Letters

Discusssion of "Microstructural characterization of "REFEL" (reaction-bonded) silicon carbides": Authors' reply

A number of points arise from the discussion of our paper [1] by Ogbuji *et al.* [2], not least of which is their misrepresentation of the "main thrust" of our original argument. We would also take issue with the evidence used by Ogbuji *et al.* to substantiate their claim to "have clearly established that the epitaxial deposit in our samples is definitely β–SiC". We will now address these issues in turn, firstly reaffirming the arguments in our original paper, secondly discussing the issues raised from them and finally presenting some experimental observations on the same samples of materials used by Ogbuji *et al.*

The question as to whether the epitaxial material in this particular range of reaction-bonded solids forms directly as α, or deposits as β and then transforms to α, is an interesting issue but was certainly not the main theme of our discussion of the microstructure of REFEL silicon carbides*. Rather, our paper was concerned with the detailed microstructural description of a selection of commercial REFEL materials together with the possible causes of variations in these microstructures. The principal conclusions were:

(i) that the new silicon carbide formed during the reaction did not take the form of a fine-grained β matrix, as had previously been reported (e.g. [3]), being neither exclusively fine-grained nor exclusively β;

(ii) that this new SiC could exhibit two distinct morphologies (associated with different nucleation sites), either occurring as an epitaxial coating (nucleated on the original α–SiC grit) or as fine-grained material appearing in the residual silicon (and presumed to have nucleated on the graphite);

(iii) that the epitaxial material, rather than the fine-grained material, was responsible for bulk cohesion;

(iv) that careful X-ray diffractometry, coupled with quantitative microscopy, revealed that the polytype distribution in the epitaxial coating in the material at the time it was examined was similar to that in the original α-grits and, therefore, that the grits had probably had a "seeding" action on the polytype distribution in the coating to produce new α–SiC;

(v) that the relative proportions of fine-grained (β) material and epitaxial (α) material in the final microstructures varied considerably due to differences in the relative importance of different nucleation sites caused by variations in green compact structures.

At the time our work was performed, there were no reported observations of REFEL which established points i to v, though epitaxial β–SiC coatings had been reported to occur in samples of reaction-bonded SiC prepared by Ford Motor Co. Research Laboratories (e.g. [4]).

The main criticism made by Ogbuji *et al.* concerns the structure of the new SiC formed as the epitaxial layer on the original grits and, in particular, they question whether the α-epitaxial layer observed by us formed *ab-initio* or developed via a transformation from an original β(3C) coating. In the absence of substantial remnants of partially transformed cubic material (which we did not observe), unambigious distinction between these two possible routes is practically impossible by observation of the final microstructure alone and, in the final analysis, is immaterial to the description of the final microstructure as observed and reported by us. For this reason, we did not include any discussion as to the possible different routes to the final microstructure of the epitaxial layer. However, we were aware of the possibility of the $\beta \rightarrow \alpha$ transformation playing a role, as is witnessed by the comment on p. 892 of the original paper that the 3C regions found to occur in the predominantly α material appeared as "occasional remnants of 3C stacking in grains which have predominantly transformed to the hexagonal (6H) structure". Further, it seemed prudent to leave discussion of this possible transformation until it had been investigated in much greater detail. This work is in process of publication, a lattice image ($\sim$ 15 Å $(0001)_{6H}$ spacing) electron micrograph of the 3C/6H interface in standard REFEL samples having been published by Smith *et al.* [5]. This

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micrograph is similar to that published by Clarke [6], who similarly concluded by selective area diffraction studies, coupled with lattice imaging techniques, that the new SiC material formed in his particular sample of REFEL was prominantly α with remnants of 3C stacking. Further aspects of the $\beta \rightarrow \alpha$ transformation, including HREM (~ 2.5 Å $(0006)_{6H}/(111)_{3C}$ spacing) observations of several α/β interfacial structures have also recently been published by Jepps and Page [7, 8, 9].

We would agree with Ogbuji *et al.* both that the $\beta \rightarrow \alpha$ transformation readily occurs in SiC during annealing (a range of structures being formed as a function of time in the temperature range 1600 to 2200° C [7, 8, 10], and that this transformation most probably occurs in the epitaxial layer during fabrication of reaction-bonded SiC. However, it is our contention that, in the range of commercial REFEL samples examined by us, any such transformation must have been virtually complete since the polytype distribution of the epitaxial coating was equivalent to that of the underlying α–SiC grits. Further, it should be stressed that our polytype identification was based on bulk X-ray diffraction data as well as highly localized TEM observation. Furthermore, whichever of the two routes is responsible for the genesis of the structure of the coating, the seeding effect of the substrate grit is critically important in governing the final polytype distribution, (as we emphasized originally). Thus, the arguments in paragraph 4 of Ogbuji *et al.* serve only to re-emphasize the seeding effect as it was described in the original publication, but do not allow any distinction to be made between seeding the epitaxial deposit during growth or during subsequent transformation.

Shinozaki *et al.* [4] have reported that the epitaxial coatings in samples of Ford reaction-bonded SiC comprise β–SiC which can be transformed to α during subsequent annealing in nitrogen in the presence of excess silicon [11]. Though we have never examined any Ford material, it seems more than likely that significant differences exist between the Ford and UKAEA (REFEL) versions of this material and have their origins in process variables such as the purity of initial materials, furnace atmospheres or thermal histories, etc. Therefore, it is interesting to note that attempts by Naylor (in collaboration with UKAEA) to confirm the occurence of the $\beta \rightarrow \alpha$ transformation in the epitaxial coatings, by arresting the processing of some REFEL samples at earlier stages than usual, still showed the epitaxial coating to be of mixed α polytypes with only slightly more β than normally occurring in the original α grits [12].

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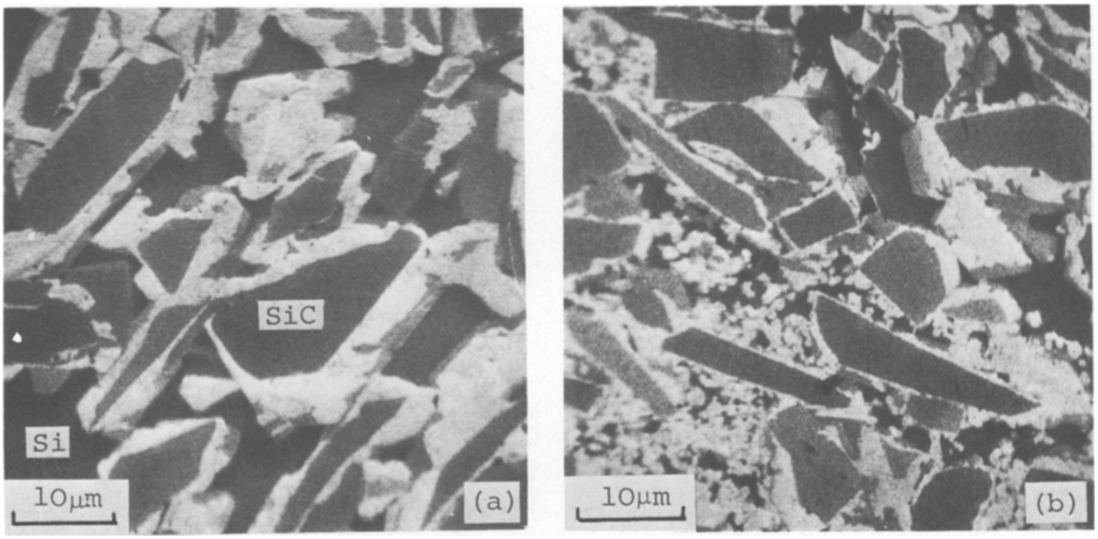


Figure 1 (a) and (b) Scanning electron micrographs of uncoated polished sections of the REFEL sample described in [2]. The secondary electron images clearly show the (predominantly lighter contrast) epitaxial coatings on the original α-grits [1], while (b) also shows some of the isolated regions of fine (β) SiC crystals occurring in the residual silicon. The irregular darker areas in (a) are silicon and this can be confirmed by back-scattered imaging [1].

the discussion of our work by Ogbuji *et al.* we requested a sample from the REFEL specimen used in their investigations. Both Professor Heuer and Dr. Shinozaki kindly sent us small samples (supplied by UKAEA c. 1974) and we have now had an opportunity of examining these in some detail. Both samples were similar and examination of several polished sections, using both optical and scanning electron microscopy (SEM) techniques (employing the purity sensitive contrast in the secondary electron image [1]), confirmed a homogeneous microstructure (similar to that of specimen SC8B in our original paper, but with a slightly larger overall grain size) with virtually all the new SiC comprising epitaxial coatings on the original α-grits (e.g. Fig. 1a). The sample from Professor Heuer also showed occasional instances of isolated clusters of fine crystals (presumed β) occurring in the silicon (e.g. Fig. 1b). Further, Table I shows the results of an X-ray diffractometry study performed on several sections cut from Professor Heuer's sample, while Table II shows the results of quantitative analyses of the series of SEM micrographs taken from the sample. These methods are described in reference [1] and the likely errors stated, though, remembering that the estimation of the fraction of 3C by X-ray diffractometry relies on peak subtraction (the 3C peaks all being common with those of other polytypes), the 3C figure may be somewhat less reliable than the rest. Hence, of the SiC present, ~ 60% is in the form of epitaxial coatings while only ~ 4% of the SiC material is of the 3C polytype. Thus, comparison of these two sets of results clearly establishes that, as observed on the sections we have examined and allowing for any errors in the X-ray analysis, *it is simply impossible for any substantial proportion of the epitaxial coatings to be cubic (3C).* The polytype distribution is again very similar to that expected in the original grit seeds [1].

TABLE I X-ray diffraction data [1]

Polytype	Occurence as a % of the total volume of SiC
6H	~ 86
4H	~ 2
15R	~ 9
3C	~ 4

(likely errors ~ 2% of the total volume)

TABLE II Quantitative microstructural analysis [1]

Feature	Volume Fraction %	
	Whole Sample	SiC only
Silicon	12.6 ± 1.8	
Original SiC grit	35.1 ± 1.8	~ 40
Epitaxial SiC	52.3 ± 4.3	~ 60
Fine SiC	insignificant	

With regard to transmission electron microscopy (TEM) studies of these structures, we would like to re-emphasize the point made in our original paper; namely that, while TEM is excellent for the examination of local microstructural character and defects, the features shown in isolated micrographs can be totally misleading in cases such as this and bulk structure must be interpreted in terms of self-consistent results arising from a number of quantitative microstructural techniques. From continuing work performed in this laboratory, it has been established that it is relatively easy to find remnants of 3C stacking in REFEL SiC (e.g. [5]), but very difficult to reliably distinguish whether or not these belong to the original seeds or to the new epitaxial material. This is not simply a stereological (sectioning) problem, but rather a question of independently establishing the detailed extent, geometry, and continuity of the epitaxial material in any grain which is being examined in an arbitrary thin section. Thus, not only are there difficulties in attempting to unambiguously correlate the various structural regions shown in the TEM micrographs of Ogbuji *et al.* with the macroscopic structural features of Fig. 1, but these micrographs/diffraction patterns show no significant fraction of wholly untransformed β–SiC. Thus, we would suggest that Ogbuji *et al.* should at least confirm the polytype distribution in their sample by a means other than TEM before claiming from this evidence alone that all the epitaxial material is still cubic. Given these reservations, it may be that Ogbuji *et al.* have examined some uncharacteristic areas of their REFEL samples by TEM, particularly, since, in a letter to us, Dr. Shinozaki stated that his samples "were not homogeneous and thus it was difficult to select a suitable area as a starting sample to observe development in microstructures as annealed in molten silicon".

We have been able to prepare two foils for TEM investigation from Professor Heuer's sample and these were extensively examined in a Philips EM

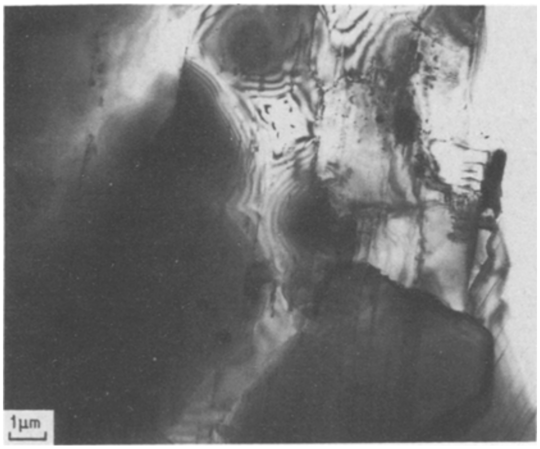


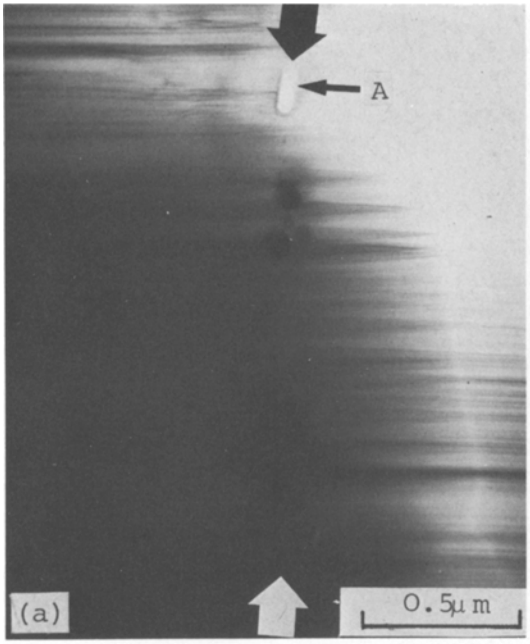
Figure 2 A bright field transmission electron micrograph showing a general view of part of the polycrystalline SiC aggregate in a specimen prepared from the REFEL sample discussed in [2]. Most grains display varying degrees of faulting, but nothing stereologically consistent with partially transformed or faulted 6H epitaxial coatings surrounding the original grain cores. However, extensive grain by grain examination using lattice imaging technique, revealed small regions of 3C stacking, α/β transformation interfaces and mixed stacking sequences (see Figs. 3 and 4).

300, operating at 100 kV, following our standard polishing and ion-beam milling procedures [1]. In areas thin enough to allow 100 kV TEM observations to be made, we have been unable to reproduce the observations of Ogbuji *et al.* in that no extensive regions of either untransformed or partially transformed 3C material were found nor were any features observed which could be correlated with "grain cores" etc. (e.g. Fig. 2). Also no diffraction patterns from predominantly cubic materials were observed (c.f. Figs. 2 to 4 of [2]). However, Fig. 3 shows "typical" observations from an area believed to possibly contain an epitaxial interface (as suggested by the line of voids/inclusions shown in Fig. 3a (c.f. Fig. 6 of [1]). Fig. 3b shows the diffraction pattern common to both sides of the interface while Fig. 3c is a lattice image showing the continuity of the ~ 15 Å $(0001)_{6H}$ fringes (i.e. α-6H stacking including a high density of stacking faults) across the region. However, we would stress that this image is specific to this region and a large number of similar images would have to be taken to unambiguously determine the exact structure (in terms of amount of 3C remaining, degree of faulting, twinning etc.) of any epitaxial coating (assuming its location could be reliably determined). In the same way, Fig. 4 shows features which are relatively easy to observe in many REFEL samples, namely, small untransformed regions of 3C material bounded by stepped $\{112\}$3C/6H interfaces together with regions displaying a range of α stacking sequences, faulting and long period structures (as further witnessed by the extraneous spots and streaks along (c* in diffraction patterns). Such regions probably account for all the 3C content of this sample and often occur both in extensive, otherwhise perfect 6H regions and in the vicinity of grain boundaries – an observation suggesting that they may be a feature of the epitaxial material.

As a consequence of our TEM investigations reported both here and elsewhere, we would suggest that lattice imaging is a rather more quantitative means of specifying the structure of local regions of SiC specimens than the selected area diffraction evidence used throughout reference [2]. Most powerful of all would be a combination of high resolution electron microscopy to fully elucidate local stacking sequences [13] coupled with secondary electron information (to locate the coatings/grits) in STEM. However, as described in [1], we have had no success in obtaining impurity contrast images from very thin foils (presumably due to reduced electrical conductivity leading to slight specimen charging).

Thus, while Ogbuji *et al.* may feel that we are guilty of an error of omission in not discussing, in more detail, the possible role of the $\beta\rightarrow\alpha$ transformation in microstructural development in REFEL SiC, we certainly have not either overlooked or misrepresented the experimental fact that in the REFEL materials originally studied, together with the sample in question here, the epitaxial coating consists of mixed α polytypes (predominantly 6H or 15R) with occasional remnants of twinned, faulted or partially transformed 3C. In the final analysis, the epitaxial coatings either never have been, or are no longer, *predominantly* cubic.*

*A more ready means of investigating both the character and relative orientation of the coating/seed is to examine REFEL thin sections using polarized transmission (or reflection) light microscopy. Such observations establish that there is no evidence for isotropic coatings on individual grains which appear uniformly birefringent. Further, the optic orientation appears uniform within each crystal [10]. However, these observations are subject to the same reservations regarding sectioning etc. as using TEM (see text).



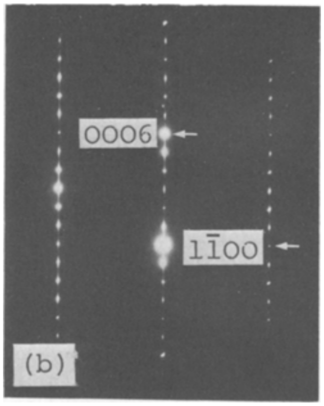


Figure 3 (a) Part of one grain in the thin sample of REFEL silicon carbide shown in Fig. 2. The row of voids/inclusions (arrowed) probably delineates an epitaxial interface between the original grit and the SiC formed during reaction-bonding. Extensive stacking faults can be seen to cross this interface. (b) The diffraction pattern observed on both sides of the interfacial area after tilting the grain close to an exact $\langle 11\bar{2}0\rangle$ beam direction [1]. Both the streaking along c* and the alternate sharp and diffuse appearance of the $000l$ and $1\bar{1}0l$ reflections suggest extensive faulting of the 6H material together with the presence of arrays of three-layer twins [8]. (c) A lattice image of the area around the prominent cavity (A in Fig. 3a) taken axially using 0000, 0001_{6H} and $000\bar{1}_{6H}$ and showing the ~ 15 Å periodicity of the $(0001)_{6H}$ planes. The faulted 6H structure can be seen to completely continuous across the possible epitaxial interface.

A further point also calls for comment in that Fig. 1 of Ogbuji *et al.* which shows an optical micrograph of REFEL SiC, is described as showing "the epitaxial deposits of the β–SiC on the α–SiC C crystals... revealed by electrolytic etching...". The accompanying text is somewhat contrary to this stating that "Fig. 1 ... does not reveal the polymorphic modification of the epitaxial deposit" and we would like to confirm that this latter statement is the correct one since the use of etching to distinguish the polytypic modifications of SiC is wholly unreliable [14]. Indeed, the very means of action of the commonly-used etchants (i.e. formation of silica) renders their behaviour far more sensitive to purity and crystallographic orientation than to polytype [10]. Thus the partition of

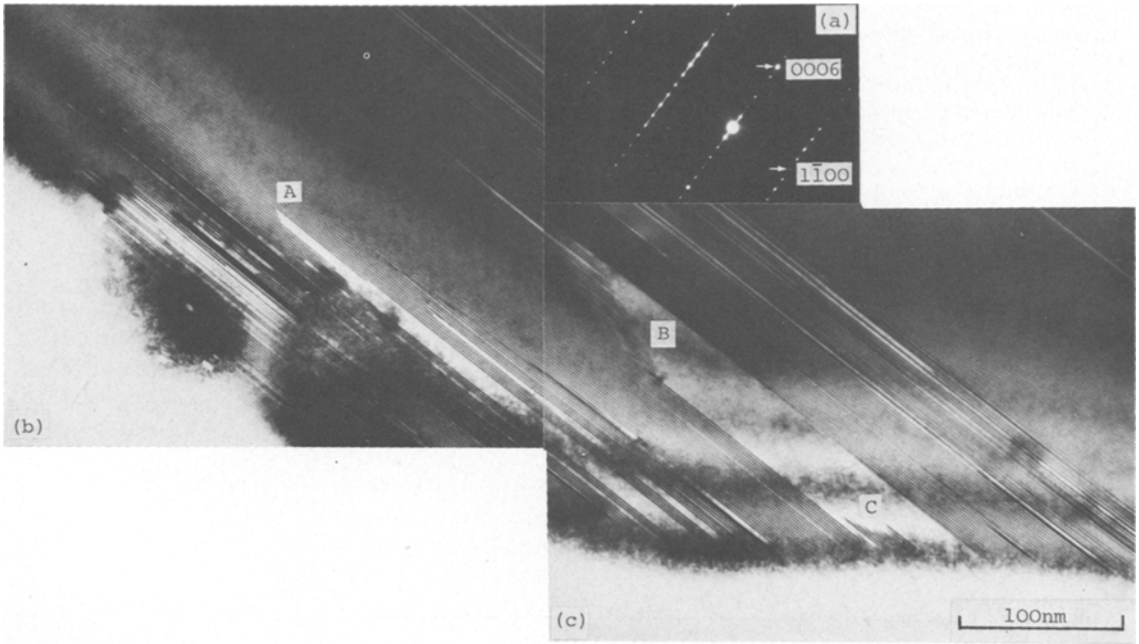


Figure 4 (a) A $\langle 11\bar{2}0\rangle$ diffraction pattern from a region found to show some remnants of 3C stacking. (b) and (c) Axial lattice image micrographs (taken using $0000, \pm 0001_{6H}, \pm 0002_{6H}$) showing the ~ 15 Å spacing of the $(0001)_{6H}$ planes together with some areas of ~ 7.5 Å fringes. The area can be seen to comprise regions of perfect 6H stacking, a number of regions showing faulted 6H stacking together with various other structural periodicities and some small (featureless) remnant regions of 3C stacking bounded by 3C/6H interfaces exhibiting $(0001)_{6H}$ unit-cell-high steps. (e.g. A, B and C).

impurities between different polytypes, or even the stabilization of particular polytypes by particular impurities, is the probable basis of the apparent phase sensitivity of various etches. However, since differential etching behaviour can be caused by different impurity distributions/levels in regions of uniform crystal structure (as here, where the α-epitaxial coatings are usually purer than the seed), no unambiguous correlation can be made between the features exhibited by etched SiC surfaces and phase distributions without recourse to confirmatory structural evidence [10].

In conclusion, we would agree with Ogbuji *et al.* that polytypic transformations almost certainly play an important role in determining the distribution of crystallographic structures observed in REFEL, and other reaction-bonded forms of SiC. However, a fully quantitative understanding of the microstructure of these materials, particularly with regard to the location of the various polytypes, requires self-consistent deductions to be made from a range of microstructural techniques at differing levels of resolution. In such cases, the examination of restricted specimen volumes by TEM alone can provide misleading results.

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A dielectric study of cellulose fibres

It appears from the literature that little work has so far been reported on the dielectric properties of cellulose fibres. Cellulose is one of the most important organic substances and has been subjected to thorough analysis by various techniques [1–3]. The directional dependence of the properties of fibres is now of wide interest as a means of producing desirable properties by inducing preferred orientation. A study of the dielectric property is of importance as it provides a measure of the amorphous fraction of the material and is sensitive to orientation effects, mobility effects and to the number and interactions of the dipoles participating. In view of this we have extended our previous work on electrical anisotropy [4] to the case of cellulose fibres. The result of measurements along both the longitudinal and transverse directions of some natural cellulose fibres are reported.

Natural cellulose fibres of ramie, hemp and jute were chosen for this study. A study of its crystallinity defects, etc., has been reported [5]. These fibres were first purified and delignified. The samples were prepared in the same way as reported earlier [4]. Dielectric measurements were carried out on a precision capacitance bridge GR716 in the frequency range 10^5 Hz by applying a resonance curve method.

The results are illustrated in Figs. 1 to 3. It is found that the dielectric constant and loss factors are highest for jute, followed by hemp and ramie. All these fibres possess the same molecular structure. i.e. cellulose I structure. The difference is mainly due to differences in the amorphous and crystalline fractions in the fibres. Thus we can conclude that the amorphous fraction is the greatest in jute, followed by hemp and ramie.

The most interesting features of the results are a sharp increase of dielectric constant and a fall of loss factor along the fibre direction, i.e. the longitudinal direction compared to the transverse direction. This is certainly not due to an increase in amorphous fraction, as in that case the loss factors would also increase. It is an established fact that the crystallinity is greater along the fibre direction in these fibres, thus we can conclude that dipoles are arranged in these molecules along the longitudinal direction, i.e. the chain direction, and the higher mobility of the dipoles along the longitudinal direction compared to the transverse direction, is the cause of anisotropy in the fibres.

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