STEREOCHEMICAL ASPECTS OF CRYSTALLINE SYNTHETIC MACROMOLECULES

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Abstract—The most relevant conformational aspects of different skeletal sequences of macromolecules in the crystalline state are discussed. The general importance of the minimum intramolecular energy rule is stressed. Because of the higher energy barriers separating the rotational isomers, sequences of C atoms show a much greater tendency to regular (i.e. "staggered") conformations than those involving CH_2–O or CH_2–N bonds. This is reflected in the surprisingly large variety of conformational polymorphs observed especially in polyoxides and in polyformals.

Interest in the conformational knowledge of polymer chains in the crystalline state, as resulting from X-ray diffraction studies, has been growing in recent years for several reasons. First of all, the assumption that the intramolecular potential energy attains a minimum in the crystals is even more justified for polymers than for low molecular weight compounds, due to the smaller proportion of intermolecular interactions. In fact, the theoretical prediction of the crystalline conformation of polymer chains has been so frequently successful. Furthermore, the analysis is favoured by the relatively low number of geometrical parameters defining the chain shape, as dictated by the postulate of geometrical equivalence among the monomer units.[1] Then, the existence of a relatively limited variety of groups whose sequence constitutes the macromolecular chain improves the chance of transferring the geometrical parameters previously known to a new polymer chain. Finally, the relatively accurate knowledge of the lowest energy conformation, as observed in the crystal, is frequently a useful guide to predicting the probable conformations of the polymer in the free state (i.e. in solution or in the melt).

For the above reasons we believe it useful to review in the present paper the geometrical features of some atomic sequences frequently occurring along the chain skeleton of crystalline synthetic polymers. We will point out the influence of the side groups, without dealing in much detail with their conformations, primarily because these are usually less accurately derivable from the X-ray data than the conformations of the main skeleton.

We want to stress that the following discussion is not intended to cover in any exhaustive way all the relevant aspects of the crystal structure of poly-

mers. In particular, reference to the papers describing polymer structures is by no means complete, since we felt essentially motivated to an analysis of what we believe to be the most interesting conformational aspects concerning short chain sequences, as said above. For the same reason, recent papers have been referred to with special emphasis. On the other hand, we did not strictly limit our attention to the structural results concerning crystalline polymers as such, since information on polymer conformations derived from inclusion compounds or from unperturbed solutions has also been utilized, inasmuch as it might shed additional light on the nature of the most stable conformations.

We shall distinguish the most characteristic sequences occurring along synthetic polymer chains into the following categories, discussing each of them separately:

(I) –C–C–C–C–,   all C atoms saturated;

(II) –C–C–C–C–,   one or more atoms being double-bonded to side groups;

(III) (C)–C–C=C–C–(C),   (polydienes, polyalkenamers);

(IV) –C–O–C–C–
    –C–S–C–C–
    –C–O–C–O–   (polyoxides, polyformals, polysulphides);

(V) (C)–C–O H–C–(C),   (polyamides);
          C═N   (with C double-bonded to N and single-bonded to H)

(C)–C–O–O–C–(C),   (polyesters);
        C (double-bonded)

(C)–o–O H–C–(O),   (polyurethanes).
         C═N

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I *Skeletal sequences of saturated carbon atoms* (–C–C–C–C–)

This is by far the most common sequential group in synthetic polymers. Not only is it encountered in polyethylene and substituted polyethylenes, in vinyl- and vinylidene polymers as well as in some crystalline ethylene copolymers, but also in unsaturated carbon polymers such as the polyalkenamers, in polyamides, in polyesters etc. The conformation of these sequences is largely dictated by the tendency towards a staggered orientation of adjacent carbon atoms (Fig 1), which on its turn is a direct consequence of the minimum potential energy requirement.[1] Indicating respectively with T, G^+ and G^- (i.e. *trans, gauche plus* and *gauche minus*) the rotation angles 180°, 60° and 300° ($\cong -60°$) around a C–C bond (Fig 1), departures larger than 10–15° from these values are found only when a significant steric hindrance is induced by bulky and/or densely distributed side groups. In this as well as in the following sections we will use the symbols T, G^+ and G^- regardless of the possibility that the respective rotation angles may be distorted from the above values, provided they are comprised within the same potential energy well.

To our knowledge, in all the polymer crystal structures reported hitherto the (–CH$_2$–CH$_2$–CH$_2$–CH$_2$–) sequence has been found in the *trans*-planar conformation. Theoretical in-

vestigations on polyethylene in unperturbed solutions seem to indicate that the energy of the *gauche* arrangement is about 0·5 kcal/mole higher.[2] Perhaps it may be worth mentioning that this energy appears to be lowered to about 0·1 kcal/mole for the linear alkanes when present in the channel inclusion compounds obtained from the full equatorial isomer of perhydrotriphenylene. Tendency towards the densest filling of the channels is said to be responsible for this effect.[3] Of course, deviation from the *trans* arrangement must occur where the chain folding occurs, in polymer crystallites.[4]

In the crystalline isotactic vinyl polymers, (–CH$_2$–CHR–)$_n$, the succession of the rotation angles along the main chain has always been found as ...TGTG..., where T and G stand for more or less distorted *trans* and *gauche* rotations, the distortion being related to both the size and the shape of the side group. More specifically, referring to Figs 1 and 2 and enclosing in parentheses the pairs of rotations around bonds departing from the same –CH$_2$– group, possible sequences are $(TG^+)_n$ or $(G^-T)_n$ (proceeding from left to right, see Fig 2), which represent helical conformations of opposite handedness, mutually related by a center of symmetry[5] (Fig 3). In the presence of non-chiral side groups, the existence of equivalent arrangements related to inversion symmetry is consistent with the chain configuration being optically compensated, except for negligible end effects. Giving the chain a 180° reversal so that the two ends are interchanged, it is easy to see that the possible helical sequences now correspond to $(G^+T)_n$ and $(TG^-)_n$. In conclusion, two pairs of equivalent helical conformations of the same chain may be obtained, each pair consisting of two opposite arrangements (*up* and *down*, see Fig 3) of the side groups, with the *same* handedness. Statistical replacement of the two conformations belonging to each pair has been frequently observed, while *in no case does it involve conformations with opposite handedness.*[5]

The distortion of the skeletal rotation angles from the exactly staggered conformations (i.e. 60°, 180° and 300°) is the largest when the first atom of the side chain carries two non-hydrogen substituents. With reference to Table 1, we see that de-
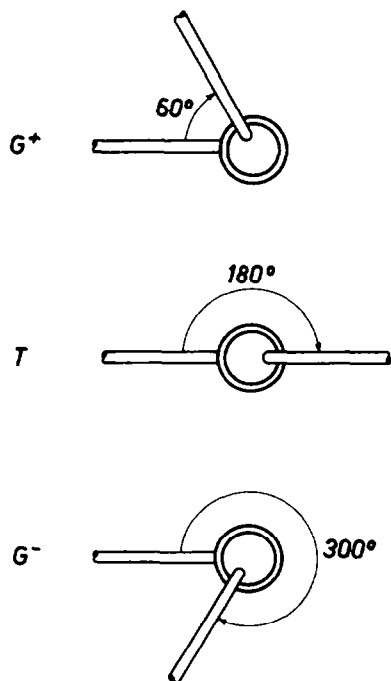

Fig 1. "Staggered" conformations of a C—C—C—C sequence, in a Newman projection. Here and in the following figures the hydrogen atoms are omitted.
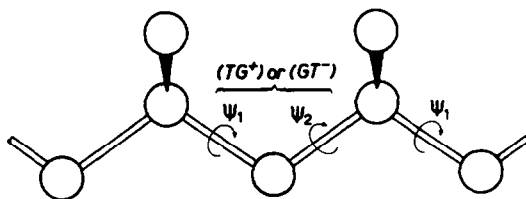

Fig 2. A sequence of isotactic polypropylene in a supposed zig-zag planar conformation. The possible rotation angles observed in the crystalline state are shown.
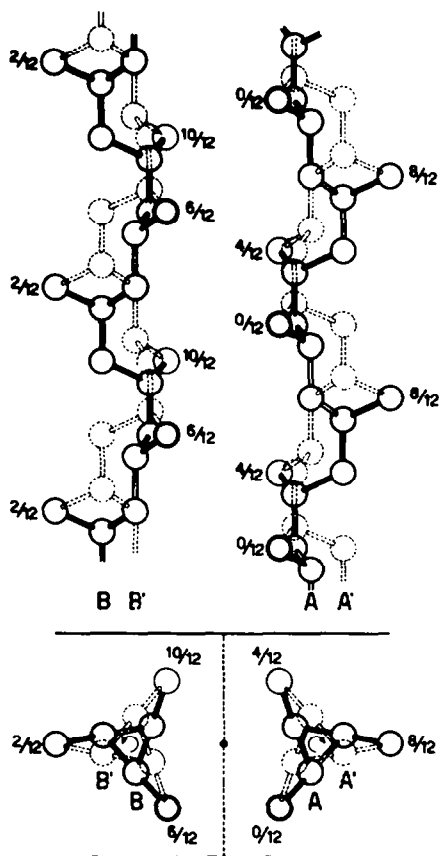
Fig 3. Isomorphous replacement in the crystalline state between isotactic polypropylene chains with either *up* or *down* orientation of the side groups.

viations as high as 30° from the above values are observed in poly (3 - methyl - 1 - butene)[6] and in poly ((S) - 3 - methyl - 1 - pentene).[7] The distortions are significantly reduced when the double substituted atom is the second of the side chain, as it may be seen in Table 1 for poly (4 - methyl - 1 - pentene),[8] poly (4 - methyl - 1 - hexene) (both racemic and optically active forms),[8] poly(allylcyclopentane),[9] 1,2 poly (4 - methylpentadiene - 1,3),[10] and for the two isotactic polyvinylethers, poly(isopropyl vinyl ether) and poly((sec-butyl) vinyl ether) (both racemic and optically active forms).[11] If the substituted atom is further away from the main chain (*cf* poly(5 - methyl - 1 - hexene) and poly(5 - methyl - 1 - heptene), both racemic and optically active forms, Table 1[12]), the distortion is still smaller, tending to the essentially staggered conformation found for isotactic polypropylene.[13]

From inspection of Table 1 two additional considerations may be derived: (i) the distortion is such that both T and G tend to be larger than the staggered values 180° and 60°; (ii) the deviation from the *trans* conformation is tendentially larger than from

the *gauche* conformation. A relatively simple, although qualitative, explanation of these facts may be offered by analysis of Fig 4, where a short section of the helical chain is shown, the side groups being considered for simplicity as spherical bodies at a bonding distance of 1·54 Å from the chain atoms (1·54 Å is the normal C–C bond length). Three among the most important interactions between the side groups and other groups separated by at least three bonds are evidenced in the figure, where the corresponding distances for the ideal (180°, 60°)$_n$ $(= (\psi_1\psi_2)_n)$ conformation are also shown. It is not difficult to realize that distance I may be increased through an increase of ψ_1 only, while distance II is lengthened by an increase both of ψ_1 and ψ_2. As for distance III, this is not seriously influenced by a limited change of ψ_1 and ψ_2. It is not surprising, therefore, that substantial alleviation of the intramolecular strain may be achieved through the observed distortion of the skeletal rotation angles in the presence of bulky side groups.

An interesting class is represented by the alternating ethylene - *cis* - 2 - butene[14,15] and ethylenecyclopentene copolymers,[14,16] whose chemically repeating unit is ⊦CH$_2$–CH$_2$–CHR–CHR⊦. They have been assigned an *erythro*-diisotactic structure, and all the chain rotation angles are *trans* except the one around the CHR–CHR bond which is *gauche*. The consecutive units are related by centers of symmetry. While in the case of the cyclopentene copolymer the *trans* rotation is sterically impossible because of the hindrance produced by the 5-membered ring connecting together the adjacent R groups, in the *cis* - 2 - butene copolymer it may appear to be possible without any apparent strain (Fig
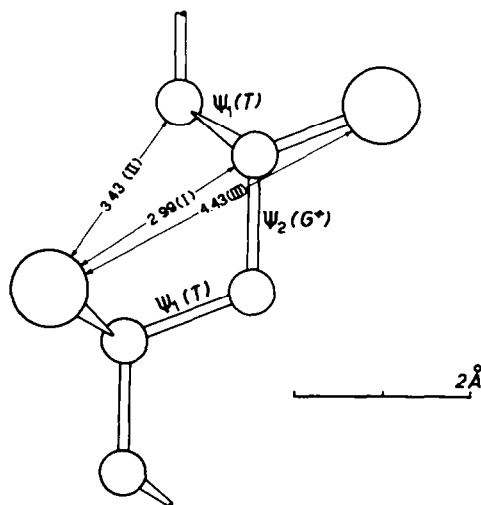

Fig 4. Chain conformation of an isotactic vinyl polymer corresponding to a (180°, 60°)$_n$ succession (a threefold helix). Some interatomic distances (Å) involving the side group are put into evidence (see text).

Table 1. Interaction rotation angles ψ_1 and ψ_2 and helical symmetry (expressed as N_M, i.e. no. of monomer units per turn) of some isotactic vinyl polymers (chain conformation $(\psi_1\psi_2)_n$)

Polymer name	Ref	Formula	ψ_1	ψ_2	N_M
Polypropylene	13	$\text{+CH}_2\text{—CH+}_n$ $\mid$ CH_3	180°	60°	3_1
Poly(1-butene)	5	$\text{+CH}_2\text{—CH+}_n$ $\mid$ C_2H_5	180°	60° (in one crystalline modification)	3_1
Poly(3-methyl-1-butene)	6	$\text{+CH}_2\text{—CH+}_n$ $\mid$ CH $CH_3 \quad CH_3$	211°	80°	4_1
Poly((S)-3-methyl-1-pentene)	7	$\text{+CH}_2\text{—CH+}_n$ $\mid$ CH $CH_3 \quad C_2H_5$	211°	81°	4_1
Poly(4-methyl-1-pentene)	8	$\text{+CH}_2\text{—CH+}_n$ $\mid$ CH CH CH_3 CH_3	193°	72·5°	7_2
Poly(4-methyl-1-hexene)	8	$\text{+CH}_2\text{—CH+}_n$ $\mid$ CH_2 CH CH_3 C_2H_4	196°	72·5°	7_2
Poly(allylcyclo-pentane)	9	$\text{+CH}_2\text{—CH+}_n$ $\mid$ CH_2' CH $H_2C \quad CH_2$ $H_2C\text{—}CH_2$	193°	70·5°	24_7
Poly 1,2(4-methyl-pentadiene-1,3)	10	$\text{+CH}_2\text{—CH+}_n$ $\mid$ CH $CH_3\text{—C—}CH_3$	188·5°	77·2°	18_5
Poly(isopropyl vinyl ether)	11	$\text{+CH}_2\text{—CH+}_n$ $\mid$ O $\mid$ R $R = \begin{cases} \text{—CH} \begin{matrix} CH_3 \\ CH_3 \end{matrix} \\ \text{or} \\ \text{—CH} \begin{matrix} C_2H_5 \\ CH_3 \end{matrix} \end{cases}$	190°	70°	17_5
Poly((sec-butyl) vinyl ether) (both racemic and optically active)					

Table 1—*Continued*

Polymer name	Ref	Formula	ψ_1	ψ_2	N_M
Poly(5-methyl-1-hexene)		$+CH_2—CH+_n$			
	12	CH_2	176°	62°	3_1
Poly((S)-5-methyl-1-heptene)		CH_2			
		R			
		$R = \begin{cases} —CH\diagdown_{CH_3}^{C_2H_5} \\ \text{or} \\ —CH\diagdown_{CH_3}^{CH_3} \end{cases}$			
Poly((S), (R)-5-methyl-1-heptene)	13	(as above)	168	64°	19_6

5). The reason why the energy difference between the *trans* and the *gauche* arrangements must be very small has been discussed by Thomas and Gwinn with reference to 1,1,2,2 tetrachloroethane.[17] They relate it to the tendency of the Cl–C–Cl angles to be larger than the tetrahedral value, with the consequence that the contact distances between Cl atoms three-bonds apart are shorter in the *trans* than in the *cis* arrangement (Fig 5).

Poly(α-olefins) which have been unambiguously characterized as syndiotactic are polypropylene[18, 19] and 1,2 poly(butadiene-1,3).[20] While the chain conformation of the latter is close to the *trans*-planar arrangement, two different crystalline modifications have been described for the former, the most stable of which is a twofold helix with the rotational succession ... $(TT)(G^+G^+)(TT)(G^+G^+)$... (or ... $(G^-G^-)(TT)(G^-G^-)(TT)$...), the other one corresponding to the completely *trans*-planar chain (Fig 6). It is noteworthy that the second modification of isotactic polypropylene was foreseen on the basis of minimum energy calculations well in advance of the experimental finding.[18, 19]

The only reported case of a halogenated ethylene polymer showing a significant amount of regularity in the succession of its stereoisomeric centers is syndiotactic poly(vinyl chloride).[21] In this case, too, a *trans*-planar conformation is observed which, therefore, appears to exist in the crystalline state of the three vinyl syndiotactic polymers known hitherto. As it may be seen from inspection of Figs 4 and 6, a sequence comprising five atoms with pendant side groups of a vinyl polymer chain attains
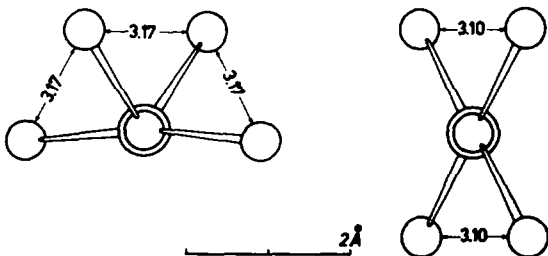

Fig 5. The two staggered arrangements of a 1,1,2,2,-tetrasubstituted ethane molecule corresponding to a *gauche* (left) and to a *trans* (right) conformation of the skeletal bond between tertiary C atoms of the ethylene - *cis*-2-butene alternating copolymer. The shortest C–C distances for all C–C–C angles equal to 112° are shown.
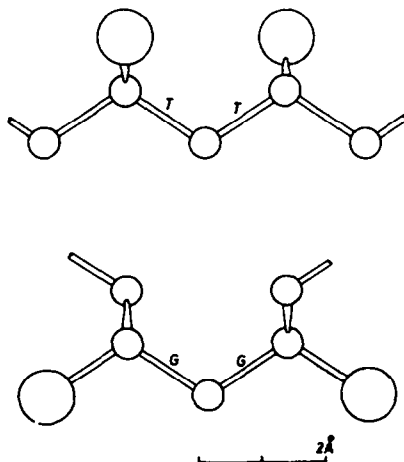

Fig 6. The (most stable) (TT) and (GG) conformations of a syndiotactic vinyl polymer chain.

approximately the same spatial arrangement whether with a (TG) conformation and an isotactic structure or with a (TT) or (GG) conformation and a syndiotactic structure, which are in fact the actual conformations found in the crystalline state.

With the possible exception of poyl(vinylidene fluoride) (PVF$_2$), the vinylidene-type crystalline polymers show relatively large deviations from the ideally staggered chain conformations; Table 2 reports the most characteristic chain parameters of polyisobutylene,[22] isotactic poly(methyl methacrylate)[23,24] and syndiotactic poly(α-methylvinyl methyl ether).[25]

An unusually large value of the C–CH$_2$–C bond angle ($>$ 120°) on the main chain of polyisobutylene has been obtained from conformational energy calculations;[22] it compares well with the corresponding value obtained through X-ray analysis of the model compound 2,2,4,4-tetramethyladipic acid[26] and it appears to be confirmed by a complete structure factor analysis of the crystalline polymer.[27] Because of this bending deformation the intramolecular distances relating the C(methyl) atoms with other C atoms 3 or more bonds apart are not less than 3 Å. The flexibility of this bond angle also allows a large number of chain conformations to be attained in unperturbed solution, with relatively low energy barriers separating the rotational isomers, as was predicted by Flory.[28] As a result, in spite of the severe intramolecular repulsions, the chain exhibits a rather high flexibility.[22]

The chain conformation of isotactic poly(methyl methacrylate) in the crystalline state, corresponding to a 5$_1$ helix[23] (Table 2), is surprising insofar as it is about 3 kcal/mol (per monomer unit) higher than the lowest minimum, corresponding approximately to the fully extended chain conformation.[24] There should be little doubt that polar interactions between packing chains are responsible for stabilizing the conformation observed.[24]

Contrary to the vinylidene polymers listed in Table 2, poly(vinylidene fluoride) (PVF$_2$) may assume an essentially extended chain conformation in the crystalline state.[29] Favoured by the relatively small size of the fluorine atom, such conformation

is found in fact for two of the three crystalline modifications of this polymer reported hitherto (i.e. mods. I and II).[30-33] However, in a recent X-ray refinement Hasegawa *et al.* propose a twisted chain model, with alternate values of the skeletal rotation angles corresponding to $180° \pm 8.4°$,[33] for both modifications I and II. The twisting provides some release (from 2·56 to 2·60 Å) to the shortest F ... F intramolecular contacts. The same result is obtained in a more effective way (shortest F ... F distance: 2·70 Å) in modification II, where the chain conformation is described by the succession ... TG$^+$T'G$^-$ ... with T $\equiv$ 179°, T' = $-$T, G$^\pm$ $\equiv$ $\pm$45° (Fig 7). Contrary to the other modifications, where
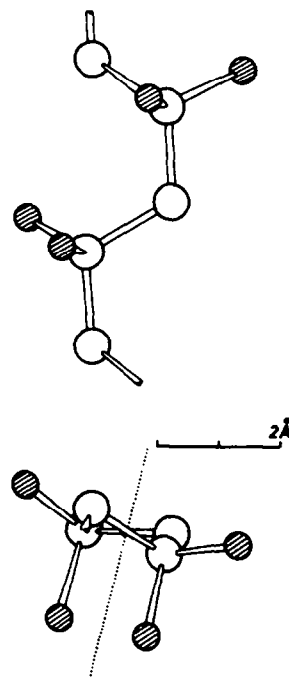

Fig 7. The ... TG$^+$TG$^-$ ... conformation of poly(vinylidene fluoride) (modification II). Fluorine atoms are shaded. The glide plane relating consecutive units is shown as a dotted line (end view, below).

Table 2. Chain parameters of some vinylidene polymers

Polymer name	Refs	Formula	ψ_1	ψ_2	C–CH$_2$–C	Chain symmetry
Poly(isobutylene)	22	$+CH_2-C(CH_3)_2+_n$	156·7°	47·5°	124°	8$_3$ helix
Poly(methyl methacrylate) (isotactic)	23, 24	$+CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C}-})_n$	185·5°	106·9°	124°	5$_1$ helix
Poly(-methylvinyl methyl ether) (Syndiotactic)	25	$+CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle OCH_3}{C}-})_n$	157°	59°	117°	5$_2$ helix with tranverse twofold axes ($s(5/2)2^{43}$)

the C–C–C angle is about the normal value of 112°, in modification II it appears to be significantly enlarged (~ 117°).

The relatively small size difference between oxygen (van der Waals' radius ~ 1·40 Å), fluorine (v.d.-W.r. ~ 1·35 Å) and hydrogen (~ 1·25 Å) is the basic reason why both poly(vinyl alcohol) and poly(vinyl fluoride) (PVF)[35] may be obtained as highly crystalline samples in spite of the irregular (i.e. atactic) placement of the substituents. In particular, poly(vinyl alcohol) can be considered as the first reported example of macromolecular isomorphism involving monomer units with opposite geometrical configuration.[36] In both cases the chain is *trans*-planar. Crystalline PVF is strictly isomorphous with PVF$_2$, modification I, and mixed crystals with this structure may be obtained both from VF/VF$_2$ copolymers and from co-crystallization of the two homopolymer chains.[31] Another example of a halogenated ethylene polymer which is capable to crystallize in spite of an irregular configuration is atactic poly(chlorotrifluoroethylene).[37] In this case the size of the substituents (v.d.W.r. of Cl ~ 1·70 Å; of F ~ 1·35 Å) is not as similar as in the previous cases. The chain conformation is fairly close to the *trans*-planar arrangement, the rotation angles being slightly shifted (about 10°) from the exact value of 180° so that the chain undergoes a uniform twist producing a helix with about 16·8 monomer units per pitch. This has some analogy with the case of

poly(tetrafluoroethylene) (PTFE), which has been shown to exist in at least four crystalline modifications. Two of these correspond to a 15$_1$ helix, another one to a 13$_1$ helix,[38] while the chain is *trans*-planar in the fourth modification, favoured by a high pressure (> 5 K bars).[39] It may be of interest to remark that modifications I and III of PVF$_2$, with a substantially planar chain arrangement, are also favoured by a high pressure.[32] On account of these facts, it is no surprise that the (predominantly) alternating ethylene/tetrafluoroethylene (TFE) crystalline copolymer also has a planar chain conformation.[40] The same arrangement was also found for the VF/TFE random copolymers, isomorphous with PVF, at least in the 0–75% molar composition in terms of TFE units.[31]

II Skeletal sequences of carbon atoms with side double bonds

The two polymers we will refer to in this section are poly(allene) (PA) and poly(dimethyl ketene) (PDMK). While both of them possess a helicoidal structure with two monomer units per turn (2$_1$ helix) in the crystalline state, PDMK may also be obtained in a crystalline modification (α-form), approximately characterized by a (TG$^+$G$^+$ TG$^-$G$^-$)$_n$ conformation[41] (Fig 8). Perhaps the most remarkable feature of this polymer conformation is that two adjacent monomer units are not symmetrically related, contrary to what is usually
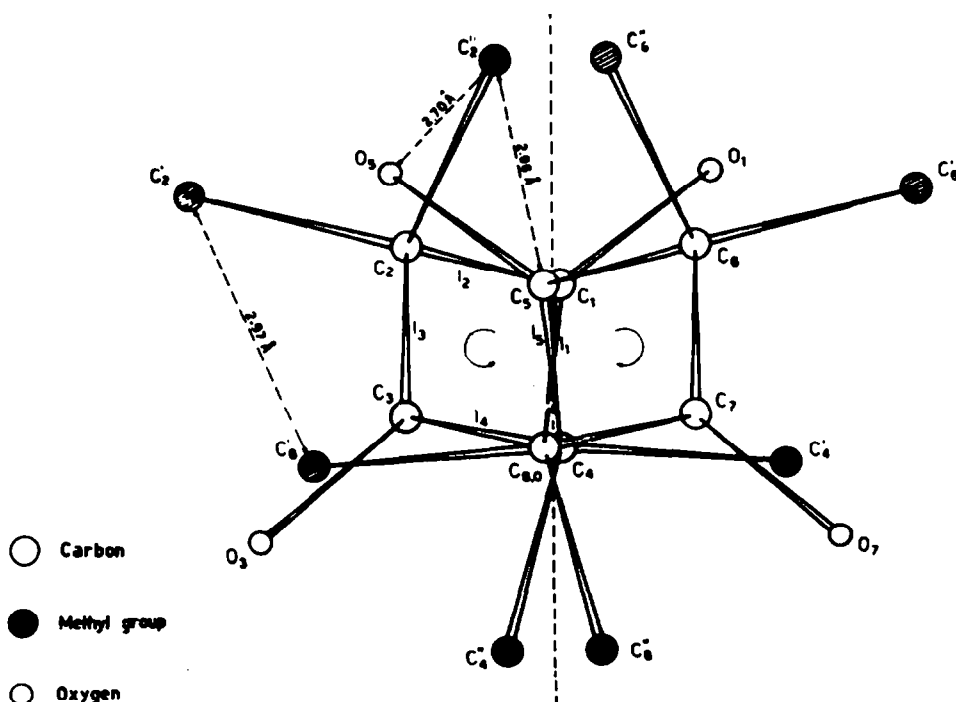

○ **Carbon**

● **Methyl group**

○ **Oxygen**

Fig 8. Chain conformation of the α-form of poly(dimethyl ketene) (end view). (Figure reproduced from Ref 41).

observed.[1] The asymmetric unit consists of two consecutive monomer units, and the polymer chain is generated through a glide-plane symmetry operation, as it may be seen in Fig 8. The G^+ rotation angles are 73° on the average, i.e. close to the value (72°) observed in the β-form, characterized by the 2_1 helix (Fig 9).[42] Both in this form and in the only reported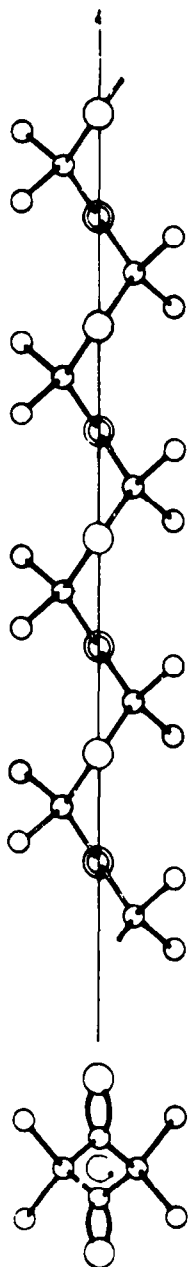 structure of PA,[43] the rotation angles have the same values throughout (uniform helix), so that in both cases twofold axes of symmetry arise, at right angles with the axis of the chain (Fig 9). The rotation angle found for PA is smaller than for PDMK (65° vs 72°), probably due to intramolecular repulsions involving the methyl groups in the latter polymer.

III Sequences of C atoms with double bonds along the main chain

Polydienes, Polyalkenamers. In this section we will deal with the crystalline polymers which can be obtained by catalytic polymerization either of conjugated dienes through 1,4 addition (poly - 1,4 - dienes) or of cycloolefins, through ring cleavage (polyalkenamers).[44] Poly(1,4 - buta - 1,3 - diene) may be regarded as belonging to both groups, since it may be obtained by polymerization of cyclobutene (polybutenamer)[44] as well as of butadiene.

The presence of double bonds along the chain entails a twofold consequence: (i) they are bound to a rigid configuration, either *trans* or *cis*, depending on the nature of the monomer and on the mechanism of polymerization; (ii) the potential energy minima inherent to the rotation around a C–C bond adjoining an unsaturated carbon correspond to $+ 120°$ (S$^+$, *skew plus*), $- 120°$ (S$^-$, *skew minus*) and 0° (C, *cis*) (Fig 10). Because of strongly unfavourable non-bonded interactions, the *cis* rotational isomer is not possible if the adjacent double bond is *cis* (Fig 10).[45]

Considering first the polydiene group, although there are reasons to believe that the *gauche* and *trans* conformations of the $(=)C–CH_2–CH_2–C(=)$ sequence should approximately have the same
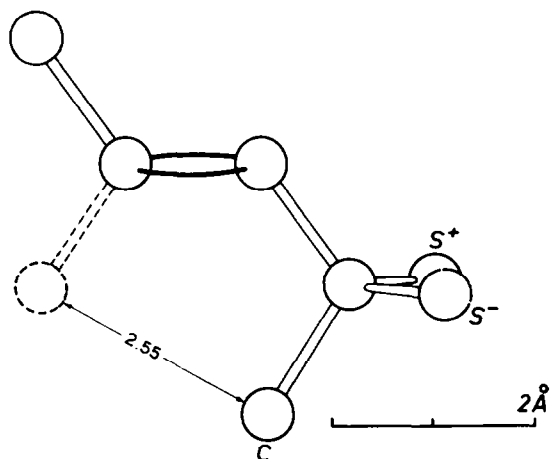

Fig 9.   Chain conformation of the β-form of poly(dimethyl ketene). (Figure reproduced from Ref 41).

Fig 10.   The *skew plus* (S$^+$), *skew minus* (S$^-$) and *cis*(C) conformations around a single C–C bond, adjacent to a double bond. The *cis* conformation is impossible if the double bond is also *cis* (see part of the figure shown with dashed lines).

energy content,[46] no *gauche* conformation has been reported hitherto in the crystalline state.

If the double bond is *trans* the most frequent chain conformation is described by the sequence $(S^-TS^+, trans)_n$ (Fig 11). Actually, this is related to the fact that most polymers of this type with asymmetric chain C atoms have been found to be isotactic: in fact, the above conformation would not satisfy the requirement of geometrical equivalence for a syndiotactic polymer and should therefore be improbable in that case. The only *trans* polymer which a syndiotactic configuration has been assigned to is tritactic, di-syndiotactic poly(di-isopropylmuconate), whose proposed chain conformation is $(S^+TS^-, trans, S^-TS^+, trans)_n$.[47a] A *cis* conformation around a C–C(=) chain bond has been found for α-guttapercha (chain conformation: $(CTS^+, trans, CTS^-, trans)_n$)[48] while β-guttapercha has the usual $(S^-TS^+, trans)_n$ structure.[49] This *cis* conformation is likely to appear in other stereoregular 1,4 substituted polybutadienes with 1,4 enchainment.[47b] A very interesting case for which *cis* rotational states have been proposed is the high temperature ($> 70°C$) modification of poly($trans$ - 1,4 - buta - 1,3 - diene) ($trans$-PBD).[50] The chain conformation, although being essentially disordered in itself, is characterized by a nearly cylindrical shape and by a nearly constant axial repeat between consecutive units. It appears to be satisfactorily described as $(XTY, trans)_n$, where X and Y stand for any of the three rotational states C,
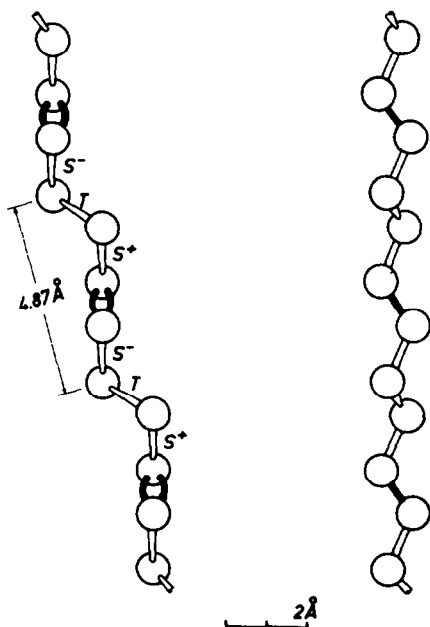

Fig 11. The $(S^-TS^+ trans)_n$ conformation found in the crystalline state for many polydiolefins with 1,4-*trans* enchainment (side views).

S^+ and S^-, under the condition that the centers of gravity of the consecutive monomer units do not deviate too much from a straight line. This constraint does not appear to lead to a severe reduction of the conformational degrees of freedom: a rough calculation of their number gives about $2 \cdot 5^{2n}$, compared with the theoretical value 3^{2n} for the unconstrained chain (n = number of monomer units). The experimental value of the entropy change involved in the solid–solid transition between the (ordered) modification stable at low temperature to the high-temperature form of *trans*-PBD, is consistent with the above model, being about twice as large as the calculated value (per monomer unit) $2R\ln2 \cdot 5$. Another *trans*-diene polymer whose chain conformation is not given by the usual $(S^-TS^-, trans)_n$ succession is poly($trans$ - 1,4 - 2 - n - propyl - buta - 1,3 - diene), where two possible conformations have been suggested, both in agreement with the observed chain repeat of $9 \cdot 2 \pm 0 \cdot 1$ Å, i.e. $(S^+TS^-, trans, S^-TS^+, trans)_n$ and $(S^+TS^+, trans, S^-TS^-, trans)_n$,[51] the first of which is identical to that proposed for poly(di-isopropylmuconate).[47] Another example of a *cis* conformation on a single bond adjoining an unsaturated carbon atom is provided by isotactic poly ($trans$ - 1,4 - penta - 1,3 - diene) ($trans$-PPD), where the *cis* arrangement involves the side methyl group, and the chain conformation is the usual one[52] (Fig 12). Contrary to this case, the C–C bond connecting the main with the side chain is in a *skew* arrangement for the two analogous polymers having an ethyl[53] and a propyl[54] instead of a methyl group (Fig 12). Interestingly enough, the conformation observed for *trans*-PPD could not be obtained in the other two polymers without close contacts ($< 2 \cdot 7$ Å) between the second C atom of the side group and the chain carbons.[52]

Among the poly(1,4-dienes) with a *cis* configuration of the double bond, poly(cis - 1,4 penta - 1,3 - diene) (cis-PPD) has been obtained both as an *iso*-[55] and as a *syndio*tactic[56] polymer. In the latter case the chain conformation is given by $(S^+TS^-, cis, S^-TS^+, cis)_n$, i.e. a glide-plane structure, analogous to that found for poly(cis - 1,4 - buta - 1,3 - diene)[57] (Fig 13). The most important polymer of this class is natural rubber, or poly(cis - 1,4 - isoprene), which a disordered structure involving XTY conformations (X, Y being either S^+ of S^-) has been recently proposed to (Fig 14), in agreement both with the X-ray data and with the rather low entropy of melting of the polymer.[58] Finally, the unusual conformation proposed for poly(cis - 1,4 - (2 - t - but) - buta - 1,3 - diene) is to be recalled (Fig 15). It corresponds to a 11_3 helix (i.e. eleven monomer units in three turns), whose rotational succession is close to $(S^+TS^+, cis)_n$.[59]

All the crystalline polymers obtained hitherto from catalytic ring-cleavage of cyclo-olefins show a *trans* configuration of the double bond.[44,60–62] The chain conformation in proximity of the double bond

C=4·85 Å

b)

Fig 12. Chain conformation of isotactic poly(*trans*-1,4-penta-1,3-diene) in the drystalline state. The asymmetric carbon atoms are shown with a star; the chain repeat is indicated. (Figure reproduced from Ref 52).
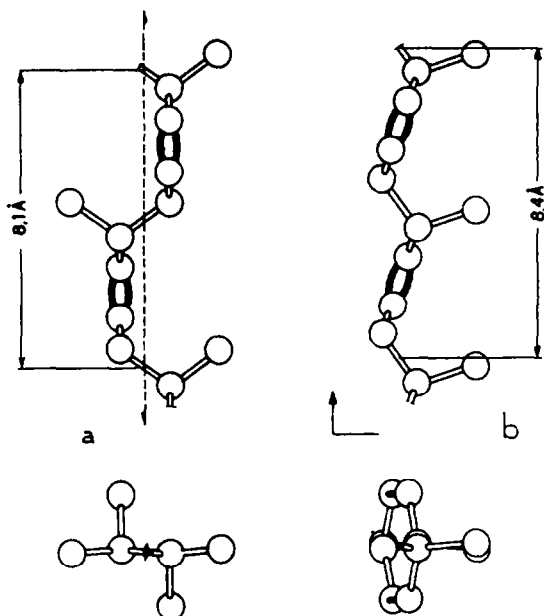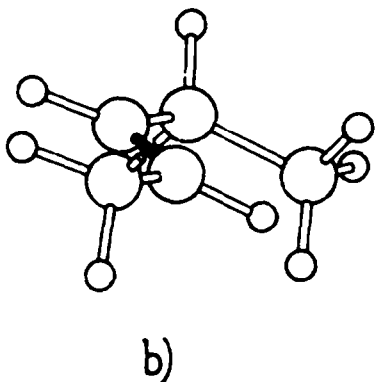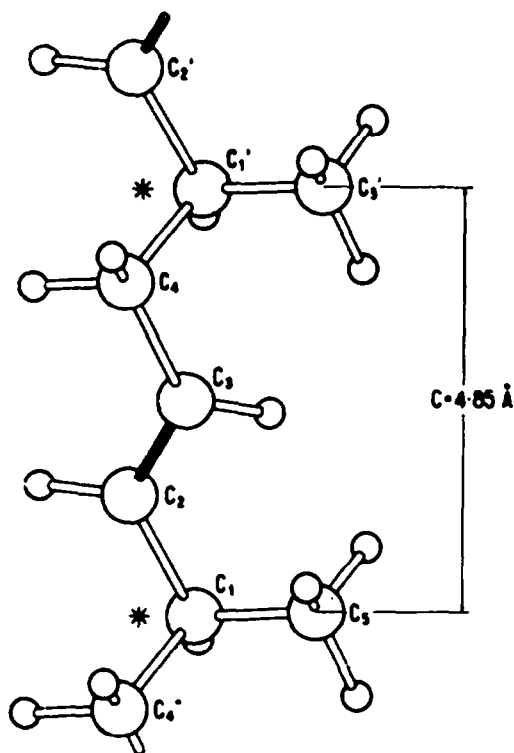

8.1Å

a

8.4Å

b

Fig 13. Chain conformation of isotactic (left) and syndiotactic (right) poly(*cis*-1,4-penta-1,3-diene) in the crystalline state. (Figure reproduced from Ref 56).

are related by twofold axes with mirror planes orthogonal to the chain ($s(2/1)m$ symmetry[63]). The polymers of the even series may crystallize in either of two different modifications, one of which strictly resembles the mode of packing of orthorhombic polyethylene.

IV *Skeletal sequences containing oxygen, or sulphur and saturated C atoms*

Polyoxides, polyformals and polysulphides. The conformation in the crystalline state of oxygen containing polymer chains of the above type as opposed to those consisting of C atoms only, is essentially characterized by the following rules.

(i) The intrinsic, threefold rotational potential associated with the C–O bonds, with minima at T, G^+ and G^-, is characterized by a much lower barrier (~ 1 kcal/mol) than that corresponding to the C–C bonds connecting saturated atoms (~ 3 kcal/mol).[64] As a consequence, the rotation angles around C–O bonds are more easily displaced from the exact staggered values; in particular, the average value of the *gauche*$^+$ (or *gauche*$^-$) rotation is larger than 75° (smaller than 285°).

(ii) The relatively small van der Walls' radius of the oxygen atom (~ 1.4 Å) compared with that of the methyl or methylene groups (~ 2 Å), together with the spontaneous tendency towards a compact space filling,[65, 66] make the *gauche* conformation of the O–CH$_2$–CH$_2$–O sequence preferred over the *trans* conformation, in spite of the electrostatic repulsion between the O atoms.

is invariably (S$^+$, *trans*, S$^-$) (or the opposite rotations), while the single C–C bonds not adjoining unsaturated atoms are all T. A remarkable general difference between the even and the odd series is that in the first case the consecutive units are related by simple translation along the chain with centers of symmetry (*t i* symmetry[63]), while in the second they'
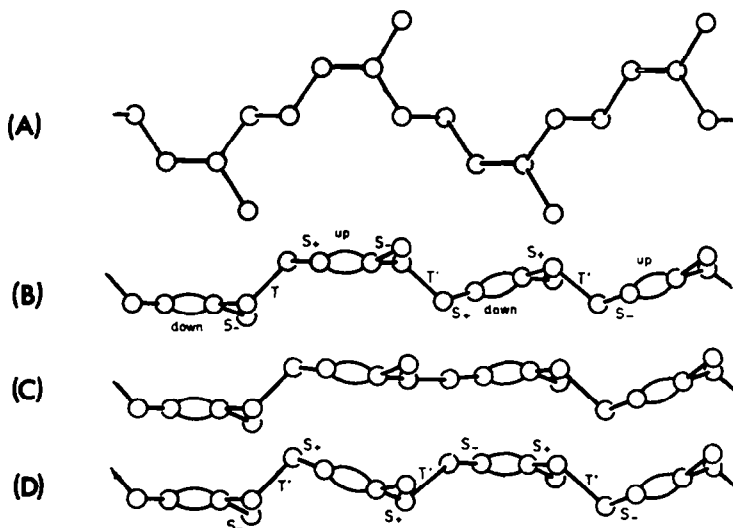
Fig 14. Model of the chain conformation of poly(cis-1,4-isoprene) in the crystalline state as viewed along an axis orthogonal to the average plane of the double bonds (A) and along an axis lying in this plane (B, C, D). B and D are nearly isosteric, differing because of the exchange of an S^-TS^+ with an S^+TS^- sequence. C represents a possible intermediate conformation. (Figure reproduced from Ref 58).
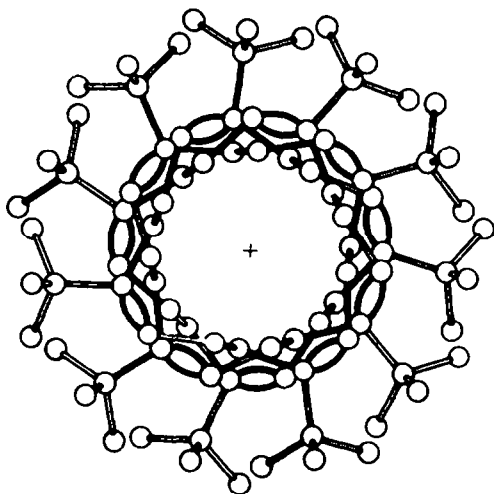

Fig 15. Chain conformation of poly(cis-1,4-2-t-butyl-butadiene), end view. (Figure reproduced from Ref 59).

(iii) Electrostatic interaction,[67] together with the above discussed steric factors, is responsible for the $O-CH_2-O-CH_2$ sequence being found always in a *gauche* arrangement. This is not the case for the $O-CH_2-CH_2-CH_2$ sequence, which is sometimes found in the *trans* conformation, possibly because in general the positive charge induced on the last methylene group is smaller for this sequence than for the previous one.

The rather shallow rotational potential minima [see the above point (i)] and the presumably low energy difference between *gauche* and *trans* states

of both the $O-CH_2-CH_2-O$ and the $O-CH_2-CH_2-CH_2$ sequences [cf the above points (ii) and (iii)] seem to be reflected in the large variety of polymorphic structures involving different chain conformations. Poly(oxymethylene), $(CH_2-O)_n$, exists in two modifications, both corresponding to uniform helices, one of which contains about 9 monomer units in 4 turns (constant value of the rotation angle $\psi = 78\cdot2°$),[68] while the other contains two units per turn ($\psi = 64\cdot2°$).[69] Poly(oxyethylene), $(CH_2-CH_2-O)_n$, is found in three crystalline modifications, two of which are complexes with $HgCl_2$.[70,71] The chain conformation of the pure polymer corresponds to a distorted helix with 7 monomer units in two turns.[72] The distortion is so appreciable that the largest difference between corresponding ψ values belonging to different monomer units is larger than 40°, showing once again that the conformational minima are quite broad if the packing forces may have such a large influence. The average conformation of the single monomer unit is approximately described as (TGT)$_m$, the *gauche* rotation angle being around the C–C bond. Both the complexed modifications have a chain structure containing a glide plane of symmetry (Fig 16). The first of them may be represented by the (TTTTTG$^+$TTTTTG$^-$)$_n$ succession, where the *gauche* rotations still correspond to C–C bonds and the asymmetric unit of the chain comprises two monomer units.[70] The other modification is approximately represented by (G$^+$G$^+$TG$^-$G$^-$T)$_n$, where T is around a C–O bond, and the asymmetric unit reduces to a single monomer unit.[71] Furthermore, it is worth mentioning that poly(oxymethylene) can take other conformations in the channel inclusion
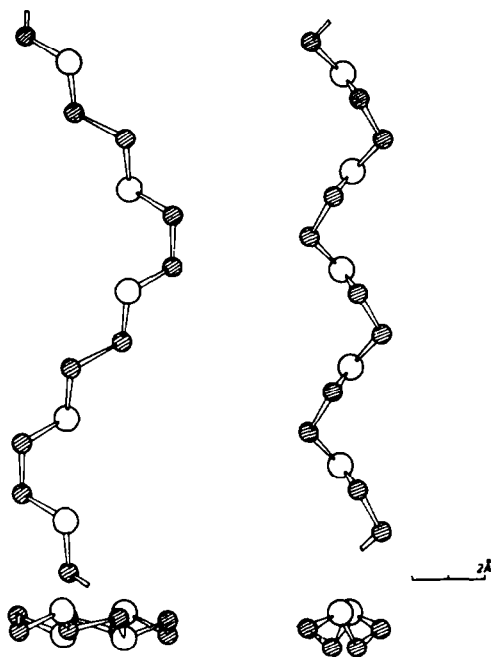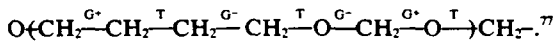
Fig 16. Chain conformations of two crystalline modifications of poly(ethylene oxide) complexed with $HgCl_2$ (mod. I, left; mod. II, right). Carbon atoms are shaded.

compounds with urea,[72] thiourea[73] and perhydrotriphenylene,[74] in the last case being close to the planar zig-zag conformation. Three crystalline modifications of poly(oxacyclobutane), $\{(CH_2)_3-O-\}_n$, have also been described.[75, 76] In the hydrated form (modification I) the chain is planar zig-zag, and chains of hydrogen-bonded water molecules join the macromolecules pairwise, giving rise to a ribbon-like structure.[75] Modification II is of the glide-plane type, with a $(TTTG^+TTTG^-)_n$ sequence, and the *gauche* conformations belong to $(CH_2-)CH_2-CH_2(-O)$ bonds. Finally, the chain conformation of modification III is characterized by a 2_1 helix and corresponds to a $(G^+G^+TT)_n$ succession, where the *trans* rotations belong to the C–O bonds. Both in mods. II and III the asymmetric unit coincides with the monomer unit.[76] Poly(1,3-dioxolane), $\{OCH_2O-(CH_2)_2\}_n$, is also reported to occur in three crystalline modifications, characterized by different repeat distances along the chain axis and therefore necessarily having different chain conformations.[65] The structure of modification II is described in detail:[65] the chain contains a crystallographic glide-plane which relates each monomer unit having a conformation of the type

$$\{O\overset{G^+}{-}CH_2\overset{G^-}{-}O\overset{T}{-}CH_2\overset{G^-}{-}CH_2\overset{S}{-}\}O,$$

with the following unit which is the mirror image. The rotation connoted with the symbol S (*skew*) ac-

tually corresponds to 94°. Such a large deviation from the exactly staggered value may be explained with the consideration that it favours a very compact chain arrangement and, on the other hand, it is a further proof of the low value of the inherent potential energy barriers around the C–O bonds. The chain conformation of poly(1,3-dioxepane), $\{OCH_2O-(CH_2)_4\}_n$, is also characterized by a crystallographic glide plane, the rotational sequence within the asymmetric unit being of the type

$$O\{CH_2\overset{G^+}{-}CH_2\overset{T}{-}CH_2\overset{G^-}{-}CH_2\overset{T}{-}O\overset{G^-}{-}CH_2\overset{G^+}{-}O\overset{T}{-}\}CH_2-.[77]$$

Poly(tetrahydrofuran), $\{(CH_2)_4-O\}_n$, is in a perfectly planar zig-zag chain conformation.[76, 78] Isotactic poly(t-butylethylene oxide), $\{CH_2-CH-O\}_n$, (with t-Bu side group)
gives two crystalline modifications, the one which is described in detail corresponding to a 9_4 helix structure.[79] Four chains are present in the unit cell of the racemic polymer as two pairs of optically opposite conformations. Each chain is either R or S, depending on the optical configuration of its asymmetric C atoms. Both the R and the S chains are present in the cell as a right-handed (d), as well as a left-handed (l) helix. In conclusion, the four chains may be classified as (R, d), (R, l), (S, d), (S, l). The two right-handed helixes—i.e. (R, d) and (S, d)—are described by the following conformations:

$$(-CH_2\overset{\psi_1}{-}CH(t-Bu)\overset{\psi_2}{-}O\overset{\psi_3}{-}CH_2\overset{\psi_4}{-}CH(t-Bu)-)$$
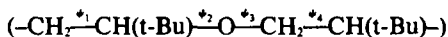
|	ψ_1	ψ_2	ψ_3	ψ_4	
(R, d) =	73°	263°	180°	73°	...
(S, d) =	263°	73°	183°	263°	...,

corresponding to potential minima with about the same energy.[79]

The crystalline isotactic polyaldehydes described hitherto all have a helix chain conformation with 4 monomer units per turn (4_1).[80] The rotation angles on the two skeletal bonds of each monomer unit are (82·5°, 225°) for poly(acetaldehyde), poly(propionaldehyde) and poly(n-butyraldehyde), while slightly changing for poly(isobutyraldehyde) (83°, 215°).[81] Especially because of the large deviation of the second rotation angle from 180°, the repeat distance per monomer unit along the chain axis is considerably smaller than for the isotactic vinyl polymers (1·2 Å *vs* at least 1·7 Å), so that the resulting conformation is very compact. Once again, the smaller size of the O atom compared with the methylene group and its electron polarization are responsible for the very tight chain structure. The shift from 225° to 215° of the second rotation angle of poly(isobutyraldehyde) produces a more extended conformation, in order to accomodate the bulky side groups.[80] The chain conformations of the three crystalline polymers poly(propylene oxide),[81]

{CH(CH₃)–CH₂–O}ₙ, poly(epichlorohydrin),[82] {CH(CH₂Cl)–CH₂–O–)ₙ and poly(propylene sulphide)[83] are closely similar and are nearly zig-zag planar, the largest deviation of the skeletal rotations from 180° being 20°.

V Skeletal sequences comprising {CO–O} and {CO–NH} groups

Polyamides, polyesters and polyurethanes. Considering the general sequence

$$-C-C'-X-C-$$
$$\underset{O}{\|}$$
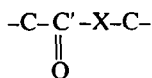
which corresponds either to the amide or to the ester group according to whether X is NH or O, it appears to be a sufficiently general proposition that all its atoms lie in the same plane. In fact, to our knowledge the largest deviations reported are less than 20°.[84, 85] As for the rotation angles around the C–C' or the X–C bonds, larger deviations seem to be possible without a significant expenditure of energy,[96, 97] although values in the neighbourhood of 180° are probably favoured by the tendency towards an extended chain conformation. For instance, polyamide chains containing even sequences of –CH₂– groups (e.g. nylon 66) assume an essentially zig-zag planar arrangement,[88] although it has been recently suggested[89] that a symmetrical shift by about 15° of both the rotation angles around C–C' and NH–C improves the formation of hydrogen bonds between the parallel chains, while being in agreement with the X-ray data. In the nylon chains with odd-numbered methylene sequences (e.g. nylon 6) two types of crystal structures have been observed (α and γ), the first of which is essentially made up by fully extended chains, making hydrogen-bonded sheets with an antiparallel arrangement.[90] In the second type the parallel chains may have the rotation angles around C–C' or NH–C shifted by as much as 100° from the *trans* value in order to improve the hydrogen-bond formation between themselves.[91] In a non-cyclic model compound of nylons, N,N'-diethyladipamide, the rotation angle around C–C' is approximately *skew* (124°).[92] Within an aliphatic polyurethane series {O–(CH₂)ₘ–OCONH–(CH₂)₆–NHCO}ₙ with different values of *m*, crystalline polymorphs similar to the α- and γ-forms of polyamides have been found, in the second of which the rotation angles around the O–CO and the N–CH₂ bonds are about 140° and 220°.[93] In the polyester, poly(ethyleneadipate), the rotation angles around CH₂–C' and O–CH₂ are 190° and 114°, respectively, implying considerable deviation from planarity.[84] In poly(pivalolactone), {CH₂–C(CH₃)₂–CO–O}ₙ, the rotation around C–CO bonds is 61° but, of course, the deviation from planarity is strongly favoured by the presence of

side methyl groups: the chain conformation is described by a twofold helix.[85]

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