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"HOMOGENEOUS" AND "HETEROGENEOUS" CELLULOSE TRIESTERS AND A CELLULOSE TRIURETHANE: SYNTHESIS AND STRUCTURAL INVESTIGATIONS OF THE CRYSTALLINE STATE*

HANS STEINMEIER AND PETER ZUGENMAIER
Institut für Physikalische Chemie der T.U.-Clausthal, D-3392 Clausthal-Zellerfeld (F.R.G.)
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ABSTRACT

Structural investigations were carried out on new cellulose derivatives prepared by heterogeneous and homogeneous reactions. X-ray examination of heterogeneously prepared crystalline cellulose triesters and a triurethane provided new insights into the packing of chains in cellulose microfibrils and in these products. The results were compared with those given by the corresponding homogeneously prepared derivatives. The side-chain conformations for various triesters deviate to some extent from the all-*trans* arrangement of the bonds of the ester groups.

INTRODUCTION

Hetereogeneous reactions on cellulose, particularly acetylations, were carried out by Staudinger to study the influence of the morphology or supermolecular structure of cellulose on the reactivity of the hydroxyl groups. Freudenberg produced cellulose derivatives with the goal of elucidating the constitution of cellulose after degradation. For morphological investigations the substitution reactions have to be carried out without degradation of the polymer, if the starting material and the product are to be compared. The acetylation of cellulose with acetic anhydride and pyridine at 60° is one example which fulfills the requirements of such a "polymer-homologous" reaction well[1]. No noticeable degradation of the cellulose backbone is observed even after a very long reaction time. On the other hand, strong degradation eliminates the differences in reaction behaviour between various cellulosic materials. Staudinger *et al.* were able to show with such experiments that various cellulose modifications such as native Ramie, and mercerized, precipitated, and inclusion cellulose exhibit different reactivities in the acetylation reaction, *i.e.* the reactivity is dependent on the morphology or supermolecular structure. A change in morphology may be difficult to detect directly,

*Dedicated to the memory of Karl Freudenberg on the centenary of his birth.

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except when such a change is accompanied by a change in the conformation or packing of the chains.

Heterogeneous cellulose derivatives have only been of scientific interest in the past. However, it has been discovered recently that these derivatives can be employed successfully in the enantioselective separation of stereoisomeric compounds[2]. The reason for this performance seems to lie in the morphology of these polymers rather than in any unusual packing of the derivatized cellulose chains.

The heterogeneous synthesis of cellulose derivatives and conformational as well as packing analysis are the subject of this investigation. The difficulty of conducting a heterogeneous reaction of cellulose is mainly in the selection of optimal reaction parameters such as reagents, temperature, preconditioning, and activation. On the one hand achievement of a high degree of substitution requires the complete accessibility of the hydroxyl groups, which become available through swelling or solvent inclusion. On the other hand strong swelling either for preconditioning or during a reaction may result in extensive or complete destruction of the supermolecular order. In the present work the heterogeneous conversions have been carried out exclusively on Ramie cellulose fibres. The heterogeneous character of a reaction on cellulose fibres can be verified, if the product is physically comparable with the starting material. The preservation of the fibres has to be evident on a macroscopic and microscopic scale, and the preservation of order has to be detected by X-ray analysis.

EXPERIMENTAL

For the heterogeneous reaction Ramie cellulose fibres (0.5 g) were treated in a mixture of pyridine (50 mL), acid anhydride (10 mL), and two drops of perchloric acid for about 14 days at room temperature. However, the reaction with benzoyl chloride and phenyl isocyanate to produce heterogeneous* tri-*O*-benzoyl cellulose (TBC I) and cellulose tricarbanilate (CTC I) was carried out without perchloric acid. The remaining fibres were then washed in aqueous methanol and subjected to X-ray analysis, which showed the original orientation of the fibres.

The homogeneous* products, tri-*O*-benzoyl cellulose (TBC II) and cellulose tricarbanilate (CTC II), were obtained by a pretreatment of cellulose (1 g, Ramie or Avicel) with pyridine (25 mL) for ~30 min at 80° to swell the material. Benzoyl chloride or phenyl isocyanate (10 mL) was then added dropwise and stirred for 12 h at 80°. The homogeneous solution was precipitated in methanol, dissolved in dichloromethane and reprecipitated in methanol.

The degree of substitution was qualitatively determined by i.r. spectroscopy, and found to be higher than 2.9 for all products. The X-ray experiments were carried out in a flat film camera with Ni-filtered CuK_α radiation and calibration

*In accord with established usage in the polymer literature, the terms *heterogeneous* and *homogeneous* are used here to designate materials produced under heterogeneous and homogeneous reaction conditions, respectively.

with CaF_2. The average degree of polymerisation for Ramie was ~7000 and for Avicel ~120.

RESULTS AND DISCUSSION

The investigated heterogeneous carboxylic acid esters and the urethane of cellulose were produced as described in the experimental section. The fibres were tested after 24 hours of reaction, when an X-ray exposure and an i.r. spectrum were taken. The i.r. spectra and X-ray patterns showed no changes as compared with the starting material when formic acid and valeric anhydride were used as reagents, despite a reaction time of up to 14 days. A small change consisting of one additional reflection in the X-ray pattern appeared when butyric anhydride was applied, probably due to a reaction at the surface of the microfibrils. As expected the heterogeneous modification of cellulose triacetate (CTA I) was obtained after a reaction time of two days with acetic anhydride as reagent. An X-ray pattern of CTA I is shown in Fig. 1a, and in Table I the *d*-spacings of the reflections are listed

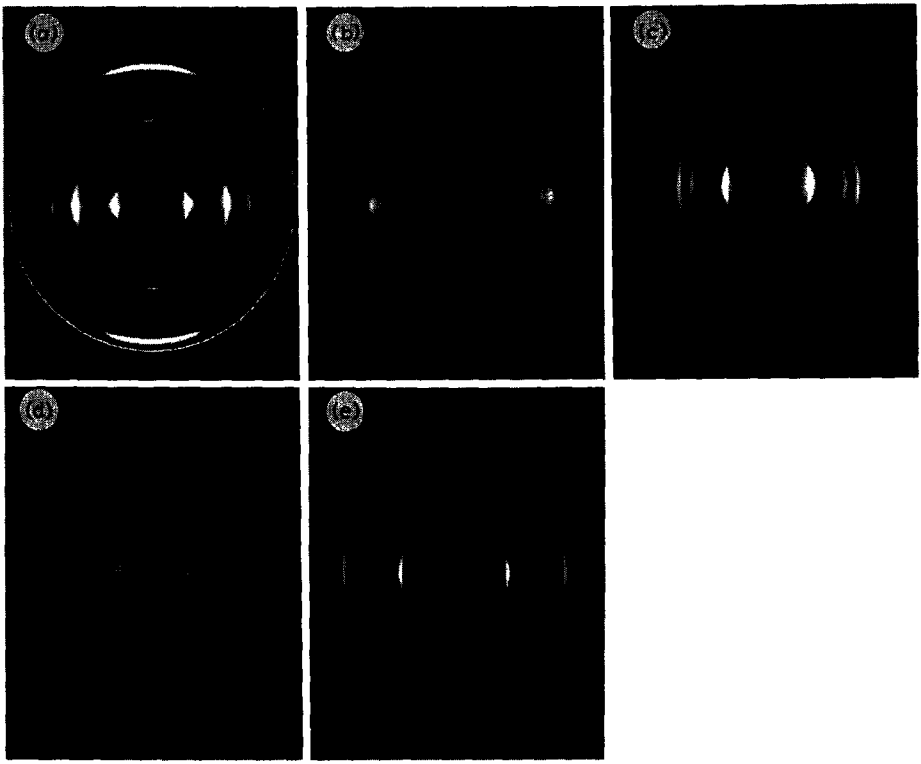

Fig. 1. X-ray fibre patterns of (a) CTA I, (b) CTP I, (c) TBC I, (d) CTC I, and (e) TBC II. Fibre axis is vertical. Calibration with CaF_2.

and compared with those reported for CTA I (refs. 3,4) and CTA II (ref. 5) in the literature. X-Ray patterns of heterogeneously prepared CTA are sometimes found to contain parts of the homogeneous pattern and amazingly show the same orientation. Traces of CTA II are visible in the form of reflections having the same arcing as those from CTA I. Such superimposed X-ray patterns seem to be present in materials examined in other studies[3,6]. The comparison of *d*-values (Table I) with those of CTA II shows that a clean heterogeneous reaction was accomplished in the present investigation.

To propose a unit cell for CTA I on the basis of an X-ray fibre pattern with a few recorded reflections is rather difficult, and any such effort has to be considered preliminary until a final structure determination is available. In one approach, we performed calculations, using a newly developed computer program[7], on data obtained by Roche *et al.*[3] for CTA I prepared from a liquid-crystalline solution. Best agreement between measured and calculated *d*-spacings was obtained with an 8-chain, orthorhombic unit cell having $a = 12.20$ Å, $b = 45.25$ Å and c (fibre axis) $= 10.45$ Å. A 4-chain unit cell with one half of the a dimension is still a possible solution. An 8-chain unit cell in which a is doubled and b one half of the above best solution ($a = 24.85$ Å, $b = 22.30$ Å, $c = 10.49$ Å) is also possible, as is a 4-chain solution with $a = 12.40$ Å (one half of the 8-chain unit cell), b and c unchanged.

An evaluation of the data from our X-ray pattern (Fig. 1a) results in similar unit-cell proposals. Two 8-chain orthorhombic unit cells having $a = 12.8$ Å, $b = 45.5$ Å, c (fibre axis) $= 10.45$ Å and $a = 25.4$ Å, $b = 22.9$ Å, $c = 10.45$ Å show almost the same overall deviations between measured and calculated *d*-spacings. A 4-chain solution also has to be considered, involving a reduction to one half of the a-dimension of the second proposal. A 2-chain unit cell for CTA I can be ruled out. A few further possible solutions for indexing the X-ray pattern have also been ruled out for various reasons. Large unit cells seem to be required for CTA I, confirming earlier findings[6]. The intensity distribution of the fibre X-ray pattern of Fig. 1a closely resembles that of tri-*O*-methylcellulose (TMC)[8], tri-*O*-methylmannan (TMM)[8], and 6-*O*-acetyl-2,3-di-*O*-methylcellulose[9], for which very elongated 4-chain orthorhombic unit cells, having $a = 4.64$ Å, $b = 43.2$ Å, c (fibre axis) $= 10.42$ Å, were proposed on the basis of an electron diffraction study of single crystals of TMC. Pairs of antiparallel cellulose chains are present in the TMC structure.

The X-ray diagram of a cellulose fibre after reaction with propionic anhydride, which results in cellulose tripropionate (CTP I), is shown in Fig. 1b. A second-order meridional reflection is clearly visible from tilted fibres of CTP I, as found for CTA I fibres (Fig. 1a). This fact, and the size of the fibre repeat (c dimension) of *ca.* 10.4 Å, point to a 2/1 helical conformation for both derivatized cellulose chains[6]. The shape of a basic unit of structure for CTA I and CTP I is represented in Fig. 2. The homogeneously prepared cellulose tripropionate (CTP II) forms a left-handed, threefold (3/2) helix[6,10], which is regarded as the stable structure because all C–C bonds in the ester groups are in *trans* positions.

TABLE I

EXPERIMENTAL *d*-SPACINGS OF THE X-RAY PATTERNS OF FIBRES OF CTA I, VARIOUSLY PRODUCED, AND OF CTA II.

CTA I[a,b]			*CTA II*[a,b]
Stipanovic and Sarkov[c]	*Roche* et al.[d]	*This study*	*Roche* et al.[e]
Equator			
11.4 vs	11.3	11.45	10.43 vs
8 m			8.40 vs
6.10 m	6.02	6.11	6.67 st
5.50 vs	5.43	5.57	5.50 m
			5.21 st
4.35 st	4.23	4.38	4.71 m
			4.09 w
3.93 w		3.98	3.85 w
			3.70 m
			3.47 w
3.35 w	3.30	3.32	3.32 w
2.73 w			
First layer line			
			9.67 w
7.70 w	7.73	7.72	7.96 w
			7.39 m
			6.53 w
			5.66 w
4.95 st	4.96	4.96	5.04 st
			4.84 m
			4.15 w
			3.89 w
3.63 w	3.66		3.62 w
			3.52 w
			3.31 w
			3.15 w
2.71 w			2.90 w
Second layer line			
4.78 w	4.74	4.84	4.79 m
			4.45 m
			4.16 w
3.95 w	3.97	3.99	3.88 w
3.65 w	3.64	3.68	3.74 w
			3.45 w
			3.29 w
3.13 w	3.11		3.07 w
Third layer line			
3.33 st	3.33	3.33	
3.02 w	3.02	3.05	
2.89 w	2.88	2.90	
2.62 w	2.60	2.63	

[a]Spacings in Å. [b]Intensities: vs, very strong; st, strong; m, medium; w, weak. [c]Ref. 3. [d]Ref. 4. [e]Ref. 5.

For a 2/1 helix such a side-group conformation has high potential energy because of very short contacts between the ester groups at C-3 and C-6 of adjacent residues. This problem of short contacts within a cellulosic 2/1 helical chain disappears when some of the ester groups at C-3 adopt a *gauche* conformation[10], which is easily recognized in the representation of CTP I in Fig. 2b, and which leads to higher conformational side-group energy. The 2/1 helix of the CTP I crystalline structure is a metastable form of packing, which can be converted into a stable 3/2 helical form by melting and recrystallizing the sample. The constraints that produce the metastable CTP I must reside in the supermolecular structure of the microfibrils of Ramie cellulose. These constraints hinder conversion into the stable CTP II structure. This argument also holds for the transformation of CTA I into CTA II. Although both forms of CTA are represented by 2/1 helices, they show small but significant differences in the deviations of their cellulose chains from an exact 2_1 screw axis. This is mirrored in different intensity distributions of weak, odd-numbered meridional reflections.

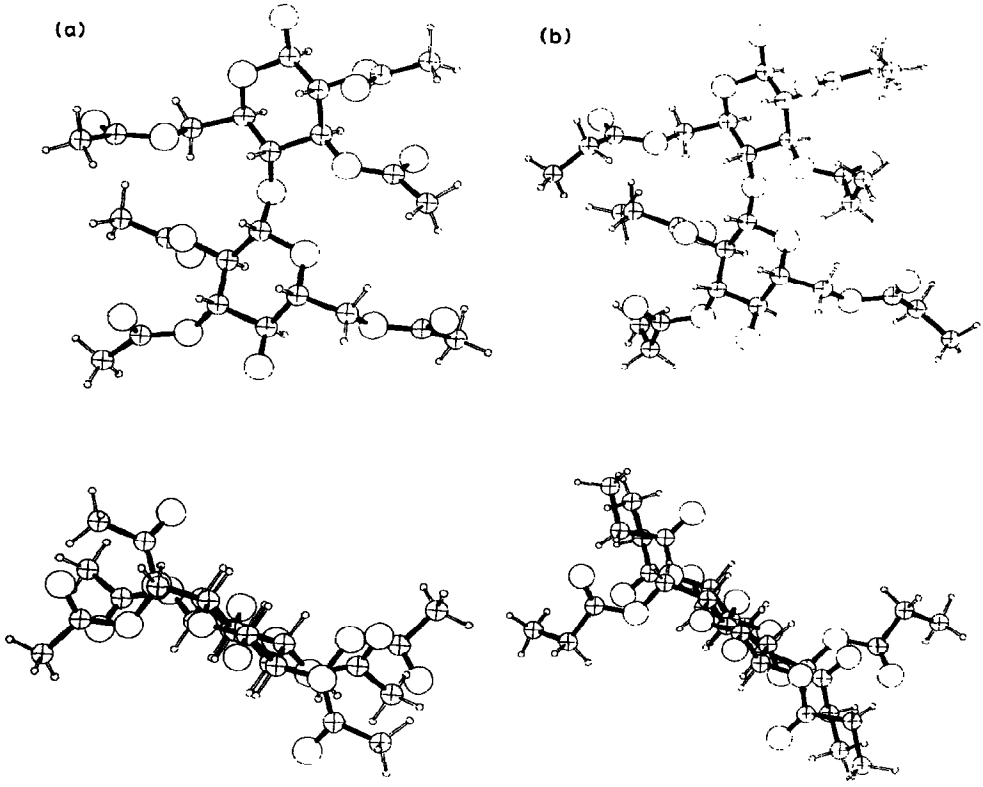

Fig. 2. Basic unit of the conformation of (a) CTA I or CTA II (2/1 helix) and of (b) CTP I (2/1 helix) in two projections.

The X-ray diagrams of heterogeneously prepared tri-*O*-benzoylcellulose (TBC I) and cellulose tricarbanilate (CTC I) are shown in Fig. 1c and d. The homogeneous crystalline fibres of TBC II and CTC II have been previously analyzed, and the results have been presented in detail elsewhere[11,12,13]. Threefold, left-handed (3/2) helices have been established for both TBC II and CTC II, and these are also present in TBC I and CTC I as shown by X-ray patterns almost

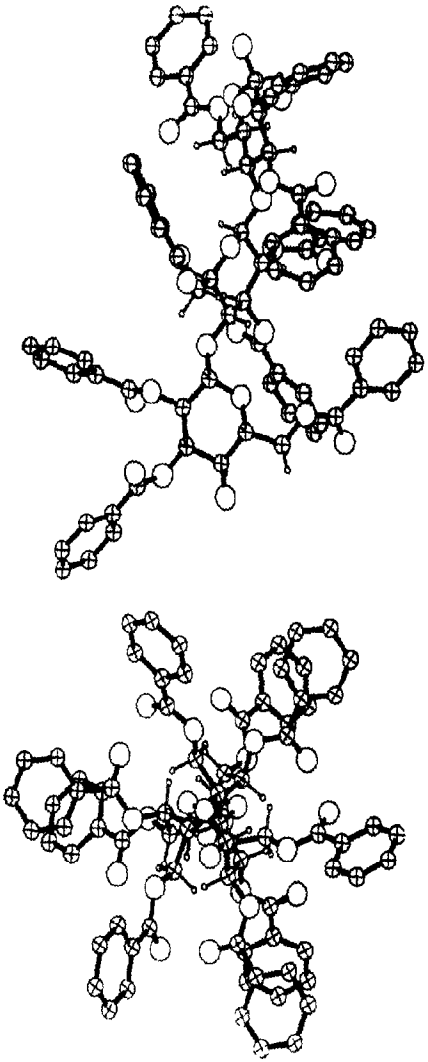

Fig. 3. Basic unit of the conformation of TBC I or TBC II (3/2 helix) in two projections.

identical in intensity distribution, including a third-order meridional reflection, and in *d*-spacings. The TBC II pattern is reproduced for comparison in Fig. 1e. The orthorhombic unit cell for TBC I contains two chains and is of size $a = 20.7$ Å, $b = 11.9$ Å, c (fiber repeat) $= 15.2$ Å, while that for TBC II is about 5% larger in volume, having $a = 21.2$ Å, $b = 12.2$ Å and $c = 15.2$ Å. In the X-ray diagram of CTC I (Fig. 1d) the layer lines are missing as in the pattern of CTC II. However, the appearance of the two patterns and the *d*-spacings on the equator are the same for a dry fibre.

The crystallographic unit for TBC (Fig. 3) may serve as a representative example for a 3/2 helix. TBC I and TBC II on the one hand and CTC I and CTC II on the other hand show negligible differences in their X-ray reflection intensities and, remarkably, in the size of their unit cells confirming the idea that the only difference between the heterogeneous and homogeneous fibres of Ramie cellulose may be their respective supermolecular structures and not different chain polarities. A diffusion of chains from different cellulose microfibrils with opposite polarities as proposed for inclusion complexes of cellulose[14] can be ruled out for the heterogeneous derivatives. Such large perturbations during a chemical reaction should lead to the stable products and conformations and are contradicted by the behaviour of the CTA I and CTP I structures.

CONCLUSIONS

Almost 60 years ago the primary chemical structure of cellulose was resolved with the strong involvement of Freudenberg. However, the question of chain polarity in the microfibrils of cellulose is still debated today, and although a parallel packing of chains is favoured by many authors, experiments were performed, the results of which cannot be explained by a parallel chain arrangement[15]. Our structural investigation on a newly heterogeneously derived triester of cellulose (TBC I) and on cellulose tricarbanilate (CTC I) clearly points towards an antiparallel packing of the chains in the crystalline fibre, and consequently towards an antiparallel chain arrangement in the native Ramie cellulose fibres. Both derivatives, TBC I and CTC I, exhibit a 3/2 helical chain conformation and unit cells almost identical with those of the homogeneously derived fibres of TBC II and CTC II, respectively. A similar distribution of atoms of the chains in the two differently produced fibres is necessarily inferred from the two X-ray diagrams, which show closely comparable intensity patterns. An antiparallel packing of the chains of the homogeneously prepared polymers is commonly accepted. An identical unit cell of any materials, produced in different ways, requires the same packing interactions, and hence one must assume the same chain arrangements in TBC I and TBC II or CTC I and CTC II. A chain inversion between the starting material, Ramie cellulose, and the heterogeneous triesters can be ruled out for the reasons given earlier in this paper.

An agreement in unit cell size and intensity distribution similar to that found for TBC and CTC is observed with differently treated cellulose triacetates (CTA).

The X-ray patterns of heterogeneous CTA I (Fig. 1a), drawn fibres from a liquid crystalline solution[4] (*cf.* Table I), and heterogeneously acetylated cellulose II (ref. 16) are comparable. Since antiparallel chain polarity should be present for the material which passed through a homogeneous process, an antiparallel packing of chains for CTA I is also suggested by these results.

The heterogeneous and homogeneous esters of cellulose show a clear distinction in their activity for the selective separation of stereoisomeric compounds. In unit cell size, and sometimes in the intensities of the meridional reflections, small differences have been established between heterogeneous CTA I (Fig. 1a) and CTA I from cellulose II or fibres drawn from the liquid crystalline state, and between TBC I and TBC II (Fig. 1c and e). All these observations point to differences in the supermolecular structure, which could be visualized *e.g.* as differences in the twist of bundles of chains in the microfibrils. The existence of various polymorphs of cellulose, CTA, and CTP is consistent with this idea. A certain supermolecular structure may provide specific surface configurations inside the holes which are always present in native cellulose, and these configurations may lead to the selective separation of stereoisomeric compounds when heterogeneous cellulose esters are used.

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