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Oriented Overgrowth (Epitaxy) of Macromolecular Organic Compounds

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In the field of oriented overgrowth (epitaxy) of low molecular weight organic compounds, extensive observations had already been made at the end of the first half of this century[1]. The efforts to effect oriented overgrowth of macromolecular compounds, however, met with their first success not before 1957 with the discovery of the epitaxy of polyethylene onto NaCl[2].

Our knowledge of the capacity of macromolecular organic compounds for undergoing oriented overgrowth has meanwhile been considerably enlarged. More recently several research teams have started to study this 'phenomenon'. This newer results are widely scattered in the literature. This review is a summary of the previous development and the present state of research in this field.

The first development period

(1) After successful attempts to produce single crystals of linear polyethylene[3,4] and to effect oriented overgrowth[5] of crystals of low molecular weight paraffins[6], the crystal structure of which resembles that of polyethylene, it was obvious to choose the system of linear polyethylene-NaCl for checking whether macromolecular organic compounds are capable of undergoing oriented overgrowth. Experiments carried out with a linear polyethylene (Marlex M = 105,000) were indeed successful. The polyethylene was applied in a highly diluted solution to the cleavage plane (001) of a rock salt crystal heated to 90°C; the polyethylene was oriented on (001) of NaCl in needles with the long axis of the needles $\parallel$ [110] and $[1\bar{1}0]$. Figure 1 shows a light micrograph of the needles which have a length up to several μ[2].

The structure of deposit films consisting of these needles and the orientation thereof to the position of the substrate crystal were thoroughly investigated by means of electron diffraction and electron micrographs (1958)[7]. Figures 2a and 2b show the electron diffraction pattern of a film oriented normally to the beam and that ascertained from the known structure of polyethylene[6], with indices of the reflections of one of the 2 reflection systems rotated around one another by 90°. The further evaluation of the pattern by means of the reciprocal lattice shows that the crystals of the polyethylene are overgrown with their (110) planes on the cleavage plane (100) of NaCl. The axes of the polyethylene chains [001] are oriented along the unicharged ion rows [110] and $[1\bar{1}0]$ of the rock salt. In this orientation the plane net areas of the 2 partners which correspond to a unit cell do not coincide with each other. Quasi-identical network meshes result, however, by comparing 3 periods of polyethylene (PE) with 1 period of NaCl. In this case a linear misfit of -4.5%, referred to the substrate, is obtained in the direction $[001]_{\mathrm{PE}}$, and perpendicular thereto in the direction $[110]_{\mathrm{PE}}$ a misfit of $+11.8\%$. Reference is made in this connection to the ideas, once more intensely discussed, which have been developed about the importance of structure correlation between the contacting surfaces in epitaxy[8–10].

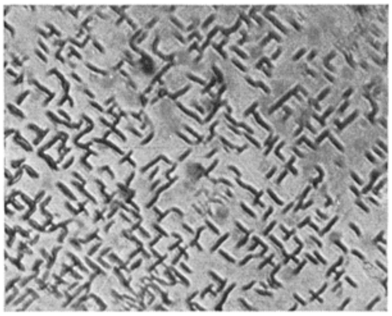

Fig. 1. Light micrograph of the oriented overgrowth of polyethylene on (100) NaCl.

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[1] J. H. Van der Merve, Discuss. Faraday Soc. *5*, 206 (1949).

[2] J. Willems and I. Willems, Experientia *13*, 465 (1957).

[3] R. Jaccodine, Nature *176*, 305 (1955).

[4] P. H. Till Jr., J. Poly. Sci. *24*, 301 (1957).

[5] J. Willems, Naturwissenschaften *42*, 176 (1955).

[6] C. W. Bunn, Trans. Faraday Soc. *35*, 482 (1939).

[7] E. W. Fischer, Kolloidzeitschrift *159*, 108 (1958).

[8] M. L. Royer, Bull. Soc. fr. Minér. Cristallogr. *51*, 7 (1928).

[9] D. W. Pashley, Adv. Phys. *5*, 233 (1956).

[10] H. Mayer, *Physik dünner Schichten* (Wissenschaftliche Verlagsgesellschaft, Stuttgart 1955), p. 110.

The polyethylene appears in the electron microscope as well as in the light microscope in the form of oriented more or less thick 'needles'. Diffractions from small selected areas have shown that the molecule chains are arranged perpendicular to the axis of the needles. Carbon replicas indicate that the needles are built up of vertically arranged laminae of a thickness of about 100 Å. These are the same laminae considered to be the morphological fundamental form which are also obtained in the crystallization from a free solution or a melt of polyethylene. Since the thickness of the laminae is in the order of magnitude of 100 Å, but the chains of polyethylene are arranged perpendicular to the plane of the thin laminae, which has been demonstrated by electron diffraction patterns, the polyethylene chains must be folded in such a manner that the turning points are positioned in the front and reverse side of the laminae, since maximally stretched chains have a length of about 1000 to 10,000 Å depending on the molecular weight[4,11,12].

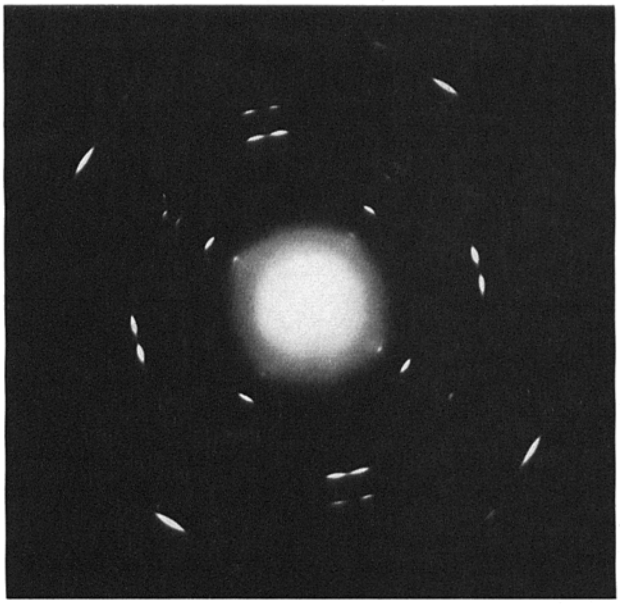

Fig. 2a. Electron diffraction pattern of an oriented polyethylene layer overgrown onto (100) of NaCl.

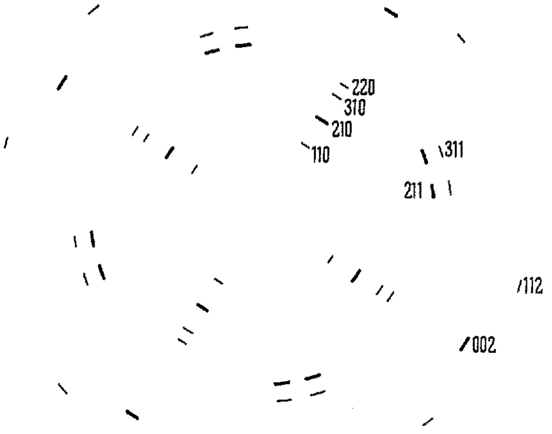

Fig. 2b. Indexes of 1 set of spots in the pattern of Fig. 2[7].

(2) Whereas, as mentioned above, polyethylene grows in the form of small needles which are observable in the light microscope, no oriented aggregates of macromolecular organic compounds observable in the light microscope could be found in further systematic overgrowth experiments using compounds of various types and various substrate crystals. New cases of epitaxial orientation of macromolecular organic compounds could be demonstrated only by a newly developed method which allows detection of epitaxy phenomena of macromolecular compounds at substrate surfaces even if the oriented particles are beyond the visible limit of the light microscope. This method consists of applying a macromolecular compound in the form of a solution or a melt as a thin film to the surface of the substrate, and, after the substrate has been detached, determining by overgrowth experiments with suitable low molecular weight deposits on the contact surface of the film whether orientation, and if so what kind of orientation, has occurred. The experience gained in the field of epitaxy of low molecular weight organic compounds on macromolecular organic compounds[13] is helpful in selecting suitable deposit crystals. A needle-like pattern of the deposit crystals is of course especially advantageous to detect orientation. In the case of extremely thin films, oriented overgrowth takes place both on the contact surface and on the reverse side thereof, so that any detachment of the film from the surface of the substrate is not required in such cases to prove orientation if the orientation of the deposit crystal on the film occurs otherwise than on the substrate.

(a) The first results with the aforementioned 'contact film method' were obtained in the polyamide series (1958)[14]. By applying a highly diluted solution of Nylon 6 (polyamide of ε-aminocaproic acid) on (100) of KCl at 195 °C, it was possible first to produce a film on whose surface, after dissolution of the KCl crystals in water, the needle-shaped crystals of evaporated pentachlorophenol are oriented in 4 positions; the axes of the needles form angles of 38°, 52° and 90° with one another (Figures 4a and 4b).

Thus, we have 4 systems (I to IV), the 2 systems I and II on the one hand, and the systems III and IV on the other hand, forming an angle of 19° with the edge [010] of KCl.

(b) Oriented contact films were likewise obtained on (100) of KCl with the polyamides of hexamethylene diamine and adipic acid (Nylon 6,6) (Figure 9) as well

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[11] A. KELLER, Phil. Mag. *2*, 1171 (1957).
[12] E. W. FISCHER, Z. Naturf. *12a*, 753 (1957).
[13] J. WILLEMS, Discuss. Faraday Soc. *25*, 111 (1950).
[14] J. WILLEMS, Experientia *15*, 175 (1959).

as sebacic acid (Nylon 6,10). Also other substrate crystals have proved to be suitable for this purpose; for example Nylon 6,6 produces films with good orientation on (100) of KBr and Nylon 6 on (100) of sucrose[15].

(c) Finally, the question was investigated, by means of the contact film method, whether the capacity of epitaxial orientation depends on a high crystallization power of the high molecular weight deposit substance. Polyacrylonitrile was chosen as a deposit substance in the investigation (1960)[16]. While polyethylene and the various types of nylon are readily crystallizing substances, polyacrylonitrile exhibits a very slight crystallization power which does not become observable until the material is stretched. It is the more remarkable that the contact surfaces of the deposit films of polyacrylonitrile on (100) of KCl and NaCl, with pentachlorophenol evaporated thereon, show an oriented overgrowth which is not inferior in quality to the epitaxy phenomena on the nylon contact films. This epitaxy has more recently also been proved by means of electron diffraction[17].

(3) In the case of the overgrowth phenomena with macromolecular organic compounds as deposits, which had been found up to then, the substrates were all crystals of low molecular weight substances. The question whether high macromolecular organic compounds, which are different from one another, are capable of oriented overgrowth with one another appeared to be of considerable interest, particularly in view of the biological ultrastructures. In the course of systematic experiments, a first success was achieved with the oriented overgrowth of polyethylene on an oriented substrate of polyoxymethylene (1962)[18]. From dilute solutions, the polyethylene grows in the form of fibrillar or needle-shaped structures which frequently exhibit curves, for example upon unilaterally drawn foils of polyoxymethylene; the long axis of the polyethylene crystallites is arranged perpendicular to the direction of drawing and thus to the direction of the molecule axes of the polyoxymethylene (Figure 3).

Results of recent years

In recent years the results described above were extended in various directions by the investigations of several teams. Both the number of macromolecular compounds exhibiting oriented overgrowth and of the low molecular weight substrates was substantially extended; our knowledge of the structure of deposit films and the orientation thereof to the position of the substrate crystals was widened by light microscopic, electron microscopic and electron diffraction investigations.

The Table indicates the more recently discovered overgrowth phenomena of macromolecular weight substances on low molecular weight substrates.

It is worthy of note that the newer results, as well as the results of the first development period, are confined to synthetic macromolecular organic compounds as oriented deposits; an experimentally produced oriented overgrowth, of a naturally-occurring macromolecular compound, for example protein, which is of particular interest from the biological point of view, has so far not been achieved. Overgrowth experiments with naturally-occurring macromolecular organic compounds are carried out at present in some research laboratories. These experiments have met with experi-

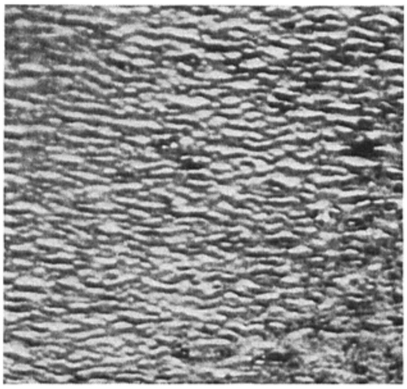

Fig. 3. Light micrograph of the oriented overgrowth of polyethylene on polyoxymethylene[18].

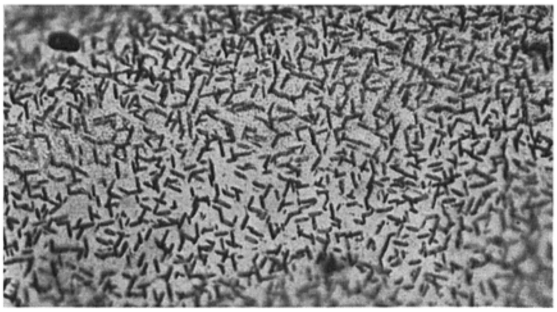

Fig. 4a. Light micrograph of the oriented overgrowth of pentachlorophenol on a contact film of Nylon 6 with (001)-KCl[17].

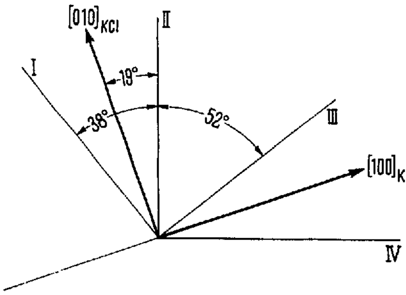

Fig. 4b. Scheme of the oriented overgrowth in Figure 4a with the corresponding directions of the edges of the substrate crystal[17].

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[15] J. Willems, Experientia *17*, 344 (1961).

[16] J. Willems, Experientia *16*, 530 (1960).

[17] E. W. Fischer and J. Willems, Makromolek. Chem. *99*, 85 (1966).

[18] J. Willems, Naturwissenschaften *50*, 92 (1963).

mental difficulties due to specific chemical and physical properties, wherein naturally-occurring macromolecular organic compounds differ from the synthetic macromolecular organic deposits mentioned in this paper. It appears that both the production and the proof of epitaxy of organic naturally-occurring macromolecular compounds require new experimental methods.

Part of the publications listed in the Table is confined to results which were obtained with the aid of the light microscope and the electron microscope. As to details, reference is made to the original literature. The present paper deals only with the fundamental principles of the newer results which are especially worthy of note.

(1) Polyethylene is oriented on the alkali metal halides listed in equal manner as on NaCl, that means in needle-shaped crystallites with the long axes thereof $\parallel$ [110] and $\parallel$ $[1\bar{1}0]$ of the alkali metal halide. The molecule axes of polyethylene are arranged in the same direction. Moreover, $(110)_{\mathrm{PE}}$ is $\parallel$ (100) alkali metal halide. In view of the great tolerance in this overgrowth series – the distance of unicharged ions in the direction of overgrowth [110] extends from 2.82 Å (LiF) to 4.97 Å (KI) – the mechanism of formation of this epitaxial overgrowth is discussed in detail; various explanations, which need to be investigated by experimental work, are considered.

(2) The long axes of the needle-shaped crystallites of pentone and isotactic styrene are likewise arranged parallel [110] NaCl; the molecule axes lie parallel to the surface of the substrate and are oriented parallel to the [110]-directions. Polystyrene grows with the $(10\bar{1}0)$-surface on (100) NaCl.

(3) The investigations with Nylon 6, Nylon 6,6, Nylon 8 and polyacrylonitrile on quartz as a substrate were carried out within the fundamental research in the silicose field. Part of the epitaxies were ascertained by means of light microscopy. The epitaxy of polyacrylonitrile was found by means of contact films and confirmed by means of electron microscopy. The orientations found are described with reference to unidimensional structure analogies between the contacting lattice surfaces.

Deposit	Substrate
Polyethylene[19]	LiF, NaBr, NaI, KCl, KI
Polypropylene[19]	NaCl
'Penton'[19]	NaCl
(Poly-3,3-bischloromethylcyclo-oxa-butane)	NaCl
Polystyrene[19] isotactic	NaCl
Polyethylene terephthalate[19,20]	NaCl
Polyoxymethylene[21]	NaCl
Polyethylene oxide[21,22]	KBr, muscovite
Nylon 6, 6, Nylon 6, 10, Nylon 8[23]	Quartz
Polyacrylonitrile[23,24]	Quartz
Nylon 7 (Figure 10), Nylon 8[17]	KCl
Polyurethane[17]	KCl

(4) The oriented overgrowths of polyoxymethylene and polyethylene oxide on NaCl and KBr are especially remarkable insofar as the molecule chains of the macromolecules are arranged not parallel but perpendicular to the substrate surface. Both substances grow in thin laminae with laminar planes parallel to the alkali metal halide. The axes of the folded molecule chains in the laminae are arranged in the same manner as explained above with reference to polyethylene, viz. perpendicular to the laminar plane, so that the turning points are on the front side and the reverse side of the laminae. Thus, the linking of the partners occurs on the part of the macromolecular deposit film by a turning plane. An epitaxial linking of the same kind was also discovered between crystal laminae of polyoxymethylene and polyethylene[21].

(5) The quite recently published paper dealing with the oriented overgrowth of polyamides on KCl cleavage planes is an instructive example for the explanation of an epitaxy discovered by the contact film method by means of light microscopic, electron microscopic and electron diffraction investigations[17].

Figure 5 shows the indices obtained on the basis of the known structure of Nylon 6[25–27], of the reflections

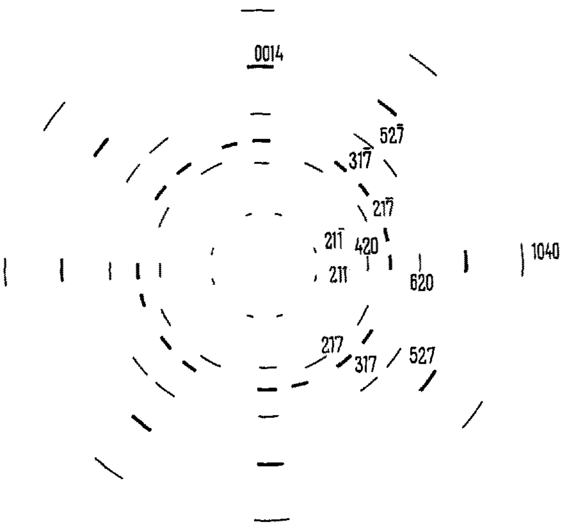

Fig. 5. Indexes of the electron diffraction pattern of an oriented Nylon 6 layer overgrown onto (001) of NaCl[17].

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[19] J. A. KOUTSKY, A. G. WALTON and E. BAER, J. Poly. Sci. *4*, 611 (1966).

[20] G. YEH, J. Polym. Sci. *4*, 611 (1966).

[21] K. KOBAYASHI and X. TAKAHASHI, Kagaku *34*, 325 (1964).

[22] T. OTA, and X. KUMOYA, Kagaku *34*, 325 (1964).

[23] H. SEIFERT and B. MÜLLER-BUSCHBAUM, Naturwissenschaften *52*, 7 (1965).

[24] H. SEIFERT and B. MÜLLER-BUSCHBAUM, Kolloidzeitschrift *205*, 46 (1955).

[25] R. BRILL, Z. phys. Chemie (B) *53*, 61 (1943).

[26] D. R. HOLMES, C. W. BUNN and D. J. SMITH, J. Polym. Sci. *17*, 159 (1955).

[27] C. RUSHER and H. J. SCHRÖDER, Faserforsch. und Text. *11*, 165 (1960).

of the electron diffraction pattern of a film oriented normally to the beam. In compliance with the light microscope observation at the contact film (Figure 4a) 4 reflection systems occur, of which 2 each are arranged perpendicular to one another and form angles of 38° and 52° respectively with the other system. The (0014)-reflections show that the molecule axes lie in the plane of overgrowth. The evaluation of the patterns obtained with perpendicular, and moreover oblique transmission using the aid of the reciprocal lattice, shows that the (020)-plane (hydrogen bonded sheet) of Nylon 6 (Figure 6a) is the overgrowth plane.

In consideration of additional light microscopic observations which are not dealt with herein in detail, the electron diffraction shows that the axes of the macromolecules of the contact film lie parallel to the long axes of the crystals of pentachlorophenol in Figure 4, that means they form an angle of 19° with the edges of the cubes of KCl.

The law of overgrowth is thereby established. Figure 6b shows the network of the mutually overgrown crystal surfaces in superposition. At an angle of 18.4° against the [100]-direction the network of the KCl cleavage plane shows a lattice line occupied by unicharged ions, the identity period of which is in satisfactory agreement with the a-axis of the nylon lattice. The difference between the 2 periods is only 0.27 Å. In the direction perpendicular thereto, the difference of the periods is so large that the structure analogy is to be regarded as unidimensional.

The electron micrograph (Figure 7) shows that Nylon 6 epitaxially grows in the form of bundles of thin fibrils forming with one another the characteristic angles of 90°, 38° and 52° which have been found with the light microscope as well as with the aid of electron diffraction. The orientation of the polyamide chains in the fibrils was determined by taking both electron diffraction patterns and electron micrographs of parts of the preparations, wherein only a single orientation existed within the range of 1 μ diameter to be diffracted.

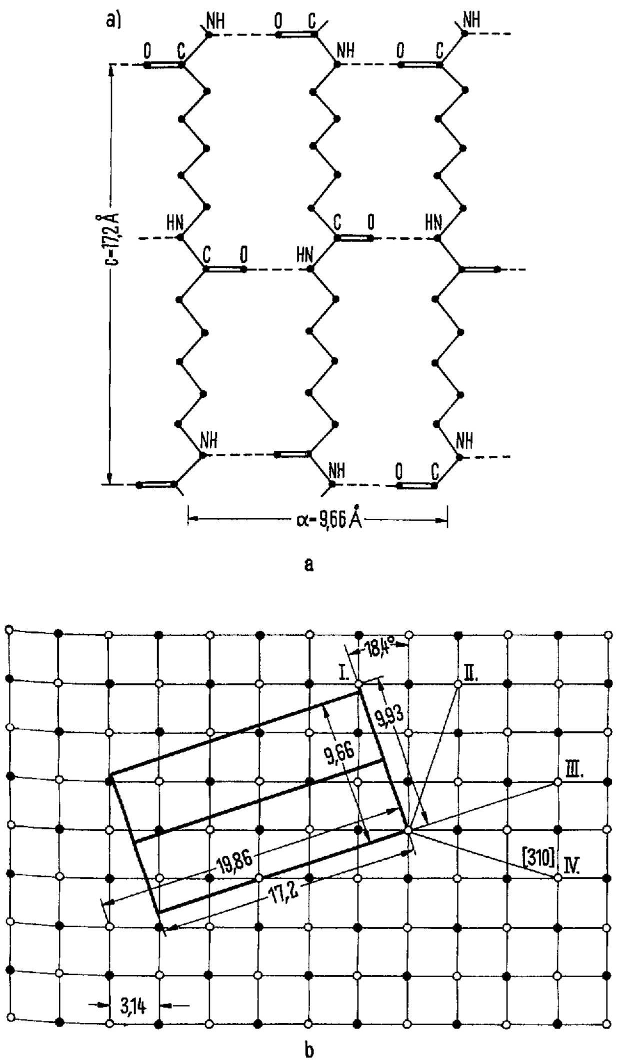

Fig. 6. Law of epitaxy of the oriented crystallization of Nylon 6 on (001)-KCl. (a) Hydrogen bonded sheet (020) of Nylon 6[25]. (b) Scheme of the plane net areas of the contacting lattice surfaces (001)-KCl and (020)-Nylon 6[17].

Fig. 7. Electron micrograph of an oriented Nylon 6 layer overgrown onto (001)-KCl with 4 favoured orientations[17].

These patterns and micrographs demonstrate that the molecule axes are arranged perpendicular to the axis of the fibrils. Since the fibrils have a thickness of about 100 Å and the molecule length is about 3000 Å, it is to be assumed that the chains in the thin fibrils are folded in similar manner as in the epitaxially crystallized polyethylene and in the known single crystals of Nylon 6[28]. The fibrils are to be regarded as degenerated laminae, preferably grown in the direction of the long axis of the fibrils.

(6) In contrast to the electron diffraction pattern of Nylon 6 (Figure 5) showing 4 orientations, the pattern of Nylon 6,6 (Figure 8) epitaxially grown on KCl shows reflections on one orientation only; this means that the latter corresponds to the pattern of a single crystal which is oriented in a certain position. Thus, the epitaxy investigations have proved to be valuable for identifying the crystal structure of macromolecular compounds, for example polyamides from which single crystals yielding sufficient reflections[29] could so far no be produced. Another example of this type is polyethylene terephthalate. A 'single crystal' pattern could previously be obtained[20] only by electron diffraction of a film epitaxially grown on (100) NaCl.

(7) In view of the considerable importance of the macromolecular compounds in the technical as well as in the biological respect, there remains the question of the results described here in the field of epitaxy in these 2 ranges. Here some first points of interest are found.

In the technical field a process should be mentioned by which surfaces of plastics are improved by applying thereto an epitaxially grown deposit[30].

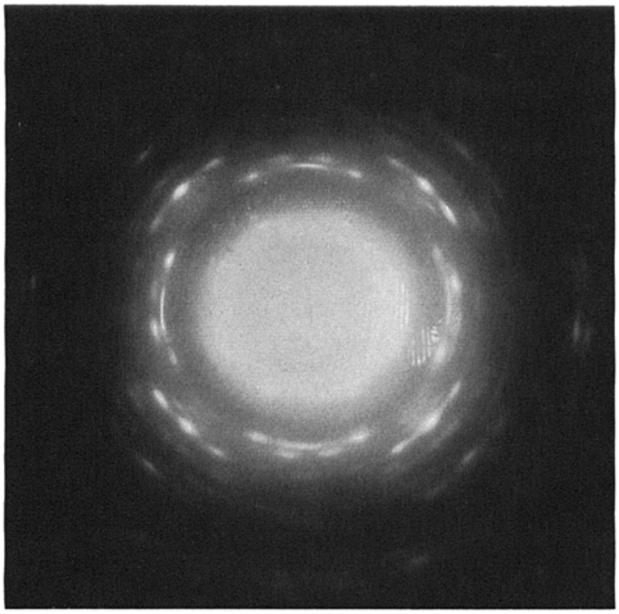

Fig. 8. Electron diffraction pattern of an oriented Nylon 66 layer overgrown onto (001) of KCl[17,29].

In the biological field, the epitaxial formation of a characteristic network of polyamide fibrils in contact with a crystal lattice plane has been proposed as a model for the production of antibodies against antigens in the organism.

In this case the formation of the characteristic fibrillar network replaces the formation of the pocket-shaped, spatial, negative print of the antigenic regions in the known theory of the production of antibodies. For details, reference is made to the original literature[15]. The conception of a model for the production of antibodies, which refers to the epitaxy of polyamides, has quite recently been discussed in connection with the general problem of transmission of chemical information[31].

Fig. 9. Light micrograph of the oriented overgrowth of pentachlorophenol onto a Nylon 66 film crystallized on (001) KCl[17].

Fig. 10. Electron micrograph of an oriented Nylon 7 layer overgrown onto (001) of KCl[17].

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[28] P. H. GEIL, J. Polym. Sci. *44*, 449 (1960).

[29] E. W. FISCHER, *Newer Methods of Polymer Characterisation*, (Ed. BACON KE; Interscience Publishers, New York, 1964), vol. 6, p. 279.

[30] F. P. 1,386,271 (1964) to Farbenfabriken Bayer AG.

[31] H. ERLENMEYER and H. BARTELS, Helv. chim. Acta *47*, 46 (1964).

Zusammenfassung. Während am Ende der ersten Hälfte dieses Jahrhunderts auf dem Gebiet der Epitaxie niedermolekularer organischer Stoffe bereits ein sehr umfangreiches Beobachtungsmaterial vorlag, führten die Bemühungen, auch hochmolekulare Stoffe zur orientierten Aufwachsung zu bringen, erst 1957 mit der Auffindung der Epitaxie von Polyäthylen auf NaCl zum Erfolg.

Das Polyäthylen wächst in Form kleiner, lichtmikroskopisch erkennbarer Nadeln auf. Nachdem die Suche nach weiteren Beispielen dieser Art mit dem Lichtmikroskop vergeblich geblieben war, gelang es, mit einem neu entwickelten, indirekten Verfahren auf Grundlage von «Kontaktfilmen» auch die Epitaxie von Nylon 6, Nylon 66 und Nylon 6,10 sowie Polyacrylnitril nachzuweisen. Zur Aufklärung des Verwachsungsgesetzes wurden vor allem die Methoden der Licht- und Elektronenmikroskopie sowie der Elektronenbeugung angewandt.

Unter dem Gesichtspunkt der biologischen Ultrastruktur ist in der weiteren Entwicklung die Feststellung der Epitaxie von Polyäthylen auf Polyoxymethylen, also von 2 verschiedenen makromolekularen Stoffen miteinander, besonders bemerkenswert.

Die Arbeiten der letzten Jahre brachten als neue makromolekulare Verwachsungspartner Polypropylen, Penton, Polystyrol, Polyäthylenterephtalat, Polyäthylenoxid, Nylon 7, Nylon 8 und Polyurethan, als neue anorganische Träger weitere Alkalihalogenide sowie Muskowit und Quarz. Eine experimentell erhaltene orientierte Aufwachsung eines natürlichen, makromolekularen organischen Stoffes, z. B. eines Proteins, die unter biologischem Gesichtspunkt von besonderem Interesse wäre, ist jedoch auch bisher nicht bekannt geworden.

Die Epitaxieuntersuchungen erwiesen sich als wertvolles Hilfsmittel zur Aufklärung von Kristallstrukturen solcher makromolekularer Stoffe, von denen es, wie bei den Polyamiden, noch nicht gelungen ist, Einkristalle herzustellen.

Auf technischem und biologischem Gebiet liegen erste Ansätze einer Auswirkung der vorliegenden Ergebnisse vor.

Auf technischem Gebiet ist ein Verfahren zu erwähnen, nach dem Oberflächen von Gebilden aus Kunststoffen durch Aufbringen eines orientiert verwachsenen Gaststoffes vergütet werden.

Auf biologischem Gebiet wurde die epitaktische Bildung eines charakteristischen Netzwerks von Polyamid-Fibrillen im Kontakt mit einer Kristallgitterfläche als Modell für die Bildung von Antikörpern gegen Antigene vorgeschlagen. Diese Modellvorstellung wurde in neuester Zeit im Zusammenhang mit dem allgemeinen Problem der Informationsübertragung diskutiert.

SPECIALIA

Versuche zum enzymatischen Abbau der «gebundenen» Gibberelline von *Pharbitis purpurea*

Bei der Untersuchung von Samen und Kapseln von *Pharbitis purpurea* auf Gibberelline wurden in den Äthylazetat- und Butanolausschüttelungen der Acetonextrakte neben den Gibberellinen A_8, A_3, A_5, stärker polare, gibberellinaktive Substanzen gefunden. Diese zeigen ein gleiches chromatographisches Verhalten wie «gebundene» Gibberelline, d.h. sie bleiben bei der Dünnschichtchromatographie auf Kieselgel G mit unpolaren Entwicklungsgemischen am Startpunkt zurück[1,2]. Wie SEMBDNER und SCHREIBER[1] sowie SEMBDNER, SCHNEIDER WEILAND und SCHREIBER[2] durch säurehydrolytischen Abbau nachwiesen, können Gibberelline an Kohlenhydrate und Eiweisskomplexe gebunden sein. McCOMB[3] sowie JONES[4] versuchten gebundene Gibberelline enzymatisch abzubauen. Sie fanden nach der Behandlung der wässrigen Rohextrakte von *Phaseolus multiflorus*-Samen mit Ficin teilweise eine Erhöhung der mit Äthylazetat extrahierbaren freien Gibberelline.

Wir haben versucht, die polaren Gibberelline von *Pharbitis purpurea*, vorläufig *Pharbitis* α und β benannt, nach dünnschichtchromatographischer Anreicherung enzymatisch abzubauen. Diese beiden Substanzen finden sich in geringer Menge in Samen, in hoher Konzentration dagegen in den Kapseln. Sie lassen sich teilweise mit Äthylazetat, vollständig mit Butanol aus dem wässrigen Rückstand der Acetonextrakte ausschütteln.

Reife und unreife Kapseln von *Pharbitis purpurea* wurden gefriergetrocknet und fein gepulvert. 51 g dieses Materials wurden zweimal mit je 500 ml Aceton und

[1] G. SEMBDNER und K. SCHREIBER, Phytochemistry *4*, 49 (1964).

[2] G. SEMBDNER, G. SCHNEIDER, J. WEILAND und K. SCHREIBER, Experientia *20*, 89 (1964).

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