Structural analysis of new basic multifunctional polymers by the comparison method

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(Received 23 July 1990; revised 5 December 1990; accepted 8 January 1991)

A method of structural analysis based on analogies and differences in the X-ray diffraction patterns of unoriented samples of chemically related polymers is proposed. By this method we study a family of new basic multifunctional polymers based on the repeat unit

$$\text{-S-CH}_2\text{-CH}_2\text{-X-CH}_2\text{-CH}_2\text{-S-CH}_2\text{-CH}_2\text{-Y-CH}_2\text{-CH}_2\text{-}$$

where the functional groups X and Y can be considered as independent variables. Eleven patterns are compared here and used in the discussion.

(Keywords: structure; comparison; multifunctional polymers; unoriented samples; X-ray diffraction)

INTRODUCTION

Recently the synthesis and properties of new basic multifunctional polymers have been reported[1-3]. Polymers of this type show a considerable actual or potential interest in several fields, finding application, for instance, as metal-ion complexing agents, as drug carriers and as components of biomedical devices. In all cases their repeat unit is given by the sequence:

$$\text{-S-CH}_2\text{-CH}_2\text{-X-CH}_2\text{-CH}_2\text{-S-CH}_2\text{-CH}_2\text{-Y-CH}_2\text{-CH}_2\text{-}$$

where X and Y are different functional groups.

Non-oriented samples of these materials have been considered for structural characterization by X-ray diffraction methods. Qualitative structural analyses for highly crystalline polymers are possible when reasonable hypotheses can be made for their molecular structures and when the corresponding diffraction patterns can be simulated by using models with a relatively high degree of order[4].

However, often, even in these simpler cases, this type of modelling cannot be performed, since the corresponding X-ray diffraction patterns are too poor. In view of these difficulties we developed a comparison method based on analogies and differences in the diffraction patterns of chemically related polymers. A preliminary and partial account of the structural results has already been presented[5-8].

EXPERIMENT AND CALCULATIONS

The preparation method for all the considered polymers has already been reported[1-3]. Intensities of X-ray diffraction patterns of unoriented samples were measured on a Philips powder diffractometer using Ni-filtered Cu Kα radiation at a scanning speed of $1^\circ\,\text{min}^{-1}$ from 3 to 40° (2θ). All the samples were in the form of powders and were pressed into sample holders so that in each case the goniometer θ–2θ axis could be put into coincidence with a sample smooth and flat surface.

For the derivation of reference structural models, the Chem 3D program for the Macintosh SE personal computer was used with the following standard parameters: bond lengths, CC = 1.52 Å, CN = 1.52 Å, CS = 1.79 Å, CO = 1.50 Å, C=O = 1.34 Å, SO = 1.75 Å, OC(Ph) = 1.34 Å, C=C = 1.34 Å; and bond angles, CCC = 109.47°, CNC = 109.47°, CSC = 109.47°.

THE COMPARISON METHOD

Small chemical differences in the monomers may give rise to large and characteristic differences in the polymer diffraction patterns, as a consequence of corresponding different packing of the polymer chains.

A method of structural analysis can be based on this fact, if those chemical differences can be introduced systematically into the monomers, thus 'designing' a family of polymers structurally related to each other. In this way, by an analogical procedure, taking advantage of possible parallelism of various features of the diffraction patterns, one can work out reasonable structural models. In order to study the capabilities of this 'comparison' method, we chose the family of new basic multifunctional polymers mentioned in the 'Introduction' and based on the repeat unit:

$$\text{-S-CH}_2\text{-CH}_2\text{-X-CH}_2\text{-CH}_2\text{-S-CH}_2\text{-CH}_2\text{-Y-CH}_2\text{-CH}_2\text{-}$$

where the functional groups X and Y can be easily introduced into the starting monomers and, therefore, can be considered as independent variables. Thus it is possible, for any given X, to study the effect of changing Y on the diffraction pattern and therefore on the degree of order. In order to clarify this procedure, the diffraction

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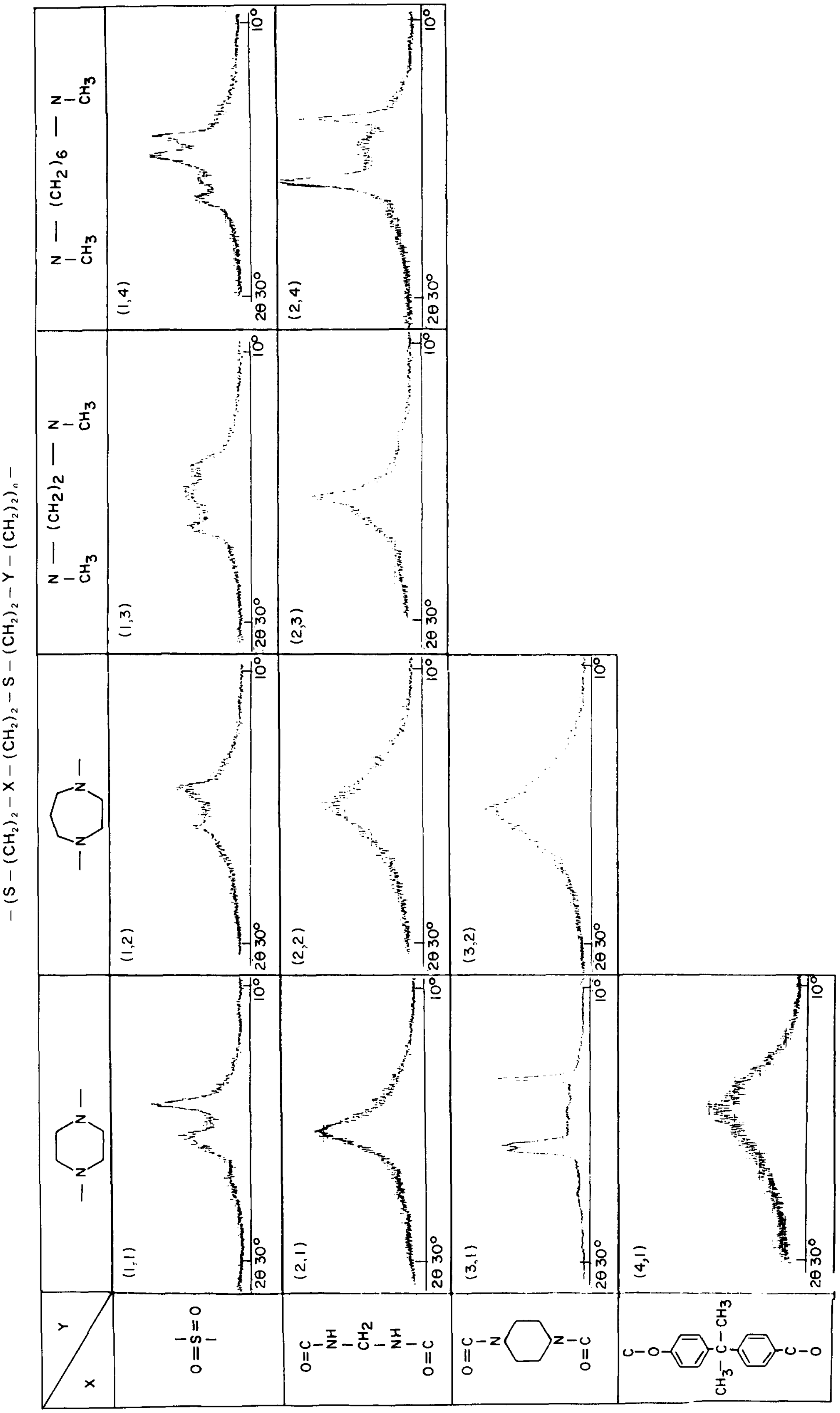


Figure 1 Analysed patterns in matrix form

Table 1 Calculated and observed chain lengths of the analysed polymers

Pattern	Chain length (Å) Calc.	Chain length (Å) Obs.
1,1	16.2	16.0
1,2	16.9	–
1,3	17.4	15.4
1,4	20.6	18.6
2,1	20.2	17.3
2,2	20.5	–
2,3	20.9	16.9
2,4	25.9	20.3
3,1	20.9	20.5
3,2	22.1	–
4,1	22.0	–

Table 2 Calculated and observed chain lengths (Å) of polymers (1,3), (1,4), (2,3) and (2,4)[a]

	(2,3)	(2,4)	Δ
c_{calc}	20.91	25.94	5.03
c_{obs}	16.9	20.3	3.4
δ	4.0	5.6	
	(1,3)	(1,4)	Δ
c_{calc}	17.38	22.43	5.05
c_{obs}	15.4	18.6	3.24
δ	2.0	3.8	

[a] δ values are differences between calculated and observed chain lengths; Δ values are differences between $(j,3)$ and $(j,4)(j=1,2)$ chain lengths

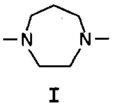
patterns obtained so far for this structural family are given in matrix form (see *Figure 1*).

In view of the fact that the proposed method is based on a comparison among diffraction patterns of materials constituted by very similar chain molecules, the hypothesis is implicitly made that all differences due to physical parameters, such as crystal growth rates, nucleation, etc., are a more or less direct consequence of the differences derived from the chemical substitution in X and Y and are therefore, in any case, distinctive of the latter factor.

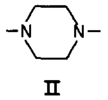
DISCUSSION

In the initial derivation of reference structural models the assumption was made that the molecules had an extended-chain conformation. Obviously the observed chain-length values are always smaller than the calculated ones, the only two possible explanations being (i) a helicoidal conformation or (ii) a monoclinic type of inclination of the molecular axes. In most cases (*Table 1*) the chain lengths calculated from the extended model are very close to the chain lengths derived from the position of an observed peak in the diffraction pattern. In these cases we have the important result that the molecular conformation is properly described by that of the reference model.

*Substitution of Y=***I** *for Y=***II**



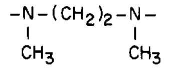
I



II

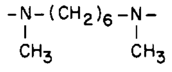
Comparison of these patterns clearly indicates that the packing of molecules containing the diazacycloheptane group (**I**) is more difficult. Indeed (1,1) vs. (1,2) and (2,1) vs. (2,2) show a clear broadening of the peaks, and in the case of (3,1) vs. (3,2) the considered substitution brings about destruction of the relatively high degree of order present in (3,1). It may be interesting to note that in the three cases the piperazine cycle (**II**) does not 'disturb' the zig-zag conformation of the rest of the chain, while the diazacycloheptane group (**I**) causes distortions in the molecular structure.

*Substitution of Y=***III** *for Y=***IV**



$-\underset{CH_3}{\underset{|}{N}}-(CH_2)_2-\underset{CH_3}{\underset{|}{N}}-$

III



$-\underset{CH_3}{\underset{|}{N}}-(CH_2)_6-\underset{CH_3}{\underset{|}{N}}-$

IV

In (2,3) one has two reflections (one broad and one sharp) and in (2,4) one has three reflections (one broad and two sharp). The broad reflections can be attributed to lateral packing of the molecules, while the sharp peaks can be identified as 0 0 *l*.

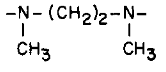
The sharpest lower angle peaks were given indices 0 0 4 and this attribution led to a *c* value of 16.9 Å for (2,3) and of 20.3 Å for (2,4). These appear to be reasonable values, implying a 'contraction' from the calculated chain lengths of the two corresponding molecules (20.91 and 25.94 Å respectively) in their extended conformations (*Table 2*).

As mentioned above, there are two possible explanations for this 'contraction', one being a monoclinic type of inclination of the molecular axes ($\beta = 130°$) and the other a helicoidal conformation. The fact that the relative contraction of (2,4) (22%) is larger than that of (2,3) (19%) favours the latter explanation, since in (2,4) a longer part of the chain can be coiled.

The difference between the two Y groups is given by a $(CH_2)_4$ chain. For this 'difference' group in a *gauche* conformation we calculated a length of 3.5 Å. This value compares well with the difference between the two c_{obs} values for (2,3) and (2,4), suggesting for the $(CH_2)_4$ group a conformation not very different from that considered. The introduction of this group generates a broadening as well as a shift towards smaller 2θ angles of the peak due to the lateral packing ($d = 4.6$ Å). Both effects can be attributed to a more difficult packing of the molecules in (2,4).

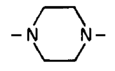
It is interesting to note that in the case of (1,3) vs. (1,4) a comparison between observed *c* values and calculated chain lengths leads to the same results (*Table 2*). Also here the relative contraction of (1,4) is larger than that of (1,3). The fact that the contraction of (1,3) and (1,4) is smaller than that of (2,3) and (2,4) respectively is an additional argument in favour of coiling as the major factor in the shortening of the chain length.

*Substitution of Y=***III** *for Y=***II**



$-\underset{CH_3}{\underset{|}{N}}-(CH_2)_2-\underset{CH_3}{\underset{|}{N}}-$

III



II

In (1,1) the first sharp peak ($d = 4.6$ Å) cannot be indexed as a 0 0 *l*, since no reasonable *l* can give a *d* value consistent with the observed chain length of ~16 Å. A reasonable 0 0 4 reflection for $d = 4.1$ Å can be identified

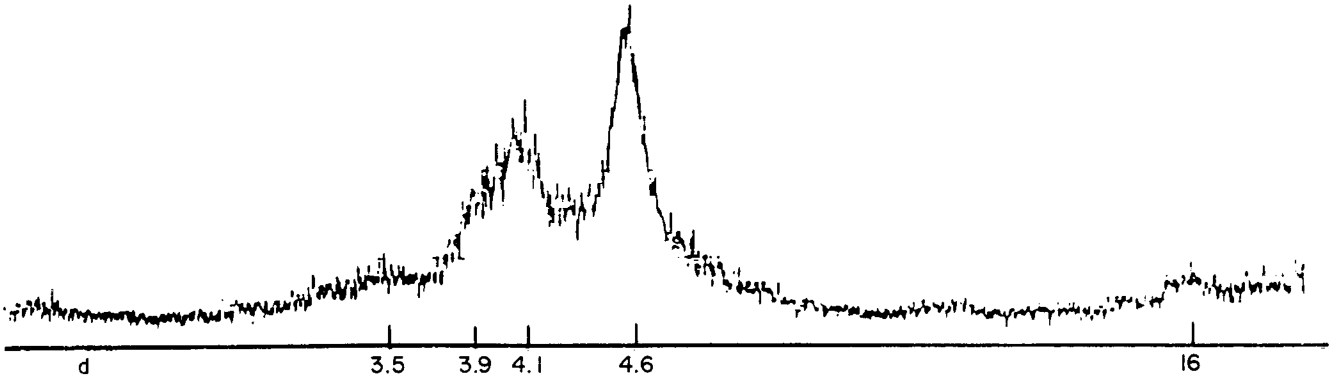


Figure 2 The (1,1) diffraction pattern

in the next peak, where another reflection is superimposed on it in its high 2θ side tail. One more peak ($d=3.53$ Å) can be clearly identified.

In (1,3) the first peak ($d=15.4$ Å) can be indexed as the 001 reflection. Thus the relatively sharp peak at $d=3.85$ Å can be identified as the 004 reflection.

In *Table 1* one can observe that while the calculated chain length is larger in (1,3) than in (1,1) the experimentally determined value in (1,3) is smaller. This fact can be explained only by admitting some coiling also in the *N*,*N*′-dimethylethylenediamine group (**III**).

In the pattern of (2,1) only one broad peak is present. In view of its shape and in view of the fact that in (2,3) the 004 reflection is detectable and that all (1,*j*) patterns show a relatively higher crystallinity, it is reasonable to assume that in the case of (2,1) the 004 reflection is superimposed on the 'amorphous' halo. In this hypothesis the conclusion reached in the case of (1,1) vs. (1,3) is confirmed.

A study of the (1,1) pattern

As stated above the first sharp peak ($d=4.6$ Å) in this pattern (*Figure 2*) cannot be given indices 00*l*. Any alternative indexing implies a high degree of order in the lateral packing of the chain molecules. Indeed the presence of two sulphur atoms in the chain and the fact that $X=-SO_2-$ (sulphonic group) make possible the bridging of adjacent molecules by oxygen atoms, thus generating a structure of superimposed sheets, kept together by van der Waals forces, or, possibly, a three-dimensional network of oxygen-bridged parallel molecules. Since bridging is possible only if a sulphonic group has the same z coordinate (the z axis is coincident with the c axis) of a sulphur atom of an adjacent molecule, the a axis must equal:

$$2\times\{2\times1.61\times\cos[(180^\circ-120^\circ)/2]\}=5.58\ \text{Å}$$

where 1.61 Å and 120° are the values of the SO bond and SOS angle, respectively, in polymeric SO_3 (ref. 9). In order to have a repeat distance in the direction of the SO bond axis, the term in braces is multiplied by 2. Two structural models are consistent with this kind of bridging. In model A the oxygen bridging occurs statistically along two mutually perpendicular directions, thus generating bundles of molecules and a tetragonal unit cell with $a=b=5.66$ Å. In model B the bridging occurs in only one direction and the sheets of chain molecules thus generated are kept together by van der Waals forces. In the latter model, for packing reasons, the superimposed sheets are shifted by $a/2$ and therefore the repeat distance along the b axis equals twice the van der Waals distance of ~4.3 Å. Thus, for this model, $b=8.6$ Å. For both models $c=16.2$ Å, as calculated for the extended chain. This value compares well with the observed chain length of ~16 Å (see above). The fact that the observed and calculated values for the c axis are so close shows that in this polymer the molecules have, in fact, an extended conformation, in agreement with the proposed model of oxygen bridging.

Table 3

h	k	l	$d_{(\text{calc})}$	$d_{(\text{obs})}$
0	0	1	16.0	16.0
1	0	2	4.6	4.6
0	0	4	4.1	4.1
1	1	0	3.9	3.9
1	1	2	3.5	3.5
1	0	4	3.3	
0	0	5	3.2	

On the basis of the above considerations the (1,1) pattern can be indexed, with all the strong reflections being only of the type 00*l* or *h*0*l* (see *Table 3*), meaning that there is no basis for choosing between model A or model B. It is interesting to note that the 102 reflection is the strongest and sharpest in the pattern. Indeed, as shown in *Figure 3*, the (102) planes are almost parallel to planes containing the strongly scattering S atoms. The same reasoning can be used for justifying the broad peak at $d=3.53$ Å (indexed as 112). For both models the structure in the *ac* plane is shown in *Figure 3*.

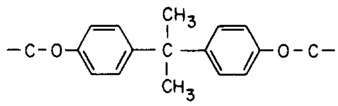
The structural model that can be obtained by considering that oxygen bridging occurs only between sulphonic S and one of the two other S atoms has an average unit cell with a c axis of ~1/5 of the chain length. However, on the basis of such a short axis it is not possible to index the pattern. The additional condition of establishing infinite –S–O–S–O–S– chains leads to the disordered model in *Figure 3*, where the c axis value is the same as that of the chain. On the basis of these cell parameters one can index the pattern as shown in *Table 3*.

The (1,1) and (1,3) patterns

While evidence was given (see above) for the coiling of the Y group in (1,3) and for the related shortening of the c axis, the model in *Figure 3* can be considered valid also in this case. However the (1,3) pattern is different from (1,1) in several important features. In the first place in (1,3) there is a very broad peak ($d = 4.36$ Å) which cannot be observed in (1,1) and also the 0 0 1 reflection clearly shows up. Moreover in (1,3) the peak at $d = 4.64$ Å (the 1 0 2 reflection) is much broader than in (1,1). All this broadening can be attributed to a disorder deriving from packing difficulties in (1,3), possibly due to steric hindrance by the bulky $-CH_3-$ groups. Following this reasoning, one may consider the (1,3) pattern as resulting from the superposition of an 'amorphous' pattern, with peaks at $d = 15.35$ and 4.36 Å (a pattern similar to those of (2,2) and (3,2)), and a 'crystalline' pattern similar to that of (1,1).

The (4,1) pattern

The conformation of X



based on the central 'tetrahedral' C atom, does not allow, for this polymer, the achievement of 'linearity' (not even approximately) in its chain. For this reason packing is difficult in this case and, as a consequence, the corresponding diffraction pattern is that of an amorphous material.

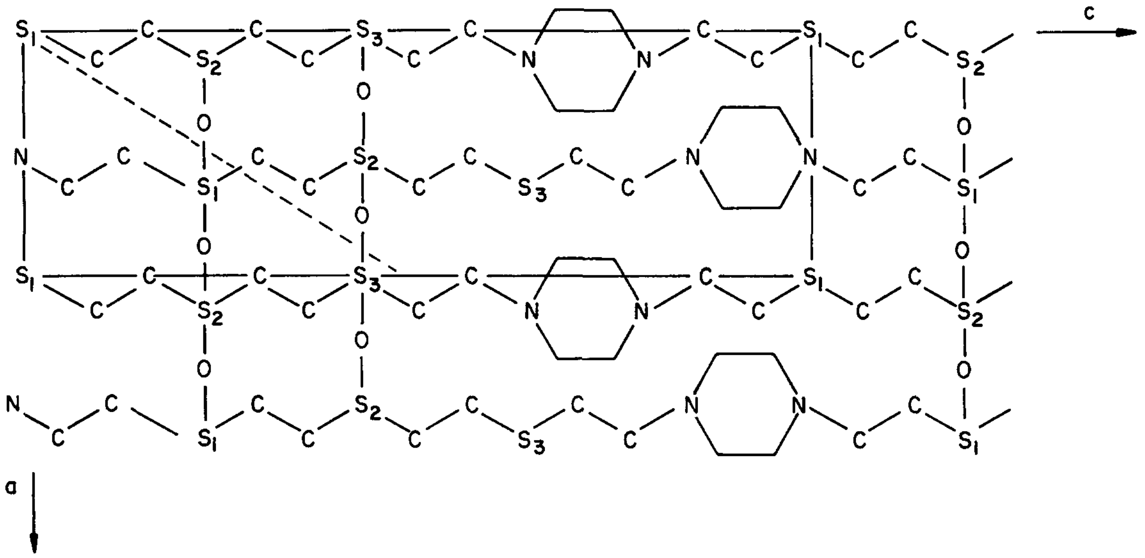


Figure 3 Structural model of (1,1) polymer. A projection of the unit cell along the *b* axis is indicated. The dashed line represents the trace of the (1 0 2) plane

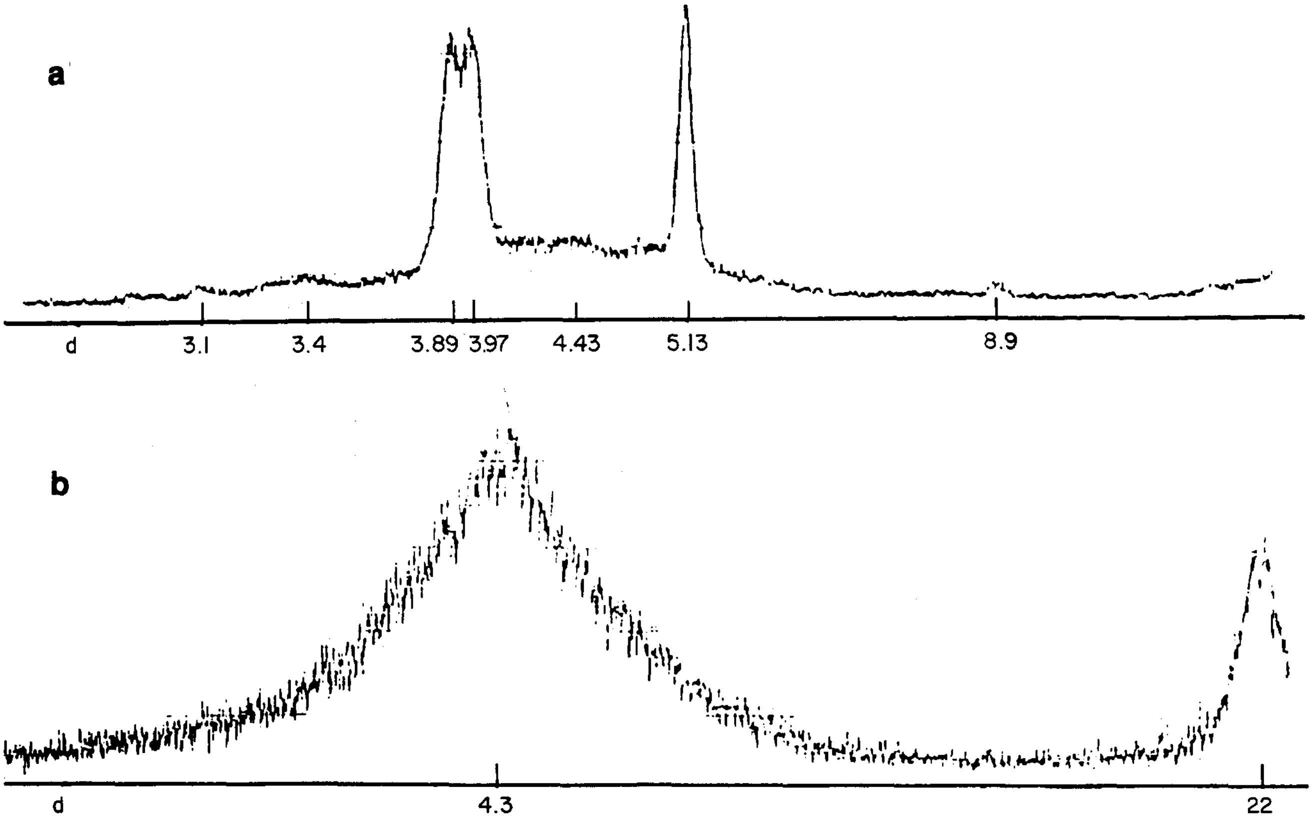


Figure 4 (a) The (3,1) and (b) the (3,2) diffraction patterns

Table 4

h	k	l	$d_{(calc)}$	$d_{(obs)}$
1	0	0	8.90	8.9
0	0	4	5.13	5.13
1	0	4	4.44	4.43
2	0	0	4.45	
1	1	4	3.98	3.97
2	1	0	3.98	
2	1	1	3.91	3.89
0	0	6	3.42	3.4
2	0	4	3.36	
2	2	1	3.11	3.1
2	1	4	3.14	
2	2	0	3.15	

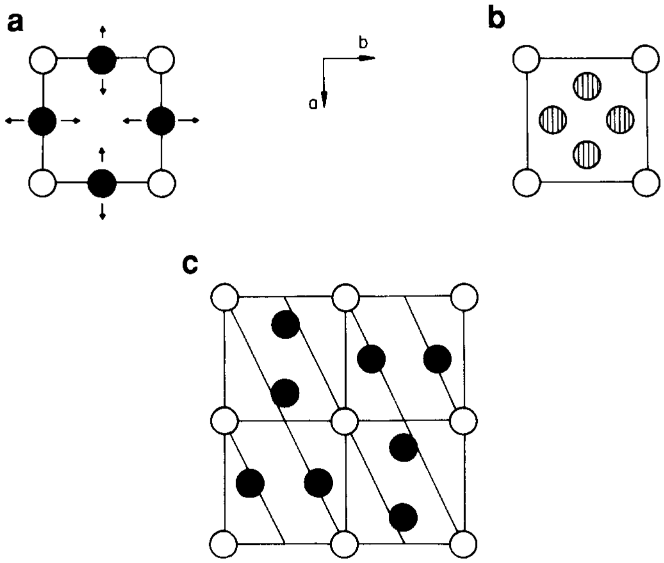


Figure 5 Structural model of (3,1) polymer projected along the c axis of the tetragonal cell (see text). The empty and filled circles represent the projections of the molecular chains. (a) The arrows indicate the splitting directions. (b) The average cell. The inner sites are occupied by chain molecules with a probability of 0.5. (c) A possible statistical structure. The (2 1 0) planes are indicated

Even the chain length does not appear to be well defined. Indeed, contrary to the case of amorphous patterns, where the identification of a low-angle reflection, whose d value can be attributed to the chain length, is common, no identification of this type is possible here, and only a very broad intensity distribution, with no peak, can be detected at low 2θ angles.

The (3,1) pattern

The (3,1) pattern (*Figure 4*) shows the highest crystallinity in all the studied systems. Three peaks (at $d = 5.13$, 3.97 and 3.89 Å) are very strong and sharp, with the last two peaks overlapping to a great extent. Four much weaker peaks are found at $d = 8.90$, 4.43, 3.4 and 3.1 Å. The sharpest peak (at $d = 5.13$ Å) can be given indices 004 if for the c axis one chooses a value of 20.5 Å, in good agreement with the value (20.92 Å) calculated for the extended-chain reference model. Obviously the fact that indices 004 can be reasonably attributed to this peak means that the conformation of the molecule is not very different from that of the model. Comparing this pattern with the (3,2) pattern due to a chemically similar molecule for which in Y a diazacycloheptane ring (**I**) is substituted for the piperazine cycle (**II**) (see also above), one should note that a very strong peak, characteristic of the chain length ($d = 22$ Å), is present in (3,2), while a corresponding peak is absent in (3,1). Owing to the similarity between the two molecules, this difference can be rationalized only by packing considerations, with the suggestion that in (3,1) the absence of 001 and the presence of a strong and sharp 004 imply packing of adjacent molecules with a relative shift of $c/4$. If the weak peak at $d = 8.90$ Å is considered as due to both the 100 and 010 reflections, indexing of all the other peaks in the (3,1) pattern is possible (*Table 4*), on the basis of a tetragonal cell with $c = 20.5$ Å. A model in agreement with this indexing of the pattern is that constituted by a pseudohexagonal packing with the molecular axes (parallel to the c axis) passing through points (0,0) and (1/2,1/2) of the cell base. However, the density, calculated on the basis of this model ($Z = 2$), equals $0.82\,\mathrm{g\,cm^{-3}}$, too low a value for a bundle of chain molecules of this chemical composition. A more reasonable value of the density for this unit cell is given for $Z = 3$ ($\rho_{calc} = 1.23\,\mathrm{g\,cm^{-3}}$). A possible model in agreement with this Z value is given in *Figure 5a*, with the molecular axes passing through points (0,0), (1/2,0) and (0,1/2). A better occupation of space could be achieved by considering the possibility of a statistical splitting of the molecules through (1/2,0) and (0,1/2) along the directions of the b and a axes respectively (*Figure 5b*). It is worth noting that for the latter model the 2 1 0 reflection is expected to be strong as it is that observed in the pattern.

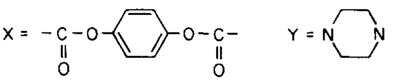
CONCLUSIONS

The proposed method, based on the systematic comparison of non-oriented diffraction patterns of chemically related polymers, led to many interesting results (see 'Discussion') that could not be achieved by a separate analysis of the measured intensity distributions.

It should be noted that in all cases, even for (1,1) and (3,1), where detailed models are proposed, uncertainties in the definition of a possible model, arising from a state of disorder, do not allow the calculation of a simulated pattern. As stated in the 'Introduction', simulation leads to meaningful results only if the model is ordered or if the disorder can be described by unambiguously well defined parameters.

In our opinion the possibilities of the method are many, the only problem being the 'design' of the family of polymers.

Work is still in progress for obtaining new results and completing the analysis of all the possible analogies and differences within the family defined in this paper. In particular, preliminary results on the polymer characterized by



are in the process of being analysed[8] and the family is being expanded, with the terms (3,3) and (3,4) in preparation.

ACKNOWLEDGEMENT

We acknowledge financial support by the Consiglio Nazionale delle Ricerche, Rome, Italy

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