observed in which the alkyl stems in the spacers are oriented parallel to each other, forming layers separated by sheets containing the ions.

Structural model for I–6–R–X ionenes, with X a divalent counterion. Polyhedric single crystals of I–6–Me–$ZnBr_4$ and its analogous trimer with dimensions up to 1 mm were obtained[2]. I–6–Et–$ZnBr_4$ and I–6–Me–$ZnCl_4$ formed single crystals as well but of smaller dimensions. These ionenes and the corresponding trimers are tetragonal I- or cubic F-centred. A simple inorganic structure with the same stoichiometry which can be used as a model is the CaF_2 structure.

The face centred unit cell contains four anions and eight cations, which are located at (0, 0, 0) and $\pm(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, respectively (*Figure 5a*). Each cation is tetrahedrally coordinated with four anions. The next cations within a spacer length are all at a distance of about 9.5 Å*, the exact distance depending on the size of the anion (*Table 4*), forming a regular cube. This distance is compatible with the spacer length, if one assumes slightly widened bond angles. The polymer chain connects with equal probability the central N atom to its eight next neighbours. Note that the cubic coordination of the cations can be viewed as two tetrahedral coordinations which are mutual mirror images (*Figure 5b*). In our model the polymer chain connecting the cation sites and two side groups occupies statistically one of the two tetrahedral orientations; the four directions belonging to the second tetrahedron remain unoccupied. The difference between the cubic CaF_2 cell and the body-centred tetragonal cell lies in the site symmetry of the cation, which is $\bar{4}$ in the latter case, i.e. here only one of the two tetrahedra of the cation–cation coordination is occupied. Since the unit cell parameters are metrically cubic with errors $\ll 1\%$, the cubic CaF_2 model is favoured. Owing to the degree of orientation disorder (i.e. only four of eight possible sites are filled with spacers and side groups), analysis of the details of the crystal structure is complicated and not yet completed. We feel, however, that there is sufficient evidence available to merit this preliminary discussion in the light of the very unusual crystallization behaviour of these polymers. *Figure 5c* shows schematically how a polymer chain can be placed into the regular CaF_2 lattice so that it performs a random walk, meeting well defined lattice sites.

The ionenes with ZnI_4^{2-}, CdI_4^{2-} and Hg_4^{2-} do not form single crystals but crystallize isomorphous with I–6–Me–$ZnBr_4$ (*Figure 6*). The X-ray powder diffractograms reveal that the dimensions of the *a* and *c* parameters of the tetragonal unit cells increase with increasing atomic radius of the halogenides in the sequence: $ZnCl_4^{2-} < ZnBr_4^{2-} < ZnI_4^{2-}$. As indicated in *Table 4*, on increasing

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* 1 Å = 10^{-1} nm

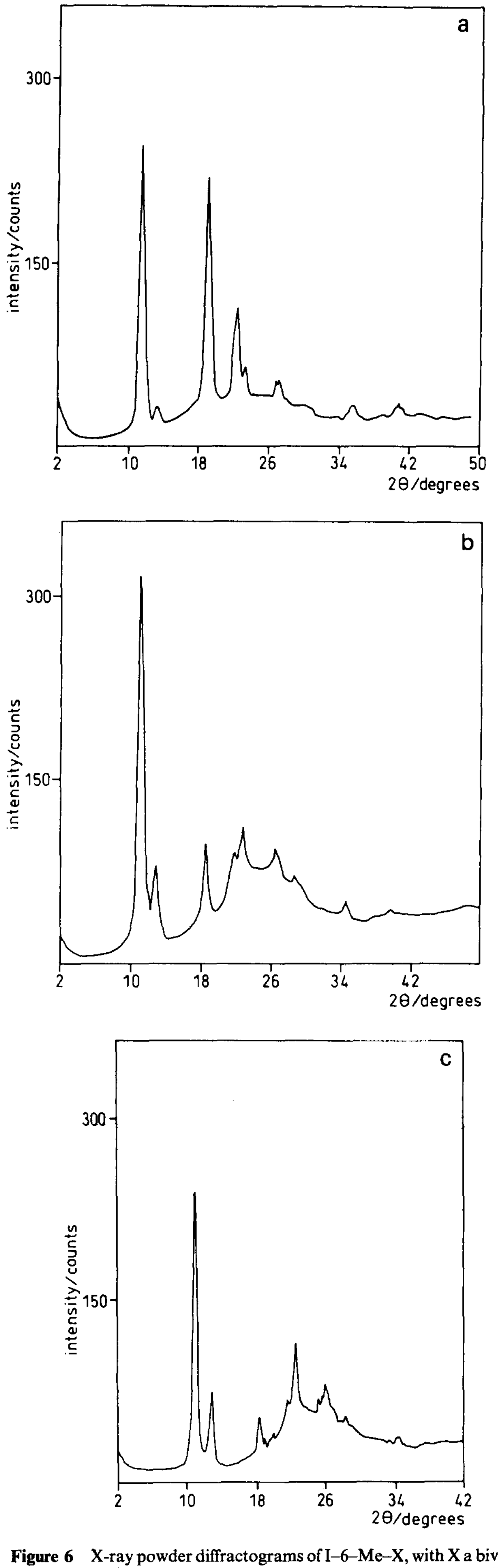

Figure 6 X-ray powder diffractograms of I–6–Me–X, with X a bivalent counterion of type MY_4: (a) I–6–Me–$ZnCl_4$; (b) I–6–Me–ZnBr; (c) I–6–Me–ZnI_4

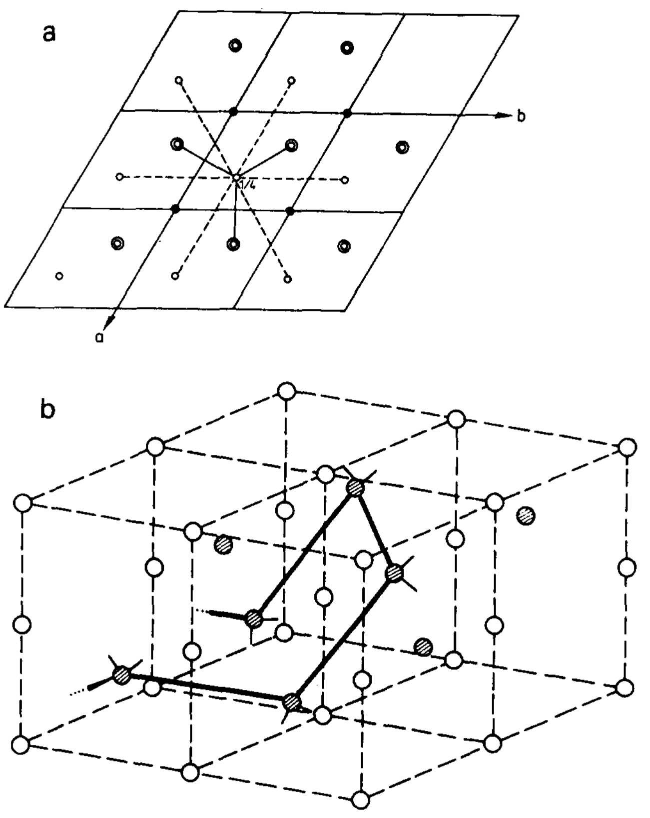

Figure 7 Unit cell of I–6–Me–X, with X a monovalent spherical anion. (a) Projection of the structural model. ●, Counterion X; ○, N atom at $z \approx \frac{1}{4}$; ◎, N atom at $z \approx \frac{3}{4}$. (b) Schematic representation of the placement of a polymer chain in the hexagonal structure

the atomic radius of the metal from Zn to Hg, *a* increases, while simultaneously c decreases.

Structural model for I–6–R–X ionenes, with X a monovalent counterion. As mentioned above, structures of this type are hexagonal. A simple structural model is the anti-NiAs structure (*Figure 7a*). Here the anions are located at (0, 0, 0) and $(0, 0, \frac{1}{2})$, and the N atoms at $(\frac{2}{3}, \frac{1}{3}, n)$ and $(\frac{1}{3}, \frac{2}{3}, n)$ with $n \approx \frac{1}{4}$. A projection of the model with the location of ionic sites is shown in *Figure 7a*. A N atom (e.g. at $(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$ has 12 nearest neighbours, six of which are at the same position in the adjacent unit cells (broken lines) at a distance of $a = 7.75$ Å. The others at $z = \frac{3}{4}$ or $z = -\frac{1}{4}$ (solid lines) are separated by approximately 7.5 Å depending on the lattice parameters (see *Table 5*). Since these distances are smaller than the length of the extended methylene spacer connecting two positively charged sites, there is no limiting restriction on the conformation of the spacers and a chain can be randomly placed into the regular ionic lattice by connecting neighbouring cation sites as shown schematically in *Figure 7b*. As in the salts of the cubic structure with divalent anions, these structures exhibit an orientational disorder, since only a small fraction of the possible sites for the polymer chain and the side groups are occupied.

The ionenes with tetrafluoroborate and triflate as counterion do not form single crystals under solution crystallization conditions, but are isomorphous with I–6–Me–PF_6 when recrystallized from the melt. Thus the dimensions of the unit cell for the ionenes I–6–Me–X with X = BF_4 and triflate were calculated from their X-ray powder diffractograms (see *Table 5*). While in I–6–Me–

BF_4 the *c*-axis remains unchanged and the *a*-axis is smaller than for I–6–Me–PF_6, both axes were larger for I–6–Me–triflate.

CONCLUSIONS

Investigation of the thermal behaviour and crystal structure analysis of ionenes has substantiated a very unusual crystal structure. In contrast to the highly regular lattice formed by the ionic sites, the structural arrangement of the polymer chains exhibits an orientational disorder, which at present can be best described as a 'random walk'. As a consequence, a lower degree of perfection of the whole lattice can be expected, which may result in a considerably lower crystalline density and unusual mechanical properties.

Further experiments to clarify the details of chain disorder and its consequences with respect to solid state properties in ionenes are necessary.

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