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Structural Aspects of Solid-phase Polymerisation

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The two main mechanisms of this new method—polymerisation in non-crystalline, armorphous zones and topochemical polymerisation—are closely connected with the morphology of the products. Especially detailed attention is paid to examples of topochemical polymerisation, by means of which it is possible in several cases to obtain single crystals of polymers. A list of 94 references is included.

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I. INTRODUCTION

Whereas the polymerisation of monomers in the liquid phase has been well studied, solid-phase polymerisation has attracted the attention of research workers comparatively recently. Such reactions should differ significantly from the corresponding reactions in the liquid, since their course is largely determined by the environment and by the orientation of the monomer molecules in the crystal. Some of the most complete surveys of various aspects of the extremely complicated process of solid-phase polymerisation are listed here[1-6]. The present Reviewers have not attempted complete coverage of all the published information on solid-phase polymerisation, but have confined their attention to structural and crystal-chemical aspects of the possibilities and extent of polymerisation in solid organic (and organometallic) compounds. For example, the Review does not consider channel polymerisation, a review of which[2] does not, unfortunately, pay due regard to the work of Soviet researchers.

The two main types of mechanism—topochemical polymerisation and polymerisation in non-crystalline zones—were first distinguished in a review[1]. Topochemical polymerisation consists in a direct transition from monomer molecules to polymer chains without disruption of the crystal lattice of the monomer and without formation of non-crystalline intermediates[1,7,8]. The opposite type of solid-phase polymerisation takes place in non-crystalline zones, formed at the monomer–polymer interface and resembling a melt or a gas phase in character. This yields an amorphous polymer, which may then crystallise. The concept of a topotactic process—i.e. one in which a solid phase is formed with its crystallographic directions related to those of the crystal of the initial substance—is used to describe reactions in the solid state irrespective of the mechanism of polymerisation: in other words, topotactic reactions involve an unambiguous correspondence between the lattices of the initial (monomer) phase and the resulting (polymer) phase.

A necessary condition for the occurrence of topochemical solid-phase reactions consists in maximum displacements of the equilibrium positions of atoms in the interacting molecules with sufficiently intense thermal motion (vibration). This is the fundamental principle of lattice-controlled reactions formulated by Schmidt[9,10], and by Kargin and Kabanov[1] in its application to solid-phase polymerisation. The molecules in a crystal of a monomer are separated by van der Waals distances, and are usually too far apart for direct formation of chemical bonds between them. Therefore the reactivity of a solid is determined in principle by the mobility of individual units of the crystal lattice, i.e. molecules. In order that polymerisation should take place by a topochemical mechanism the distances between active (reactive) atoms in neighbouring molecules firstly should not exceed a certain value, respectively[11] 4.0 Å for C...C and C...N, 3.95 Å for P...N, and 3.7 Å for C...O interactions. Monomers in whose crystals active carbon atoms of neighbouring molecules are 4.3–4.7 Å apart are unable to polymerise in the solid phase. From these results the maximum distance R between atoms A and B in neighbouring molecules at which polymerisation in the crystal is still possible can be estimated as $R = R_A + R_B + 0.5$ Å, where R_A and R_B are the van der Waals radii of atoms A and B. Secondly, solid-phase polymerisation is more probable, under otherwise similar conditions, with shorter than with longer distances between the reactant atoms in the crystal[12]. We must mention that this work[11,12] was concerned with the dimerisation of molecules, which in some cases can be regarded as a first step in polymerisation.

In the solid phase the actual polymerisation may be followed by relaxation processes, which change the morphology of the polymer formed initially[6,8]. This complicates the correlation between the mechanism of polymerisation and the morphology of the polymer obtained.

In order to make the account of solid-phase polymerisation more systematic, we shall discuss separately the solid-phase polymerisation of cyclic monomers and of unsaturated monomers containing multiple bonds. Both topochemical and non-topochemical polymerisation can take place in either group of monomers. The same division has been used previously[4].

II. POLYMERISATION OF CYCLIC MONOMERS

A mechanism based on the arrangement of the molecules in a crystal of the monomer was suggested[8] for the solid-phase polymerisation of such cyclic monomers as e.g. trioxan and hexamethylcyclotrisiloxane. These molecules form stacks (Fig. 1) with the number of contacts between atoms of adjacent molecules in a stack larger, and the corresponding intermolecular distances shorter, than those between molecules in different stacks. Therefore polymerisation takes place in a stack with ring cleavage to form extended polymeric helices.

Another limiting case is the polymerisation of monomers in layers of molecules. This should yield planar zigzag molecules.

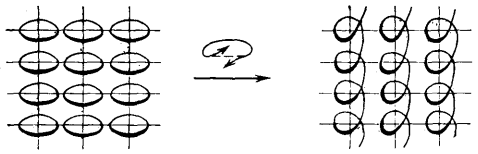


Figure 1. Polymerisation of cyclic molecules, present as stacks in the monomer crystal, to form helical polymer chains.

Table 1. Crystallographic data and physical constants of cyclic oligomers of formaldehyde and two modifications of polyoxymethylene.

Oligomer or polymer	$(-CH_2-O-)_3$ (TOX)	$(-CH_2-O-)_4$ (TEX)	$(-CH_2-O-)_5$ (POX)	$(-CH_2-O-)_6$ (HOX)	$(-CH_2-O-)_n$ (POM)	
System	trig.	mon.	orh.	trig.	trig.	orh.*
Space group	$R3c$	$C2/c$	$Pbcn$	$R\bar{3}$	$P3_1$	$P2_12_12_1$
Cell const.						
a, Å	9.320	11.455	8.135	7.917	4.47	4.77
b, Å	9.320	4.160	10.642	7.917	4.47	7.65
c, Å	8.196	12.232	7.645	11.345	17.39**	3.56**
γ or β, °	120	108.4		120	120	
Mol. in cell	6	4	4	3		
Mol. symmetry	$C_{3v}-3m$	C_2-2	C_2-2	C_3-3	one helix 9/5***	two helices 2/1***
Density, g cm^{-3}						
meas.	1.39	1.435	1.480	1.440	1.40—1.45	1.52
X-ray	1.406	1.442	1.507	1.457	1.49	1.54
M.p., °C	64	114	61	72.5	178—187	(75—80)****

*Detected only in the polymerisation of hexoxodan.
**Axis of polymer chain.
***In the notation n/m for a helix n is the number of monomer units and m the number of turns of the helix, both in the repeat distance.
****Orthorhombic–trigonal transition point.

1. Oligomers of Formaldehyde

The action of γ-rays on single crystals of cyclic oligomers of formaldehyde—1,3,5-trioxan (TOX), 1,3,5,7-tetroxocan (TEX), 1,3,5,7,9-pentoxecan (POX), and 1,3,5,7,9,11-hexoxodan (HOX)—leads to polymerisation with cleavage of the ring and formation of a crystalline polyoxymethylene (POM)† (Table 1).[13-15] In all cases the polyoxymethylene chain grows in certain crystallographic directions of the monomer crystal: i.e. a quite definite mutual orientation is exhibited by the crystallographic directions of monomer and polymer crystals. Thus the polymerisation of these monomers is a topotactic process.

† Only the trigonal modification of polyoxymethylene is formed in all cases other than in the polymerisation of the hexoxodan (see later).

The possibility of obtaining macrocrystals of polyoxymethylene by the polymerisation of crystals of the trioxan has been known for a long time[16-18]. Morphological investigations have shown that, except with gaseous surface initiation, the polyoxymethylene consists of crystalline fibres well oriented both mutually and with respect

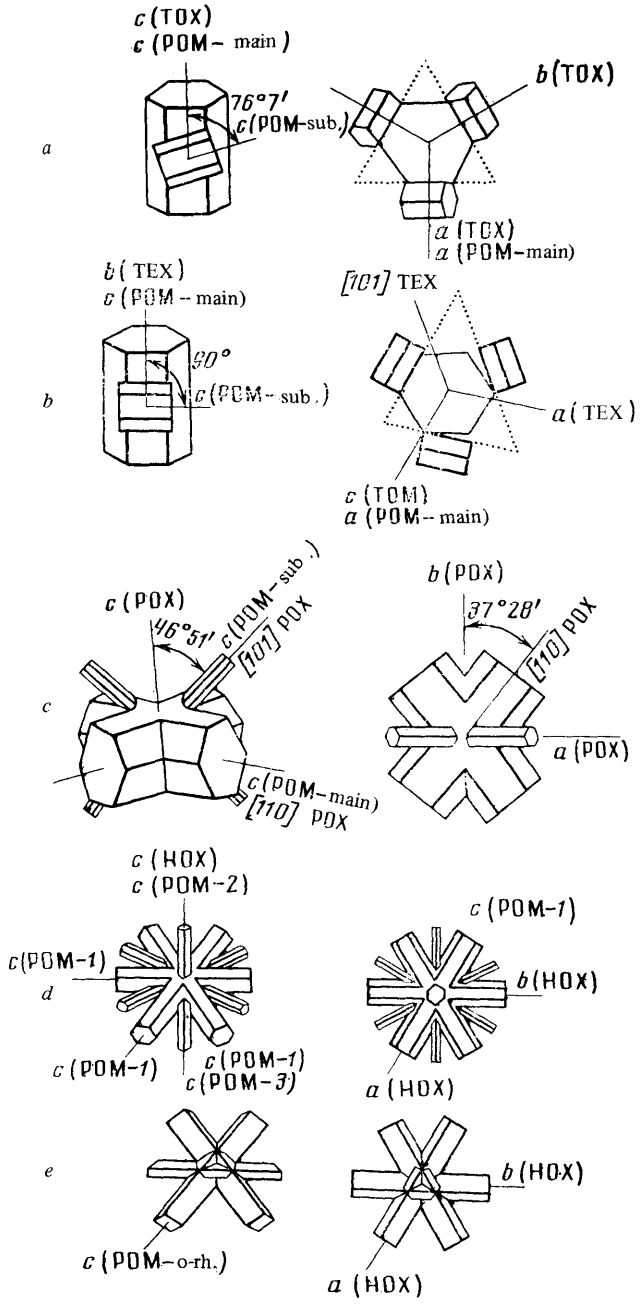


Figure 2. Diagram showing orientations of crystals of trigonal polyoxymethylene relative to crystals of: *a*) trioxan; *b*) tetroxocan; *c*) pentoxecan; *d*) hexoxodan; *e*) orthorhombic polyoxymethylene relative to a hexoxodan crystal. The dotted lines (*a* and *b*) show the relative orientations of the subcrystals.

to the crystallographic directions of the single crystal of the monomer [6,18]. Polyoxymethylene crystals obtained by solid-phase polymerisation possess unusual physical properties in comparison with crystals obtained from solutions or melts [6,19]. It was suggested [20,21] that those obtained by the solid-phase polymerisation of trioxan consist of elongated chains. A serious difficulty in studying the relation between the orientation of the growing fibres and the mechanism of the formation of polymer chains in a crystal matrix has been twinning of the polyoxymethylene: i.e. formation of a crystal having the predominant orientation (henceforward termed the "main crystal") is accompanied by that of crystals growing in other preferred directions [13,22]. The volume of such "subcrystals" becomes negligible when the temperature of polymerisation is raised. The subcrystals disappear also when the polymer is heat-treated at 170°C. [23]

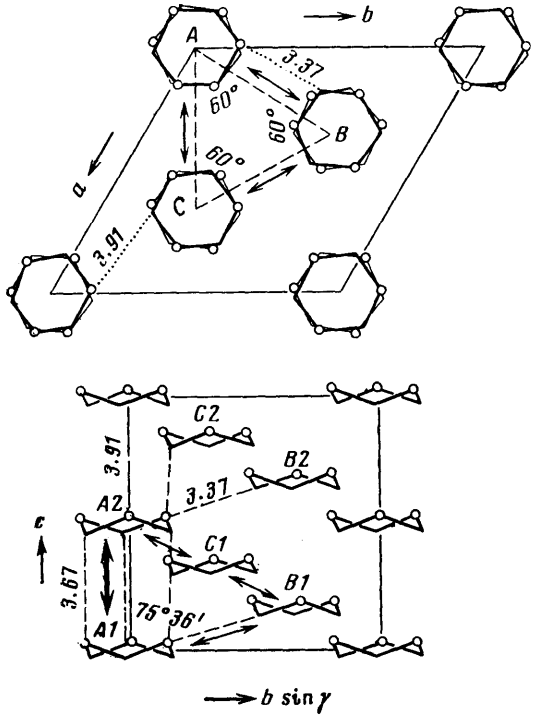


Figure 3. Packing of molecules in a crystal of trioxan. The thick and thin double arrows show the directions of the polymer chains in the main polyoxymethylene crystal and its subcrystals respectively. As also in Figs. 4, 6, and 7, the open circles indicate oxygen atoms.

The *c* axis of the main crystal of polyoxymethylene (the axis of the polymer chain) coincides with that of the initial trioxan crystal, but the (100) plane of the polymer is perpendicular to the *a* axis of the monomer (Fig. 2*a*). The *c* axes of the subcrystals are inclined to that of the main crystal at an angle of 76°7′, and their (100) planes are parallel to the (100) plane of the latter; the relative arrangement of the subcrystals corresponds to threefold axial symmetry. The tetroxocan can be polymerised [13] by precisely the same methods as with trioxan, but the morphology of the resulting polyoxymethylene is somewhat different: the *c* axis of the polymer (the axis of the chain) is parallel to the *b* axis of the monomer; and the *a* axis of the polyoxymethylene is parallel to the *c* axis of the tetroxocan (Fig. 2*b*). As in the polymerisation of trioxan, the X-ray diffraction patterns of the polyoxymethylene obtained from tetroxocan have additional, weaker reflections, indicating the formation of twin subcrystals in addition to the main crystal, but their orientation relative to the latter is different: the *c* axes of the subcrystals are perpendicular to that of the main crystal, and their (100) planes are parallel to the *c* axis of the main crystal. The directions of the *c* axes of the subcrystals are exactly parallel to the [100] (*a* axis), [001] (*c* axis), and [101] directions of the tetroxocan crystal. The twinned structure of the crystalline polyoxymethylene fibres is lost if polymerisation is conducted at temperatures above 80°C (and also when the polymer is annealed). In spite of this, however, density fluctuations are preserved in directions perpendicular to the axes of the polyoxymethylene macromolecules.

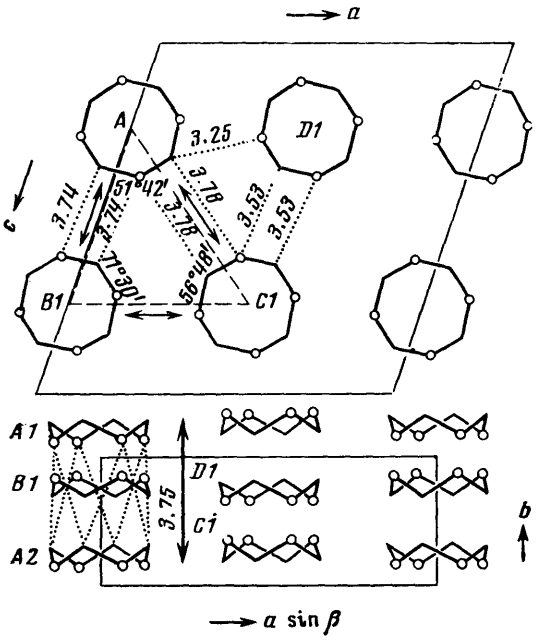


Figure 4. Packing of molecules in a crystal of tetroxocan. The thick arrow (below) and the thin double arrows (above) show the directions of the polymer chains of the main crystal and the subcrystals respectively.

Trioxan and tetroxocan molecules are stacked in the direction of growth of the polymer chain of the main crystals in such a way that the carbon atoms of one molecule are relatively close to the oxygen atoms of the neighbouring molecule (Figs. 3 and 4). The trioxan crystal includes three equivalent C...O distances of 3.67 Å in this direction (the *c* axis), and the tetroxocan crystal eight C...O distances of 3.75 Å (in the direction of the *b* axis).

Table 2. Parameters of the molecular packing of trioxan, tetroxocan, and pentoxecan in certain crystallographic directions (see Figs. 3, 4, and 6).

Oligomer	Trioxan			Tetroxocan				Pentoxecan			Polyoxymethylene			POM
Direction*	A1...A2**	A1...B1***	A1...C1	A1...A2**	A1...B1***	A1...C1	A1...D1	[100]	[010]	[001]	A...D** [110]	C...D*** [101]	A...C, B...D [011]	
Distance between mol. centres of gravity, A****	4.18	5.60	6.10	4.18	6.44	6.92	6.09	8.19	10.69	7.68	6.74	5.62	5.74;7.48; mean 6.61	—
Distance per monomer unit, A*****	1.39	1.87	2.03	1.05	1.52	1.73	1.43	1.64	2.14	1.54	1.35	1.12	1.32	1.93
Shortest C...O distance, A	3.67	3.37	3.91	3.75	3.74	3.78	3.25	4.76	6.43	6.79	3.39;3.40&3.79	3.45;3.67&3.84	3.59 & 3.76	
Mol. cross-section, A^2 ******	25.5	19.0	17.5	33.1	22.7	20.0	24.2	20.5	15.7	21.9	25.0	30.0	25.6	17.3
Angle with c (TOX) or b (TEX) axis	0°	75°36′	62°50′	0°	75°54′	88°	66°	—	—	—	—	—	—	—

*Two notations—directions between centres of gravity of molecules and crystallographic—are used. Where they coincide, both are given.

**Direction of polymer chain of main crystal.

***Direction of polymer chain of subcrystal.

****These lengths may differ somewhat from the repeat distances in the corresponding crystallographic directions. For example, the distance between the centres of gravity of the tetroxocan molecules $A1$ and $A2$ is 4.18 Å, but the repeat distance in the [010] direction (along the b axis) is 4.16 Å.

*****Distance per monomer unit if polymerisation occurs in the given direction.

******Area per molecule perpendicular to the given direction.

Table 2 shows that the distances between the centres of gravity of the molecules are shorter in these directions ($A1...A2$ and $A...B$ respectively, both of 4.18 Å) than in others. This should result in maximum probability of interaction between molecules in these directions of the monomer crystals.

Trioxan crystals belong to the polar class C_{3v}, so that the vectors of the dipole moments have the same orientation relative to the c axis. Such a structure, involving strong dipole interaction, tends to favour polymerisation [24]. Tetroxocan crystals belong to the non-polar class C_2, but molecules arranged along the b axis, the preferential direction of polymer growth, form the same stacks as in trioxan. It is interesting that X-ray examination indicates that thermal motion in the tetroxocan crystal is most intense precisely in the direction of the b axis [14]. The shortest C...O distance (3.37 Å) in trioxan is found between molecules $A1$ and $B1$ (Fig. 3). Subcrystals are formed in this direction and also in the equivalent $B1...C1$ and $C1...A2$ directions. Analysis of the reflection intensities on the X-ray patterns showed that the proportion of each of the subcrystals was ~15%, giving a total of ~45% for all subcrystals [14]. In the tetroxocan crystal the closest intermolecular contacts occur in the directions of the a and c axes, but such contacts are few. Thus the growth of polymer chains in this direction is explained by the larger number of C...O collisions during thermal motion and by the dipole interaction in the same direction.

The distance between monomer units along the axis of the polyoxymethylene helix is 1.93 Å, whereas in a "monomeric" crystal of tetroxocan, for example, four monomer units fit into the repeat distance of 4.18 Å along the b axis, so that one monomer unit occupies only 1.05 Å. This discrepancy is smaller in the trioxan crystal, 1.39 Å per monomer unit in the direction of the c axis. However, the form of the "monomeric" crystals of trioxan and tetroxocan remains unchanged on polymerisation. Resolution of this contradiction depends on elucidating the role of the subcrystals in polymerisation. The distance of 1.87 Å per monomer unit of trioxan in the $A1...B1$ direction‡ (the direction in which subcrystals are formed) is closely similar to the 1.93 Å between monomer units along the axis of the polyoxymethylene helix; furthermore, the cross-section of a molecule perpendicular to the $A1...B1$ direction is similar to that of the helix perpendicular to its axis (19.0 and 17.3 $Å^2$). Therefore the development of polymerisation in $A1...B1$ direction causes only slight stress in the trioxan crystal and seems adequate for relieving the stresses produced by growth of the main crystal [21]. At high temperatures the latter stresses can be removed by the strong thermal motion [25], with decrease in the number of subscrystals.

A relation has been discovered between the direction of dislocations in trioxan crystals and the direction of growth of polyoxymethylene [26]. If dislocations in trioxan favour polymerisation, as in many other crystalline monomers [27], a mechanism is possible in which a short polyoxymethylene chain formed initially is oriented along a dislocation, whose space it uses for its growth [6]. The formation of dislocations may well depend on a volume deficiency arising on polymerisation in the direction of the c axis in the trioxan crystal [28]. The growth of polymerisation may lead to further development of dislocations, so that these two structure-dependent processes develop in parallel.

Two alternative molecular models of the structure of crystalline polyoxymethylene fibres have been suggested [6] in connection with the molecular mechanism of the solid-phase polymerisation of trioxan and the dampening effect of subcrystals. In the first model the difference in orientation between individual segments of the polymer chain (Fig. 5a) leads to the appearance of differently oriented

‡ Polymerisation does not occur in the $A1-C1$ direction, which would appear suitable with terms of the distance per monomer unit and the cross-section of the molecules, because of the large C...O distances (Table 2).

crystallites, which form the main crystal and the subcrystals[29,30]. On the other hand, microfilaments may consist entirely of segments having elongated chains and segments having "folded" chains (Fig. 5*b*).[31] The former model (Fig. 5*a*) is to be preferred, and provides a better explanation of the behaviour of polyoxymethylene when annealed.

As along the *c* axis in trioxan, the packing of tetroxocan molecules along the *b* axis is too dense for a uniform polyoxymethylene helix to be formed in this direction without additional displacement of molecules. Furthermore, the cross-section of the tetroxocan molecule is considerably larger than that of the polymer helix (Table 2). About 50% of the molecules in the series of polymerising along the *b* axis are forced to move from their lattice positions during polymerisation[26,32].

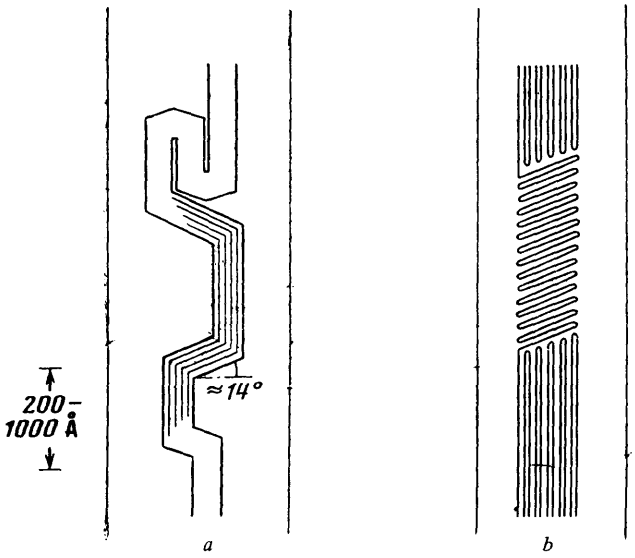


Figure 5. Alternative models (*a* and *b*) of the structure of crystalline polyoxymethylene fibres obtained by the solid-phase polymerisation of trioxan.

In the polymerisation of pentoxecan[14,33] the axis of the polymer chain (the *c* axis) lies in the [110] direction of the monomer, while the *a* axis of the polyoxymethylene is perpendicular to the *c* axis of the monomer (Fig. 2*c*). Since pentoxecan crystals belong to the orthorhombic system (Table 1), and the [110] and [$\bar{1}$10] directions are equivalent, polymer chains grow in both directions, and a twinned crystal is formed. High exposures lead to the appearance of new, considerably weaker and diffuse polyoxymethylene reflections on the X-ray diffraction patterns, which indicates other directions of growth of the polymer crystals (main crystal and subcrystals). The *c* axes of the subcrystals lie in the equivalent directions [101] and [$\bar{1}$01], while the *a* axes are located in the *ac* plane of pentoxecan, forming angles of 46°51′ with its *a* axis. Columns of molecules can formally be distinguished along the *c* axis in the pentoxecan crystal (Fig. 6), but the shortest C...O distance between these molecules (6.79 Å) is too large for chemical bonding. The C...O distances in the directions of the *a* and *b* axes are also large (4.76 and 6.43 Å respectively—Table 2). Interaction of monomer molecules with the formation of chemical bonds between them can therefore be expected only in the diagonal directions [110], [101], and [011]. In the [011] direction, however, there are two kinds of distances between centres of gravity of molecules: $A...C = 5.74$ Å and $B...D = 7.48$ Å, giving an average of 6.61 Å (Fig. 6). Only between the molecules *B* and *D* are the C...O distances sufficiently short; such close contacts are absent between molecules *A* and *C*, so that polymerisation in the [011] direction is impossible. Growth of main crystal and subcrystals in the [110] and [101] directions respectively is probably explained by the smaller difference between the distances per monomer unit in polyoxymethylene (1.93 Å) and in these directions in pentoxecan (1.35 and 1.12 Å—Table 2).

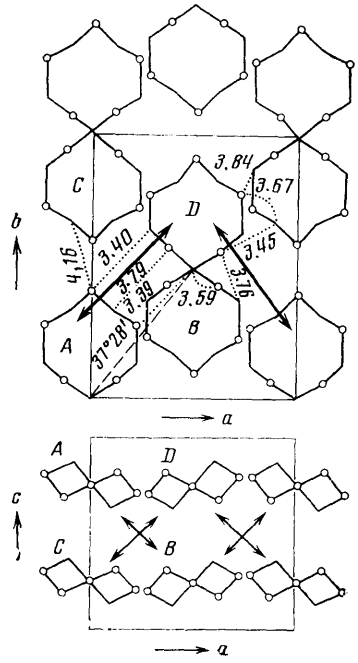


Figure 6. Packing of molecules in a crystal of pentoxecan. Thick and thin double arrows show the directions of the polymer chains in the main crystal and the subcrystals respectively.

X-Ray diffraction has revealed three orientations of the trigonal polyoxymethylene crystals formed by the polymerisation of hexoxodan. These crystals are denoted POM-1, POM-2, and POM-3 in order of their diminishing content in the specimen determined by X-ray diffraction[15]. The POM-1 crystals are elongated (the *c* axis) in the equivalent directions [100], [010], and [1$\bar{1}$0] of the trigonal hexoxodan crystal (Fig. 2*d*). The POM-3 crystals are elongated in the three equivalent directions [210], [$\bar{3}$20], and [1$\bar{3}$0]. The axis of the chain in the POM-2 crystal is parallel to the *c* axis of the monomer, so that POM-2 grows only in one direction. The powdery character of the polyoxymethylene obtained from hexoxodan is a consequence of the variety of its growth orientations. It must be pointed out that Fig. 2 shows only the directions of the crystallographic axes, and bears no relation to the actual

morphology of polyoxymethylene crystals observed e.g. by electron microscopy. In addition, an orthorhombic modification of polyoxymethylene (POM-orh.) is also formed in the polymerisation of hexoxodan. This is the first observed case of an oriented orthorhombic modification of polyoxymethylene. The axis of the chain (the *c* axis) is parallel to that of POM-1 (Fig. 2*e*). The polyoxymethylene chain forms a 9/5 helix in a trigonal crystal and a 2/1 helix in an orthorhombic crystal: i.e. the helices differ little in structure and especially in their radii. The [110] direction of POM-orh. is parallel to the *a* axis of POM-1, with very similar arrangements of the molecules in the two modifications. The reasons why two different modifications of polyoxymethylene grow in the same crystallographic direction in hexoxodan are obscure.

Table 3. Intermolecular distances *d* in the structure of hexoxodan*.

Direction	*d*, Å	Direction	*d*, Å
C(3) I...O(1) II and equiv. pairs		C(4) I...C(1) III	3.77
ные пары	3.51	C(4) I...C(1) II	3.87
C(4) I...O(1) II	3.56	C(4) I...C(2) III	3.93
C(4) I...O(5) II	3.84	C(4) I...C(6) II	4.08
C(4) I...O(1) III	3.94		

*Contacts I...II and I...III correspond to the [211] and [100] directions respectively (see Fig. 7).

The normal amplitudes of the thermal vibrations of atoms in a partly polymerised specimen of hexoxodan at room temperature, when polymerisation is fairly rapid, show that polymerisation is not accompanied by disorientation of monomer molecules that have not reacted. The twelve-membered rings that open and then combine into polymer chains should be in direct contact, at least in the initial stages of polymerisation.

It is significant that in many cases such characteristics of polymerisation as the limiting conversion, activation energy, etc. are not reproducible. Furthermore, reflections due to polyoxymethylene crystals are observed on X-ray diffraction patterns even below 5% conversion. This suggests that polymerisation is not a microscopically homogeneous process, but occurs at a multitude of individual foci, which may be for instance crystal defects.

With respect to intermolecular distances the [211] and [100] directions appear to be the most advantageous for the polymerisation of hexoxodan (Fig. 7 and Table 3). However, the initial molecule contains six oxymethylene groups, although the distance between the centres of molecules in the [211] direction is only 5.93 Å. The molecules are obviously arranged too close together in this direction for unstressed polymerisation. The formation of polymer chains not only in the [100] but also in the [210] and [001] directions, in which close C...O contacts are absent, may well be possible for monomers that polymerise by a non-topochemical mechanism, although no other such examples are known. Fig. 8, illustrating the mutual orientation of monomer and polymer molecules, shows that the arrangement of centres of gravity of each of the polymers—POM-1, POM-2, and POM-3—mimics quite well the initial lattice, which has not always been observed in trioxan and tetroxocan crystals. Perhaps study of the role of dislocations will produce clearer ideas on the mechanism of the polymerisation of hexoxodan.

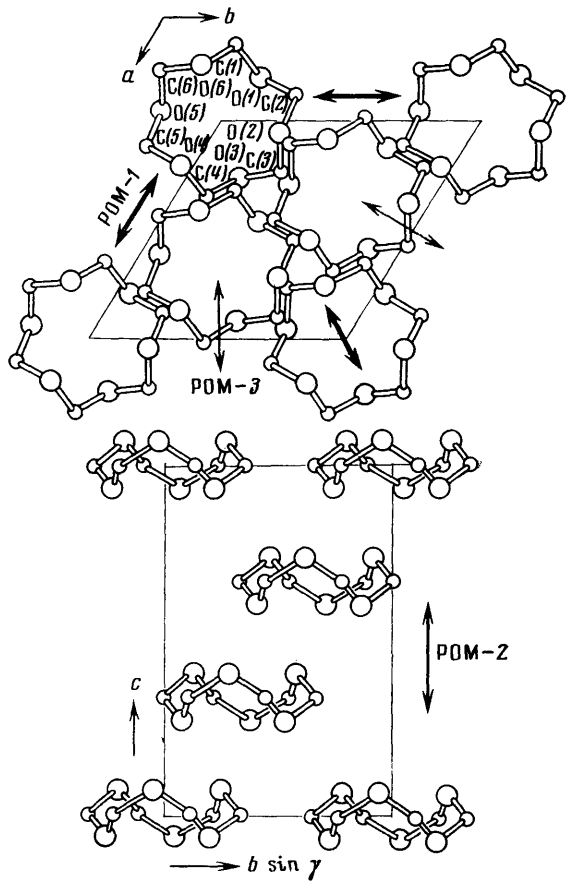


Figure 7. Two projections of the packing of molecules in a crystal of hexoxodan. The arrows show possible directions of the polymer chains.

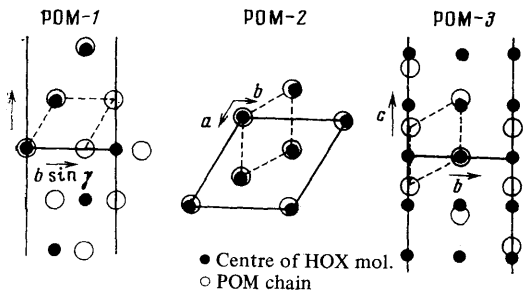


Figure 8. Diagram of distribution of HOX, POM-1, POM-2, and POM-3 molecules in projections along the axes of the polymer chains. Full and broken lines show the unit cells of hexoxodan and polyoxymethylene respectively.

In conclusion we note that the orientation and the structure of polymer crystals is determined by many factors, that transition from the initial monomer crystal to the polymer crystal involves many stages, and that it is quite difficult to establish precisely the role of the structure of the initial crystal in each stage, even if the overall process is topotactic [15].

2. Other Cyclic Monomers

Introduction of an initiator—potassium trimethylsilanoxide—enables hexamethylcyclotrisiloxane, as well as the *cis*- and *trans*-isomers of trimethyltriphenylcyclotrisiloxane, to be polymerised in the solid phase at room temperature or above [34]. Recent X-ray structural studies on hexaphenylcyclotrisiloxane [35], the above *cis*- and *trans*-isomers [36,37], and hexamethylcyclotrisiloxane [38] have led to several interesting conclusions on the possibilities and the mechanism of the solid-phase polymerisation of cyclotrisiloxanes. The organic derivatives have a characteristic layer structure (Fig. 9), with large interlayer spacings in trimethyltriphenylcyclotrisiloxane (9.48 and 9.52 Å in the *cis*- and *trans*-isomers). This completely eliminates the possibility of initiation of polymerisation between the layers, so that the polymer chain must develop in the plane of a layer, in which intermolecular Si...O contacts are sufficiently close (e.g. 4.28 and 4.51 Å in the *trans*-isomer). Thus the above "stacking" scheme of the polymerisation of cyclic monomers (suggested in particular even for hexamethylcyclotrisiloxane), according to which monomer molecules are arranged in piles in the crystal and polymerisation leads to the formation of elongated polymer helices, cannot be applied to these trisiloxanes [8].

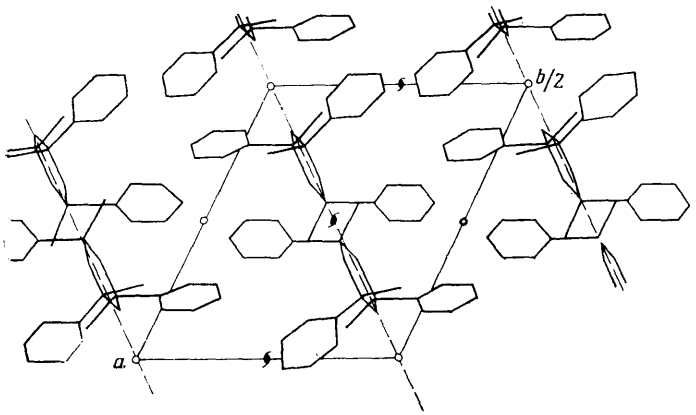


Figure 9. Packing of molecules in a crystal of *trans*-trimethyltriphenylcyclotrisiloxane. The broken lines show the direction of the layers of molecules.

Topochemical polymerisation by a single crystal of cyclic bithiazyl S_2N_2 has recently yielded an analytically pure single crystal of polythiazyl $(SN)_x$ (Fig. 10), which acts as a unidimensional metallic conductor [39-42]. The macromolecules have a completely planar structure, which with a topochemical mechanism can be achieved only by polymerisation in the layer. This evidently provides experimental confirmation of solid-phase polymerisation with ring cleavage occurring in layers of molecules.

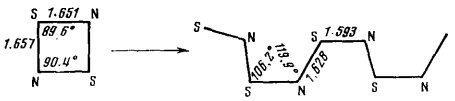
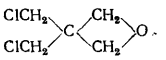


Figure 10. Polymerisation of bithiazyl. Bond lengths and angles obtained from X-ray examination of monomer and polymer crystals.

A thorough study has been made also of the polymerisation of 3,3-bischloromethyloxetan



and its analogues. It was suggested that this polymerisation is rigidly controlled by the lattice, since a highly crystalline and oriented polymer is formed [43,44]. But the formation of polymers when oxetans are exposed to X-rays leads neither to shifts in the reflections from the monomer crystals nor to the appearance of additional reflections, in contrast to for example the polymerisation of solid oligomers of formaldehyde [45] (above). X-Ray examination of the structures of bisiodomethyloxetan [46,47] and also of polybischloromethyloxetan [48] has shown that polymerisation should entail considerable displacement of the halogenomethyl groups. Such a transition must involve intermediate formation of amorphous zones. Hence the morphology and the orientation of products of the solid-phase polymerisation of oxetans are governed not by the actual mechanism of polymerisation but by secondary processes.

III. POLYMERISATION OF MONOMERS WITH MULTIPLE BONDS

The solid-phase polymerisation of molecules containing double and triple bonds differs in many respect from that of heterocyclic monomers. Transition from a cyclic molecule to a linear unit in a polymer chain involves no change in the valency configuration of the atoms, whereas the polymerisation of unsaturated compounds is accompanied by rehybridisation of the interacting atoms of the initial molecules. The mechanics of growth of the polymer chain is also fundamentally different in the solid-phase polymerisation of cyclic and of unsaturated monomers: in the former case the gap between adjacent molecules in the crystal, joining together to form the polymer chain, is filled as a result of cleavage of the cyclic molecules and straightening-out of the monomer unit in the direction of chain growth; in the case of unsaturated monomers the distance between adjacent monomer molecules forming the polymer chain should contract by ~2 Å (the difference between the intermolecular distance and the interatomic bond length in the macromolecule [4]). The "lever" mechanism of the polymerisation of rigid rodlike molecules suggested by

Wegner[5] (Fig. 11) can be applied in the latter case. The molecules, in the form of small sticks with reactive functional groups at their ends, are stacked in the crystal in such a way that two reactive groups in adjacent molecules are ~3 Å apart. Polymerisation takes place without displacement of the centres of gravity of the molecules in the lattice, either by their gradual rotation proceeding from molecule to molecule or by simultaneous rotation throughout a stack. Reactions occurring in this way are termed *topochemical* in the narrow sense.

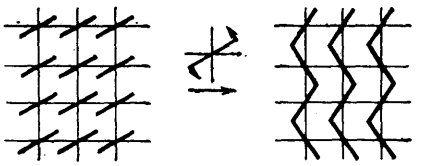


Figure 11. Simplified scheme of topochemical solid-phase polymerisation by the lever mechanism.

The solid-phase polymerisation of dienes (termed "four-centre polymerisation"), monomers containing triple bonds, and also certain other linear monomers with multiple bonds takes place by such a "lever" mechanism.

1. Four-centre Polymerisation

Molecules such as distyrylpyrazine (DSP) and derivatives of *p*-phenylenediacrylic acid§, packed "head to tail" in the crystal, yield polymers containing cyclobutane rings in the main chain and a completely ordered arrangement of substituents[49-54] (Fig. 12). Solid-phase polymerisation gives a product of exceptionally high crystallinity[55], but in solution an amorphous polymer is obtained.

Distyrylpyrazine molecules are arranged in the crystal in such a way that the relative positions and mutual orientation of the reactive double bonds are favourable for the formation of a cyclobutane ring; but crystals of another polymorphic modification (of undetermined structure) do not polymerise in the solid phase. Fig. 13*a* shows that the approximately planar distyrylpyrazine molecules are stacked along the *c* axis, which favours polymerisation in this direction. The shortest distance between the centres of double bonds in adjacent molecules is 3.94 Å (I*a*...II*b*, II*a*...III*b*, etc.). The next shortest distance, between double bonds of molecules in different stacks (5.42 Å), is too large for interaction[11]. It is therefore most probable that double bonds related by centres of symmetry react on irradiation (with the formation of cyclobutane rings), so that the polymer chains should grow in the direction of the *c* axis.

During polymerisation the X-ray diffraction pattern of distyrylpyrazine gradually changes into that of the polymer[51]. The mutual orientation of crystals of monomer and polymer has been established from the rotation photographs and the Weissenberg patterns of a partly polymerised crystal: the *a*, *b*, and *c* axes of the polymer are parallel to the corresponding axes of the monomer, but the characteristic elongation of spots on the X-ray patterns indicates some disordering of the polymer in the (001) plane. Since a single crystal of the monomer is converted by polymerisation into a polycrystal consisting of slightly disoriented fine blocks (crystallites), no X-ray structural analysis of the polymer has yet been made. Electron-microscopic study of polydistyrylpyrazine crystals has shown[56] that they consist of rodlike crystallites of square cross-sections about 1 μm thick, elongated in the direction of the *c* axis.

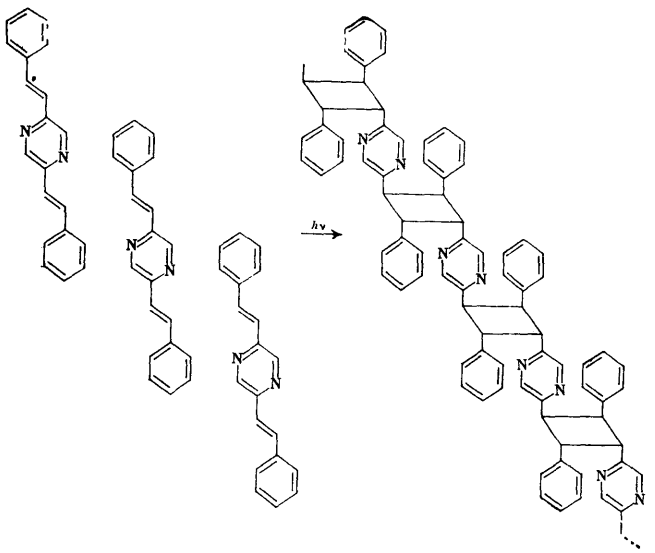


Figure 12. Four-centre photopolymerisation of dienes exemplified by that of distyrylpyrazine.

When crystals of distyrylpyrazine are exposed to light of wavelength exceeding 400 nm, polymerisation ceases at an intermediate stage: an oligomer having a mean degree of polymerisation of 5 is formed[57]. Comparison of the X-ray patterns of monomer and oligomer indicates that the latter, like the polymer, is well oriented, with its axes parallel to the corresponding axes of the monomer. The oligomer can be converted into the polymer by exposure to light of shorter wavelength. The degree of orientation of the polymer obtained from the oligomer is almost the same as that of the polymer obtained from the monomer. On conversion of the monomer into the polymer the *a* axis contracts by 11%, the *b* axis becomes 13% longer, and the *c* axis decreases by <2%. Thus the centre of gravity of the unit cell of the monomer is only slightly displaced in the direction of chain growth (the *c* axis), which is important for obtaining polymers in good yield.

The source of lattice deformations is the change in the distance between the double bonds I*a* and II*b* from the van der Waals value to the length of the σ bond in cyclobutane (1.56 Å).[58] Since the repeat distance along the *c* axis remains almost unchanged on polymerisation, the interaction of these double bonds leads to close contact of the

§ Dienes that polymerise by this mechanism are listed in Refs. 5 and 49.

second double bond II*a* with the double bond III*b*, as a result of which the excited molecule III reacts more readily with a double bond in II than in the next molecule IV. Fig. 13*b* shows how the polymer chain is superposed on the (010) projection of the monomer crystal; despite rotation of the central segment, displacement of the phenyl side-chains is insignificant.

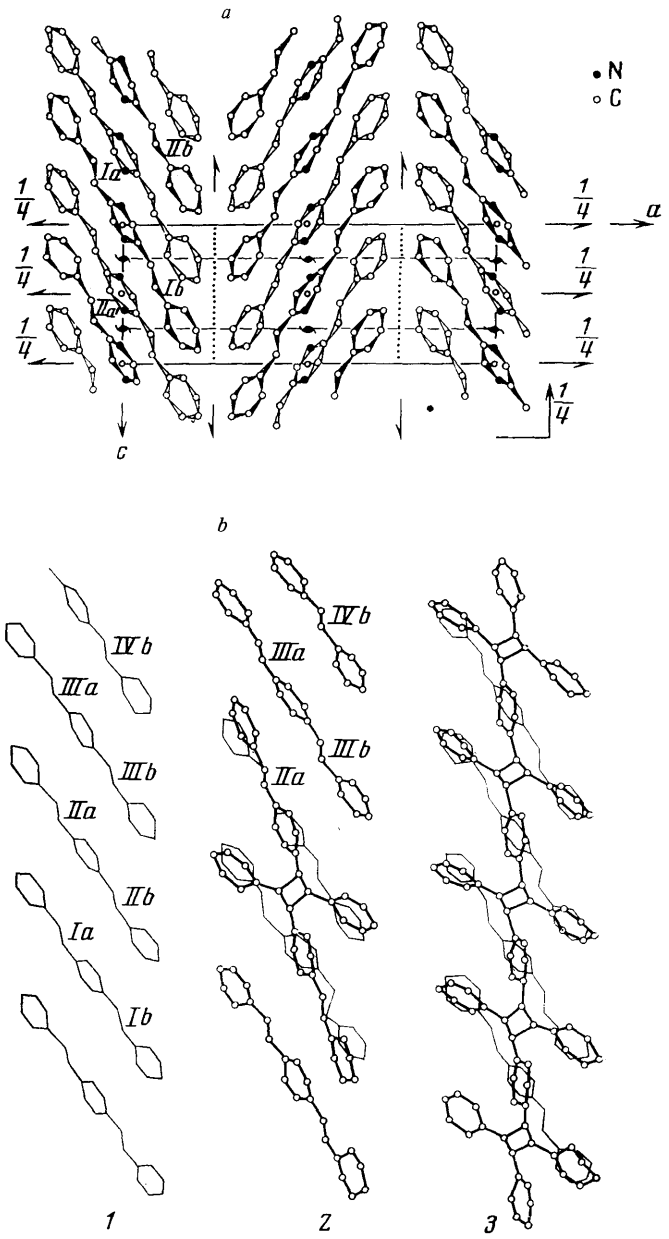


Figure 13. (*a*) Packing of molecules in a crystal of distyrylpyrazine. (*b*) Scheme of polymerisation of distyrylpyrazine shown by projections of the monomer: 1) alone; 2) combined with molecular model of dimer; 3) combined with molecular model of polymer.

Important results are obtained from a study of the behaviour of polydistyrylpyrazine on recrystallisation. The difference between the X-ray patterns of recrystallised and initial polymers[59] shows that the latter is formed under the control of the crystal lattice of the monomer and is not in the thermodynamically most stable form. It is extremely interesting that polydistyrylpyrazine undergoes thermal depolymerisation in high yield[53]. The scheme in Fig. 14 for the reversible interconversion of monomer and polymer is based[7] on thermodynamic and spectral investigations of the polymerisation–depolymerisation and a comparison of X-ray patterns obtained at various stages in these processes. Crystalline polydistyrylpyrazine is thermally more stable than the amorphous polymer, probably because the crystal lattice of the polymer protects the cyclobutane groups from thermal degradation by restricting local movement of the polymer chain.

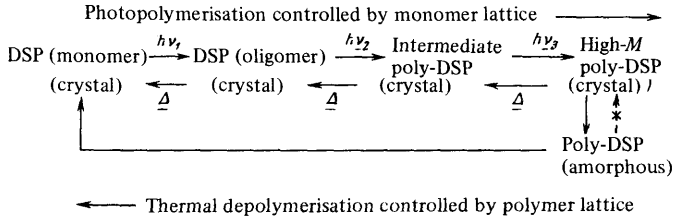


Figure 14. Scheme of reversible polymerisation of distyrylpyrazine (DSP).

In connection with the growing interest in asymmetric synthesis by topochemically controlled reactions in a chiral crystal[5,60–64] a series of 1,4-photodimerising monomers has been obtained containing as substituents "chiral handles" promoting crystallisation of these monomers into asymmetric structures[65,66]. Dimers and polymers obtained from the monomers (Fig. 15) are in fact chiral, with optical rotation of opposite sign to that of the monomer. A racemic crystal of structure similar to that of one of the enantiomers A or B (Fig. 15)¶, but containing (in equal quantities) substituents X of opposite chirality, also yields an optically active polymer on exposure. On the other hand, replacement of the chiral groups in an optically active monomer by methyl groups enhances the optical activity of the polymer. Thus optical induction accompanying polymerisation is caused by the chiral influence of the environment of the reaction centre in the crystal, not by the chiral influence of the "chiral handles".

2. Polymerisation of Monomers with Conjugated Triple Bonds

The solid-phase polymerisation of monomers containing conjugated triple bonds, discovered by Wegner in 1968, is a classic example of topochemical polymerisation by a

¶ The optically active monomer (Fig. 15) and its racemate crystallise in the $P1$ space group with closely similar cell parameters.

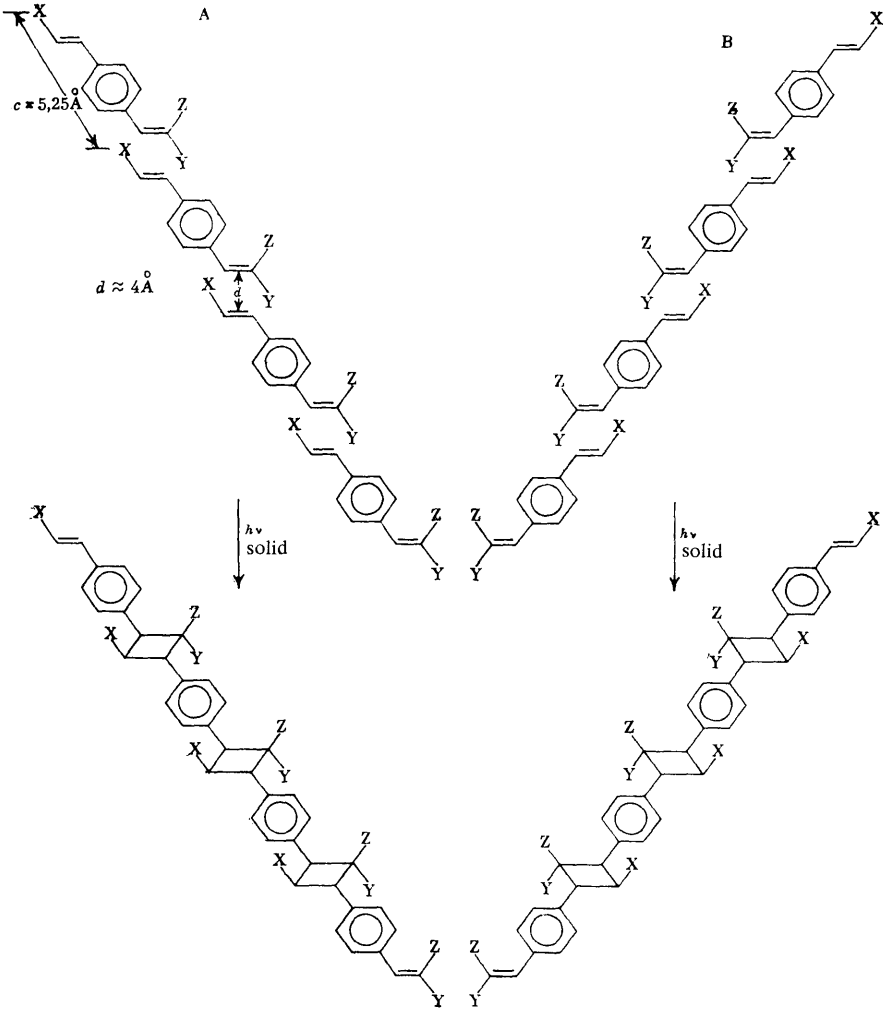
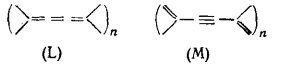


Figure 15. Structure and polymerisation in enantiomorphous crystals A and B. The suggested structure of the monomer is based on the parameters of the unit cell (molecular plane in the *ab* plane), and that of the polymer from n.m.r. data for the dimer and data for polydistyrylpyrazine.

lever mechanism [6,67-69]. The process is shown diagrammatically in Fig. 16. Equation (1) represents the formation of a polymer whose main chain, according to X-ray examination [70,71], is a planar conjugated system with a *trans*-arrangement of the substituents:

$$n\mathrm{R{-}C{\equiv}C{-}C{\equiv}R{-}R \rightarrow {-}C(R)\left[=C{-}C{\equiv}C{-}C(R)\right]_n=C{-} \quad (1)$$

The distribution of bond lengths in the main chain (Fig. 17) is described better by M of the two possible structures



for 1,4-addition products. The same distribution of bond lengths is suggested also by spectral investigation [72].

The polymerisation of diynes yields a completely ordered three-dimensional macroscopic single crystal of the polymer, in many cases of the same size as the single crystal of the monomer. For example, a polymeric single crystal weighing >1 g can easily be obtained from hexa-2,4-diynylene ditoluene-*p*-sulphonate [5]†. The polymerisation of colourless single crystals of diynes is usually accomplished by ultraviolet irradiation or by heating below the melting point, although other methods of initiation are possible, and is accompanied by a marked change in colour. Polymerisation does not take place in the melt or in solution [67].

Only imperfect microcrystalline aggregates of the polymers, often possessing a fibrous structure, are

† A list of diynes that polymerise in the solid phase will be found in Ref. 5.

obtained in the previous cases of the solid-phase polymerisation of trioxan and tetroxocan[13,14,16-18] and in four-centre photopolymerisation[55,56]. In these cases polymerisation is accompanied by breakdown of the initial monomer single crystal. This is due to the mechanism of polymerisation, which may be described as a phase transition characterised by stages of nucleation and growth of nuclei of the new (polymer) phase in a matrix of the initial crystal. This is known as heterogeneous solid-phase polymerisation. In homogeneous solid-phase polymerisation the polymer chains are "dissolved" in the matrix of the monomer crystal, and phase separation does not occur. The polymerisation of monomers containing conjugated triple bonds is such a homogeneous process[73].

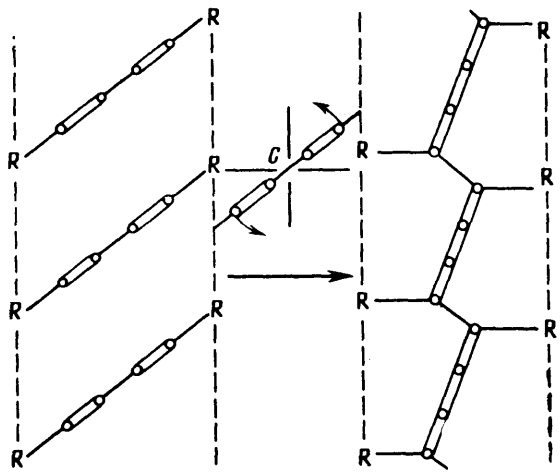


Figure 16. Polymerisation of conjugated diynes. Reaction involves rotation of monomer molecules about the centres of gravity C.

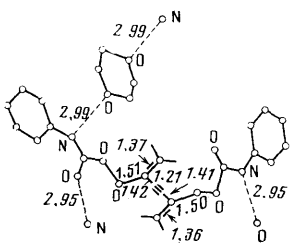


Figure 17. Structure of polymer obtained from hexa-2,4-diynylene bisphenylcarbamate. The broken lines show hydrogen bonds with neighbouring polymer chains and with molecules of dioxan of crystallisation.

In the polymerisation of certain diynes no change in density takes place, and no appreciable quantity of amorphous polymer is formed, but monomer and polymer are completely isomorphous. Such isomorphism has been noted e.g. with hexa-2,4-diynylene ditoluene-p-sulphonate[74]. However, other diynes, e.g. hexa-2,4-diynylene bis-stearoylcarbamate, give polymers possessing only two-dimensional orientation. These phenomena can be related and explained by means of the simple scheme[8] shown in Fig. 18. We suppose that a monomer passes into a polymer topochemically, by lever polymerisation, the solid product being in a modification that is not in general the energetically most advantageous, since the molecules are in an unfavourable stressed conformation. This is the transition $A \rightarrow B$. State D is thermodynamically stable for the polymer. If the monomer lattice is disturbed sufficiently, e.g. because of the difference between its density and that of the polymer, or if unchanged monomer is removed, the macromolecules relax and pass into state D. This state is not usually achieved, for the mobility of molecules is limited at the usual temperatures of polymerisation or extraction. The polymer therefore passes into a vitreous state C. Clearly, lowering the temperature of polymerisation may result in fixation of state B. This may explain the observations that, when diethynyl p-phenylenediacrylate undergoes polymerisation below 5°C, the polymer modification corresponding to state B is "frozen in", whereas at about 30°C relaxation ensues with the appearance of an amorphous structure corresponding to state C. In the polymerisation of hexa-2,4-diynylene bisphenylcarbamate and ditoluene-p-sulphonate, however, the polymer formed topochemically corresponds to the thermodynamically stable modification. Polymerisation of the bis-stearoylcarbamate follows a different course, with the resulting polymer modification stable only in the presence of the monomer lattice. This involves "forced" isomorphism of monomer and polymer, in which the monomer structure is kinetically (but not thermodynamically) preferable, for the resulting polymer, to the polymer structure possessing minimum free energy. Therefore the lattice changes accompanying polymerisation are minimal.

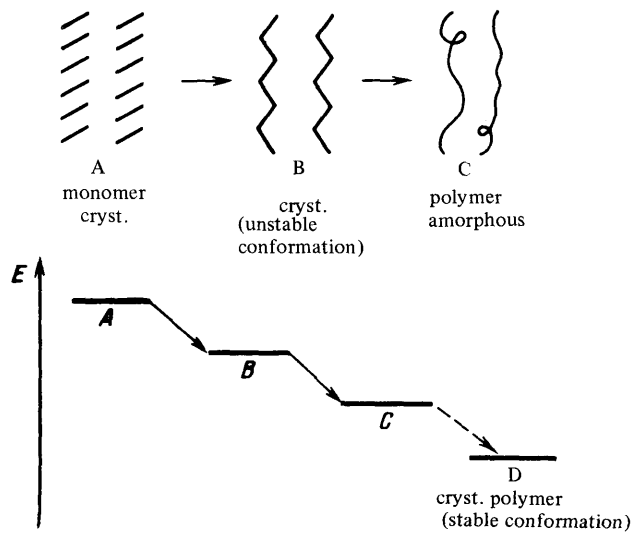
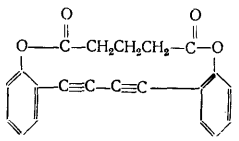


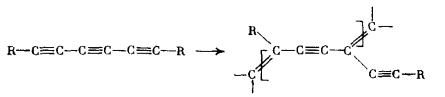
Figure 18. Relative stability of polymer chains in crystalline and amorphous polymer.

The possible isomerism of polymers obtained from cyclic diynes has been discussed[5]. If the monomer molecules are linked in the crystal only by translations, they should yield the chiral polymer shown diagrammatically in Fig. 19*a*. If, however, neighbouring molecules are linked in the direction of polymerisation by a reflecting glide plane, the achiral polymer of Fig. 19*b* should be formed, in which the side loops (rings) are alternately above and below the plane defined by the conjugated main chain. Crystals of the cyclic diyne



readily undergo photopolymerisation, but thermal polymerisation is very slow. X-Ray examination has shown that the polymer has the structure indicated in Fig. 19*b*. Unfortunately, it has not yet proved possible to select a crystalline modification of a cyclic diyne having translational symmetry only in the direction of polymerisation, although a fairly large number of reactive modifications of cyclic diynes have been described[5,75].

The solid-phase polymerisation of triynes is well known, and is easily detected from the spontaneous coloration of the monomer crystals[5,69]:



As with diynes, polymerisation is a consequence of 1,4-addition, with an acetylenic side-chain present in the monomer unit.

However, not all diynes and triynes undergo solid-phase polymerisation. The reactivity of monomers is largely determined by their packing, not by e.g. mesomeric or inductive effects. If a monomer can be obtained in different modifications, the latter usually exhibit different tendencies to undergo solid-phase polymerisation. Frequently only one modification polymerises in the solid phase, and the others do not. It is significant, for example, that crystals of hexa-2,4-diynylene bisphenylcarbamate polymerise only if they contain dioxan of crystallisation, which probably ensures that the packing of the molecules in a crystal is favourable for polymerisation[71]. Hexa-2,4-diynylene dibenzoate crystallises in two forms, one of which (S) can polymerise under the influence of high pressures, but the other (T) cannot[76]. Molecules are located at centres of symmetry and have the same conformation in both forms of crystals. However, whereas the C...C distances between triply-bonded atoms in adjacent molecules in the S form of crystal (4.02 Å) can be shortened by high pressures to the critical value at which covalent bonds are formed, the corresponding shortest C...C distance in the T form of crystal is 5.37 Å, which could not be shortened by pressure to the critical value.

Solid-phase polymerisation is possible when adjacent molecules in a crystal are arranged as shown in Fig. 20. The angle α between the translation relating the centres of gravity of adjacent reactant molecules and the direction of their conjugated bond system should be ~40°. The distance between the centres of gravity of neighbouring molecules is 4.7–5.2 Å, with an optimum of 4.9 Å for polymerisation: i.e. polymerisation is accompanied by minimal changes in the parameters of the unit cell.

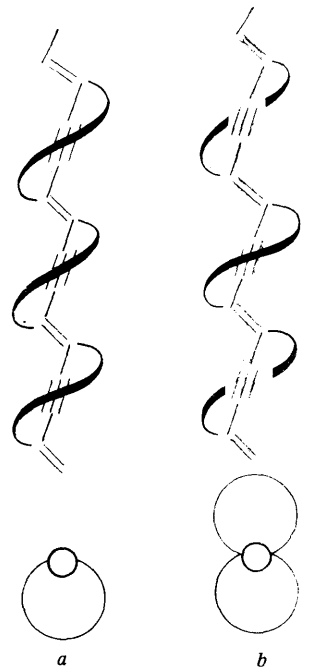


Figure 19. Structure of polymers obtained by the solid-phase polymerisation of cyclic diynes: *a*) chiral; *b*) achiral. Projections along the axes of the macromolecules shown at foot of diagrams.

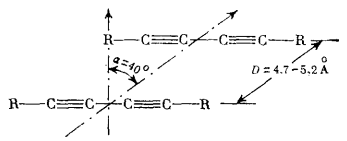


Figure 20. Arrangement of adjacent molecules in a stack in a diyne crstal undergoing solid-phase polymerisation, where D is the distance between the centres of gravity of the molecules and α the angle between the axis of the molecule and the direction of translation relating neighbouring molecules in a stack.

In this connection it is very interesting to study the difference in reactivity between two substituted diacetylenes[77]: hexa-2,4-diynediol polymerises slowly in the solid phase, but diphenylbutadiyne hardly polymerises at all. Reactant molecules in a crystal of the former are related by the diagonal translation *ac*. The molecules are joined by hydrogen bonding in the direction of the *c* axis, but no hydrogen bonds are formed in the *ac* direction. The geometrical parameters α and D (Fig. 20) are 5.34 Å and 41.4° in hexa-2,4-diynediol, and 6.04 Å and 50.9° in diphenylbutadiyne. Polymerisation of the first monomer should involve a contraction of 0.44 Å in the distance between the centres of adjacent reactant molecules, while the axes of the molecules should turn through 28°. The relative inactivity of the second monomer in the solid phase is attributed to the considerable displacement and

rotation of molecules necessary for polymerisation by 1,4-addition (respectively 1.14 Å and 37.5°). The distances between the terminal atoms of the reactive butadiyne groups are also different: 3.54 Å in the first monomer, and 4.69 Å in the second.

The relative arrangement of diyne molecules is dictated by the packing of lateral substituents. Reactive modifications should obviously be formed by diynes substituted by polar groups—hydroxyl, carboxyl, amide, and urethane—able to promote suitable orientation of the molecules in the crystal by dipole–dipole interaction or hydrogen bonding. A system of hydrogen bonds interconnecting neighbouring monomer units has been found[71] in a crystal of polymeric hexa-2,4-diynylene bisphenylcarbamate.

The parallel packing of adjacent benzene rings in the direction of the polymer chain in the crystal of poly-1,2-di(toluene-*p*-sulphonyloxymethyl)but-1-en-3-ynylene[70], which fixes the relative arrangement of neighbouring monomer units, is probably also a consequence of the dipole–dipole interaction of polar side-groups. Nevertheless, the presence of such groups is neither a necessary nor a sufficient condition for the solid-phase polymerisation of diynes. For example, octacosadiyne containing purely aliphatic substituents has a low-temperature modification which undergoes photopolymerisation exceptionally readily, whereas its high-temperature modification is inactive from 15°C up to the melting point[5]. Thus the orientation of adjacent molecules necessary for polymerisation can be ensured also by the packing of non-polar groups. On the other hand, among diphenylbutadiyne derivatives disubstituted with polar groups only the *ortho* and *meta* isomers are active in the solid phase, whereas the corresponding *para*-disubstituted compounds do not polymerise[57].

The best test of the above ideas of Wegner[5], of course, would have been a structural investigation both ot the monomer and of the polymer formed from it, but this has not yet been done. With many diynes, e.g. bisphenylcarbamates, X-ray examination is difficult because of the extreme rapidity of polymerisation on exposure. With diynes that polymerise slowly in the solid phase (hexa-2,4-diynediol, etc.) the crystalline structure of the monomers is known[74,78], but the structure of the polymer has not been investigated. On the application of large radiation doses with the aim of achieving high degrees of conversion the polymeric hexadiynediol becomes amorphous[78]. The structure of diphenylbutadiyne is known[79], but it is almost inactive in the solid phase.

Successive determination of the Raman spectra during the polymerisation of diynes[72] revealed spectral bands due to states intermediate between the initial monomer and the final polymer. The intensity of the bands due to the intermediate states increased initially, and then diminished. However, the vibration frequencies of the intermediate states were independent of the degree of polymerisation. Investigation of the ultraviolet spectra during the polymerisation of hexa-2,4-diyne-1,6-ylene revealed two intermediate spectral states differing both from the monomer, from the polymer, and from combinations thereof. However, lower intermediate products could not be identified by thin-layer chromatography[67]. The infrared spectra of partly polymerised hexa-2,4-diyne-1,6-diol show that the intermediates, present in considerable quantities, are completely hydrogen-bonded both in the monomer crystal and in the extracted polymer[72].

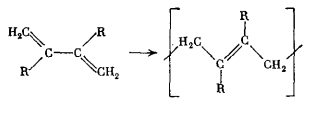
Thus spectral methods clearly establish the stepwise character of the solid-phase polymerisation of diynes, but the nature of the intermediates is obscure and requires further investigation.

3. Polymerisation of Monoethylenic Monomers

The above lever mechanism is impossible for the polymerisation of alkenes‡, and growth of the polymer chain requires considerable displacement of the molecules. Therefore topochemical polymerisation is not usually observed with these compounds[5]. The solid-phase polymerisation of vinyl monomers generally yields amorphous polymers, and the actual process takes place in "amorphous zones" or "local melts" arising from the absence of geometrical correspondence between monomer and polymer lattices.

Only the polymerisation of vinyl stearate and other quasi-crystalline long-chain vinyl and acrylic monomers takes place under definite structural control[81–83], occurring preferentially in monolayers, apart from the channel polymerisation of dienes in the form of inclusion compounds[84,85]. Polymerisation of ethylenic monomers in a quasi-crystalline state is possible if their molecules contain suitable substituents capable of being densely packed, while the ethylenic groups are situated in quasi-liquid regions and hence are highly mobile. This phenomenon is termed the "crystallinity of side-chains"[86,87]. A typical case is the polymerisation of *N*-*p*-vinylphenylbenzamide[88] or vinyl stearate, when the packing of the side-chains is largely preserved during polymerisation, but the linking of the double bonds is not specific and an atactic polymer is formed. The solid-phase polymerisation of long-chain unsaturated compounds has recently aroused especial interest, since it may occur in monolayers or in multilayer structures formed from them[82,83].

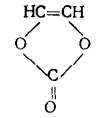
In channel inclusion compounds the "host" molecules, e.g. urea or thiourea, form an open structure, in the channels in which the molecules of a suitable monomer may be distributed. The polymerisation of alkenes in the form of inclusion compounds in urea or thiourea has been known for a long time[34,89]. Direct X-ray structural investigation of butadiene and its 2,3-disubstituted derivatives in the lattice of perhydrotriphenylene or urea as host has recently shown[62,85,90] that such derivatives are tightly packed "head to tail" in the channels. Powerful irradiation yields *trans*-1,4-polybutadiene by 1,4-addition:



The host lattice does not disintegrate during polymerisation, and an isolated stressed macromolecule is formed in each channel. After the host lattice has been cautiously dissolved, a highly crystalline fibrous product remains, comprising stressed chains[85]. The specific character of these reactions consists in the mutual isolation of the channels and the greatly restricted mobility of the monomer molecules. In a channel a monomer molecule is unable to rotate about its long axis, its mobility being reduced to the possibility of translational diffusion, which creates the necessary conditions for the formation of an ordered polymer.

‡ Because no rotation of such molecules is able to bring the ends of the double bonds within the distance necessary for polymerisation.

Crystals of vinylene carbonate



which polymerise on exposure to γ-rays, comprise layers perpendicular to the [$\bar{2}$01] direction[91]. The shortest intermolecular C...C distance between vinyl groups lies in the plane of the ($\bar{2}$01) layer (Fig. 21). But the formation of chemical bonds in this plane would have required large molecular rotations both in and perpendicular to the plane, which would have results in local stresses in the lattice. Polymerisation develops preferentially along surfaces parallel to the axes of the polymer to form a heterogeneous phase[92]. Weissenberg diagrams obtained after irradiation for 48 h established that the *a* and *b* axes of the polymer were parallel to those of the monomer. Thus polymerisation proceeds in the (110) plane. The polymer chain is a 3/1 helix extending along the *b* axis of the monomer crystal. At 10% conversion a signal due to the amorphous polymer appears on the diffractograms, at 35% only two peaks corresponding to a crystalline substance remain, and at 67% conversion the polymer is completely amorphous. The initially formed polymer probably has a thermodynamically unstable conformation and is able to exist only when a considerable crystalline environment is preserved by the monomer[92].

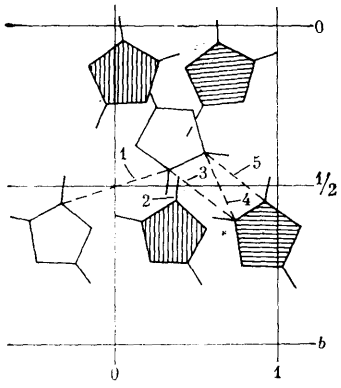


Figure 21. Packing of molecules in a crystal of vinylene carbonate projected on the ($\bar{2}$01) face (plane of layer). Molecules lying above and below this plane are shown by vertical and horizontal hatching respectively. Intermolecular vinyl–vinyl distances < 4 Å are indicated (Å): 1) 3.776; 2) 3.778; 3) 3.902; 4) 3.864; 5) 3.902.

The initial stage in the polymerisation of crystalline acenaphthylene is also a topotactic process[93,94], which, like that of vinylene carbonate, takes place not in the plane of the separating layers but in planes having $z = 0.25$ and 0.75. The polyacenaphthylene chains are oriented along the *a* and *b* axes of the monomer crystal. From the size of the identity period along the chain axis a *threo*-diisotactic structure was suggested for the polymer chain.

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The above survey has shown that solid-phase polymerisation is not necessarily controlled by the lattice and does not necessarily give a stereoregular crystalline polymer. The crystal structure of the monomer may be destroyed by the growing polymer chains, so that only the initial stages of oligomerisation take place under the control of the lattice. This yields an amorphous polymer, which in some cases (oxetans) is able to crystallise. On the other hand, the product of solid-phase polymerisation frequently does not possess the expected morphological properties, because relaxation processes, which are so characteristic of other polymer reactions, may occur in structures obtained topochemically.

Two general types of lattice-controlled solid-phase polymerisations can be distinguished. (i) Polymerisation with ring cleavage is characteristic of cyclic monomers whose molecules are arranged in stacks or layers in the crystal. Polymerisation in stacks involves the opening of rings with formation of helical polymer molecules (trioxan, tetroxocan, etc.). Monomers having a stressed-ring structure (cyclotrisiloxanes and probably bithiazyl), in contrast, undergo polymerisation in layers. (ii) Lever polymerisation is accomplished by the concerted displacement and rotation of rigid rodlike molecules. A clear example of the lever mechanism is provided by monomers having conjugated triple bonds, which on polymerisation give units with alternating double, triple, and single bonds. The polymerisation of these monomers completely satisfies Schmidt's conditions[9,10] and is topochemical in the narrow sense.

The next important step in the study of solid-phase polymerisation should be to obtain quantitative structural–chemical criteria of the process, in particular to investigate potential barriers to motion, the geometry, and the dynamics of molecular groups during the process by the method of interatomic potentials.

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