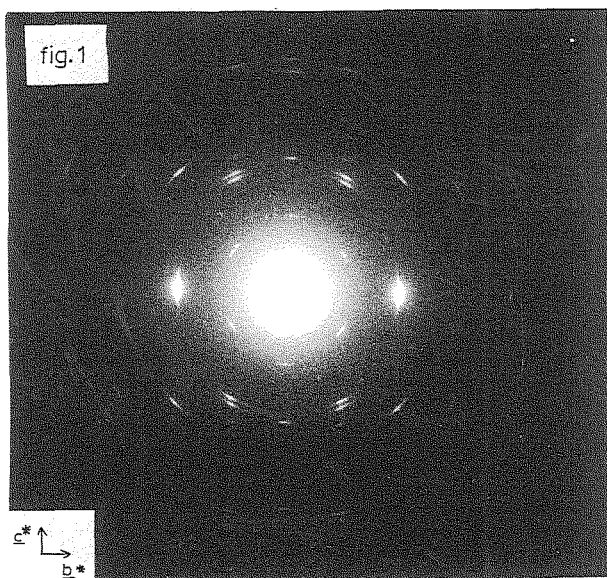


10.2-3 ELECTRON CRYSTAL STRUCTURE ANALYSIS-EPI TAXIALLY GROWN POLYETHYLENE. By Barbara Moss and Douglas L. Dorset, Medical Foundation of Buffalo, 73 High Street, Buffalo, New York 14203, U.S.A.

Epitaxial crystallization of linear polymers onto various substrates allows the possibility of obtaining electron diffraction patterns from zones other than that obtained from solution-grown specimens, from which reliable structural information can be difficult to obtain (the long projection axis enhances crystal bend effects on Bragg intensities (Cowley, *Acta Cryst.* (1961) 14, 920). Wittmann, Hodge and Lotz (*J. Polymer Sci. Polymer Phys.* (1981), 19, 1837; 1853) have described the epitaxial crystallization of polyethylene on benzoic acid. The PE chain axis is oriented parallel to the substrate surface and the  $0kl$  diffraction pattern is obtained. The reflections are rather arced. In addition,  $lkl$  and  $2kl$  type reflections are also observed due to the twisting of lamellae (Keith and Padden, *J. Polymer Sci.* (1959) 39, 101;123) or tilting of successive stacks of lamellae (Bassett and Hodge, *Proc. R. Soc. London* (1978) A359, 121) (Fig. 1). Microcrystals were examined in a JEOL 100B microscope at 100kV. The patterns were recorded on Kodak DEF-5 X-ray film. The films were scanned with a Joyce-Loebl flat bed densitometer and integrated to give Bragg intensities, from which structure amplitudes were derived:  $F=I^{1/2}$ . Typically 7 to 9 reflections from other zones were recorded in addition to 6  $0kl$  reflections. Agreement with a kinematic calculation (using coordinates derived from paraffins (Abrahamsson *et al.*, *Progr. Chem. Fats. Other Lipids* (1978) 16, 125) and down weighting reflections not from the  $0kl$  zone) gives generally poor agreement. Dynamical scattering is important in these data. This presents difficulties as reflections on the tilt axis (the 020 and 040) will have contributions from crystallites oriented in different projections. Considering only the  $0kl$  and  $lkl$  zones, the sums of intensities not on the tilt axis were used to estimate the relative importance of the two zones. At  $284\text{\AA}$  crystal thickness the  $0kl$  reflections have fair agreement ( $R=.22$ ) with the dynamical values, while the  $lkl$  data also agree reasonably ( $R=.19$ ) at  $300\text{\AA}$  thickness. It is apparent that the present analysis is hampered by the need to alter too many variables for too few data. This is in contrast to previous work on epitaxially crystallized paraffin (*J. Polymer Sci. Polymer Phys.*, submitted). Thin, flat, epitaxial crystals of a more perfect nature are required. Work supported by NSF grant DMR81-16318.



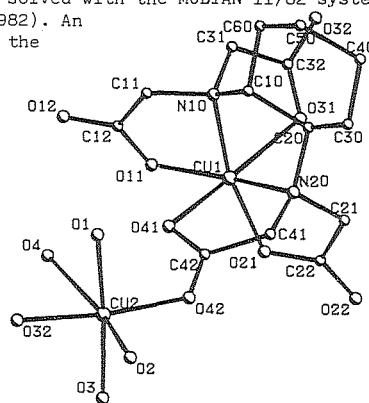
10.2-4 STRUCTURE OF IODIDE ION ARRAYS IN IODINATED NYLON 6 AND THE CHAIN ORIENTATION INDUCED BY IODINE IN NYLON 6 FILMS. By N. S. Murthy, A. B. Szollosi, and J. P. Sibilia, ALLIED CORPORATION, Corporate Technology, Morristown, New Jersey 07960 and S. Krimm, Department of Physics, University of Michigan, Ann Arbor, Michigan 48109.

Nylon 6 exists in at least two well characterized crystalline forms referred to as  $\alpha$  and  $\gamma$ . In the  $\alpha$  form the polymer has a sheet structure of fully extended antiparallel chains connected by hydrogen bonds. The  $\gamma$  form has a shorter chain length ( $2_1$  helix) and the hydrogen bonds are formed between parallel chains.  $\gamma$  form can be obtained by treating nylon 6 with an aqueous solution of iodine-potassium iodide followed by the removal of iodine. Two species of iodide ions ( $I_3^-$  and  $I_5^-$ ) are found in intermediate iodine-nylon 6 complexes. Orientation of  $I_5^-$  arrays along the chain axis and  $I_3^-$  perpendicular to the chain axis in uniaxially drawn films and in films with planar orientation suggests that there is an intrinsic relation between the direction of iodide ion arrays and nylon 6 chains. When an unoriented film of nylon 6 in the amorphous or the  $\alpha$  form is treated with an aqueous solution of iodine-potassium iodide, the  $I_3^-$  chains in the resulting iodine-nylon complex lie in planes parallel to the surface of the film, and  $I_5^-$  chains are oriented normal to the surface of the film. The  $\gamma$  form obtained by desorbing the iodine from this complex shows considerable orientation with the nylon chains oriented perpendicular to the plane of the film; this orientation is maintained during the  $\gamma$ - $\alpha$  transition. It is proposed that the iodine induced orientation of the nylon 6 chains is due to the nucleating effects of the iodide ion columns as the iodine diffuses unidirectionally into the film.

10.2-5 CRYSTAL AND MOLECULAR STRUCTURE OF COPPER CYCLOHEXYLENEDIAMINETETRAACETATE TETRAHYDRATE. By A. Fuertes, E. Escrivá, D. Beltran, E. Molins, C. Miravittles, Dep. Química Inorg. Fac. Químicas, Univ. Valencia, and Inst. "Jaime Almera" C.S.I.C., Aptdo. Correos 30.102, Barcelona, Spain.

The structure of the compound  $Cu_2(CDTA) \cdot 4H_2O$ , where  $CDTA^{4-}$  is the anion cyclohexylenediaminetetraacetate ( $C_{14}H_{18}N_2O_8^{4-}$ ), has been determined by X-Ray techniques to clarify the coordination geometry around the two copper atoms and the packing of the complex. Crystals are orthorhombic with  $a = 10.863(3)$ ,  $b = 12.074(4)$ ,  $c = 14.802(6)$  Å,  $V = 1941.3$  Å<sup>3</sup>; the space group  $P2_12_12_1$ ,  $Z = 4$ . Intensity data were collected on a CAD 4 Diffractometer using  $MoK\alpha$  radiation.

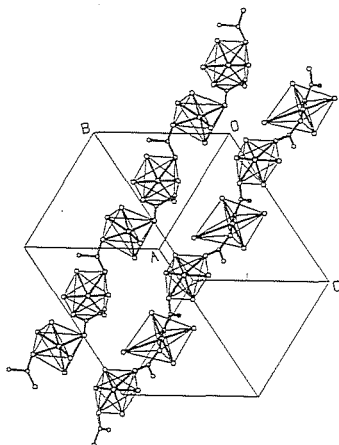
The structure was solved with the MULTAN 11/82 system (Main, P. et al., 1982). An E-map computed with the phases from the set with the highest combined figure of merit revealed peaks for nine non-hydrogen atoms and the two Cu atoms, the remaining were located with a Fourier Synthesis. The structure was anisotropically refined by means of full matrix least-squares with the SHELX-76 program (Shel-



drick, 1976). A posterior difference map revealed positions for ten H-atoms. The refinement was terminated at  $R = 0.039$ ,  $R_w = 0.036$ .

The two Cu atoms lies on a two different octahedral coordination sites. The  $[\text{Cu}(\text{H}_2\text{O})_4\text{O}_2]^{2+}$  coordination polyhedron is a slightly distorted octahedron and the  $[\text{Cu}(\text{CDTA})]^{2-}$  has a more distorted octahedral geometry.

The two coordination polyhedra are linked by carboxylate bridges forming infinite zig-zag chains along a, with the plane of the zig-zag parallel to (001).



10.3-1 INVESTIGATION ON THE  $\beta \rightarrow \alpha$  POLYMORPHIC TRANSITION IN ISOTACTIC POLYPROPYLENE. By D. Paukszta and J. Garbarczyk, Department of Chemistry, Technical University, Poznań, Poland.

In our previous works we had found, that less stable hexagonal  $\beta$  polymorphic form besides monoclinic- $\alpha$  of isotactic polypropylene is formed during crystallization from a melt in presence of a small amount of aromatic compounds having specific crystal structure /Garbarczyk, Paukszta, Polymer 1981, 22, 562/. Energetic calculations show that experimental observation of hexagonal form is made possible owing to retardation polymorphic  $\beta \rightarrow \alpha$  transition /Garbarczyk, Die Makrom. Chem. 1983 submitted for publication/.

The aim of this work was to find if the influence of the above mentioned additives /2-mercaptobenzimidazole/MBIM/, phenothiazine/PT/, Permanent Red E3B/E3B/, anthracene/AN/, phenanthrene/PNR/, triphenodithiazine/TPDT/ may cause polymorphic transition retardation. The samples were prepared during crystallization from a melt of iPP with 0,5% additive. Phase-transition from hexagonal to monoclinic form was carried out with thermal treatment in two ways: a/ step adjusted temperature in a range from 140 to 165 C, b/ variable time of heating / 1/2, 1, 2, 3, 4, 5 h./ at constant temperature close to complete transition  $\beta \rightarrow \alpha$ . Process of the transition, that is decrease of amount of  $\beta$ -form /k/, was observed on the basis of X-ray diffraction patterns. We have found, that temperature at the initial point of rapid decrease of value of k and the temperature at the vanishing point depend on the kind of the introduced additives.

In presence of E3B, AN, PNR, TPDT beginning of decrease was observed at definitely higher temperatures as compared to other additives. Opposite phenomenon that is faster decrease of value of k in shorter time of thermal treatment was observed in samples with PT and MBIM. This observation corresponds to the amount of  $\beta$ -form found in particular samples before thermal treatment. During transition we observed increase of monoclinic form. At the initial point of rapid decrease of amount of  $\beta$ -form we could see definite decrease of crystalline sizes. The results we have obtained confirm a hypothesis of mechanism of transition and lead into conclusion that the applied additives act as retardants of polymorphic transition from hexagonal to monoclinic form. The used additives have various retardation intensity of the transition.

10.3-2 LINE GROUPS

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Line groups are symmetry groups of polymers and quasi 1-dimensional crystals. Their irreducible representations have been constructed, as well as the corresponding Clebsch-Gordan series and selection rules. For application in phase transitions studies equitranslational epikernels (low temperature subgroups) were determined. It is shown that in certain cases 3-dimensional transitions can be described by the line groups only (without reference to the space groups involved). Also, magnetic line groups and their co-representations have been derived.

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