JOURNAL OF MATERIALS SCIENCE 19 (1984) 1439–1445

Epitaxial crystallization of selenium on linear polyphenyls

J. C. WITTMANN, B. LOTZ
Centre de Recherches sur les Macromolécules, 6, Rue Boussingault, 67083 Strasbourg, France

Selenium has been crystallized in the presence of linear polyphenyls, namely *p*-ter and *p*-quaterphenyl, crystals by reheating from the glassy state to temperatures in the range 80 to 180° C. Oriented growth of selenium is observed. The epitaxial relationship is based on lattice matchings parallel and normal to the selenium chains. Similarities with epitaxial growth of polyethylene on the same organic substrates are discussed.

1. Introduction

Epitaxial growth of polyethylene and linear polyesters has recently been shown to occur on crystals of two homologous series of organic substrates: condensed aromatic hydrocarbons and linear polyphenyls [1, 2]. The underlying epitaxial relationships, as established by electron microscopy and electron diffraction studies, were explained by two-dimensional lattice matchings between polymers and substrates. In view of the structural similarities between these substrates and organic salts currently used as nucleating agents for polymers, it was suggested in addition that epitaxy could account for the nucleating ability of the salts.

All the polymers investigated in the above studies have a common planar zigzag chain conformation and their crystal structures are not significantly different from that of polyethylene. In contrast, polymeric selenium is inorganic and has a quite different chain conformation and crystal structure. Despite these differences, we found it possible to epitaxially crystallize it on the aromatic hydrocarbons, in particular on the *p*-polyphenyls. The present paper is not aimed at giving a detailed description of the various morphologies which may be observed, but rather focuses on the orientations obtained in relation to the substrate structure. It will be shown that, due to a close correspondence in lattice spacings, the relationships involved in epitaxy of selenium are nearly identical to those governing the deposition of polyethylene or polyesters on the same organic substrates.

2. Experimental details

Large aromatic hydrocarbon crystals or dendrites were grown and deposited on glass slides by slow evaporation from a saturated *p*-xylene solution. The crystals were dried under vacuum prior to use. Thin, glassy selenium films were produced by evaporating small pellets of the material (99.99% purity, Fluka A.G.) at a working pressure of 10^{-5} torr on the substrate crystals held at room temperature. For electron microscopic examination (with a Hitachi HU 11CS), the samples were further backed with carbon and, after thermal treatment, the substrate crystals were dissolved in ethanol when desired. Optical examination of thicker films (300 nm thickness) was made in phase contrast and polarized light (Zeiss Photomicroscope II).

Crystallization of selenium was carried out isothermally using a Mettler FP 2 hot stage. As some of the aromatic hydrocarbons used as substrates tend to sublimate and have melting temperatures lower or only slightly higher than that of selenium ($T_m = 220.5^\circ$ C), crystallization of the latter was performed by reheating the samples from the glassy state, rather than by cooling from the molten state.

3. Results and discussion

3.1. Overall morphology of thick selenium films crystallized in the presence of linear polyphenyls

Contrary to the polyolefins and polyesters studied previously [1, 2], selenium can be quenched very

0022–2461/84 $03.00 + .12

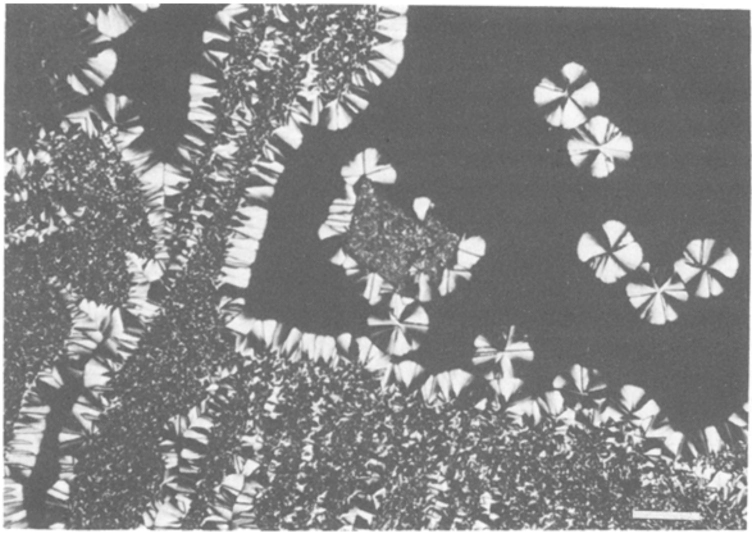

Figure 1 Selenium film crystallized by heating to $T_c = 180°$ C from the glassy state in the presence of *p*-terphenyl crystals (lower part). Crystallization has been arrested by quenching back to room temperature. Optical micrograph with crossed polarizers; scale bar: 50 μm.

easily to the glassy state and can be polymerized–crystallized from the melt or from the glassy state over a very large temperature range (from 70 to 160° C for measurable crystal growth rates [3]).

Marked oriented growth of selenium was obtained under these conditions on the large (0 0 1) basal surfaces of various aromatic hydrocarbons. Among these, *p*-terphenyl and *p*-quaterphenyl, i.e. members with high melting temperatures in the linear polyphenyl series, were found to be particularly efficient and versatile substrates, and therefore were used throughout this study.

An early stage of the crystallization of selenium in presence of dendritic or irregularly shaped crystals of *p*-terphenyl is shown on the optical microphotograph of Fig. 1. The selenium film was annealed for a short time at $T = 180°$ C, i.e. well above the maximum crystallisation rate of selenium (~ 130° C [3]), then quenched to room temperature to arrest crystallisation.

Fig. 1 displays some features which are typical of thick selenium films crystallized over the whole crystallisation range. It is characterized by:

(a) coarse grained structures of selenium in contact with the (0 0 1) basal plane of the substrate.

(b) transcrystalline selenium layers at the periphery of the *p*-terphenyl crystals. These layers bound the isotropic regions of still uncrystallized selenium.

Fig. 1 provides ample evidence for a high nucleating efficiency of aromatic hydrocarbon crystals towards selenium, comparable to that previously observed with synthetic organic polymers [1, 2]. Transcrystallization however does not help precise whether the lateral faces are operative or if the transcrystalline layers stem from nuclei formed on the basal (0 0 1) *p*-terphenyl surface. In this connection, one may note that the radius of the few isolated spherulites in Fig. 1 compares well with the thickness of the transcrystalline layers, indicating comparable nucleation efficiency of *p*-terphenyl crystals and the spherulite germs. The latter could therefore well be tiny *p*-terphenyl crystal fragments left on the glass slide after solvent evaporation.

Fig. 2, which is an enlarged view of the coarse grained structure apparent in Fig. 1, helps precise the crystalline texture of polymeric selenium on the large (0 0 1) faces of hydrocarbon crystals. The structure is in fact composed of highly birefringent domains of varying sizes and shapes. Each domain is characterized by a unique orientation of the selenium molecules since it exhibits single crystal type optical properties, with well defined extinction positions under polarized light. The domains however are divided into two populations whose extinction positions are 70° apart. Fig. 2 has been taken with the polarizer parallel to the bissectrix of the 70° angle; the two populations thus have equal birefringence.

The optical properties of the thick films therefore suggest that crystallization of selenium on (0 0 1) *p*-terphenyl surfaces leads, as already established for synthetic polymers, to two well defined and characteristic orientations of the selenium

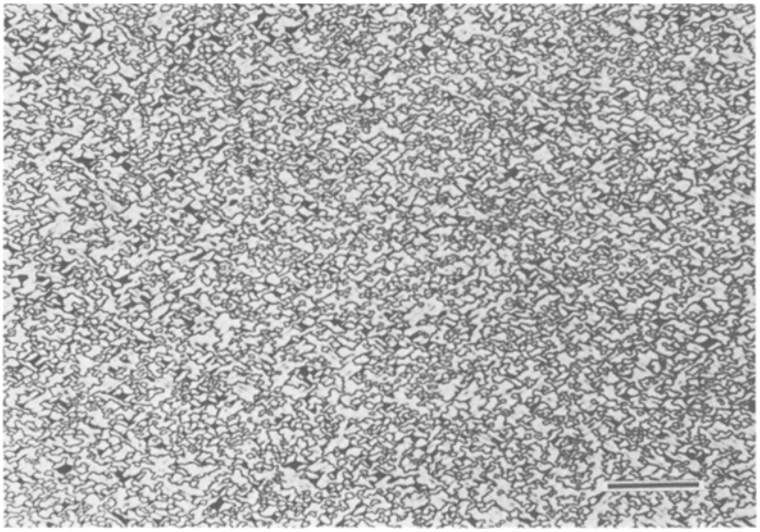

Figure 2 Optical micrograph of the selenium domain structure formed at $T_c = 120°$ C on the (0 0 1) basal surface of *p*-terphenyl crystals. Crossed polarizers; scale bar: 25 μm.

crystals which, as will be shown later, correspond to two crystallographically equivalent directions of the substrate lattice.

3.2. Crystallization of thin selenium films

Selenium condensed at room temperature to produce thin samples hardly forms uniform and continuous layers: it tends to gather into small droplets which align along steps in the basal surface of the organic substrate crystals. Fig. 3 shows a phase contrast optical micrograph of selenium-decorated *p*-terphenyl dendrites with numerous growth spirals and marked growth steps. The resulting pattern reminds one of that obtained with the gold decoration technique developed by Bassett [4] for ionic crystals, but in the present case the decorating particles are much larger (0.1 to 0.5 μm against $\simeq 5$ nm, respectively) and are actually frozen-in amorphous selenium droplets. We also observed that selenium films of slightly larger thicknesses, although uniform at room temperature, very often break up into small liquid droplets on sudden heating above the glass transition temperature ($48°\text{ C} < T_g < 58°\text{ C}$ [5]).

When *p*-quaterphenyl is used as a substrate, the nucleation of all the droplets is promoted by the (0 0 1) basal surface, leading to a uniform morphology of tiny spherical selenium crystallites. These samples are well suited for recording composite electron diffraction patterns (polymer + substrate)

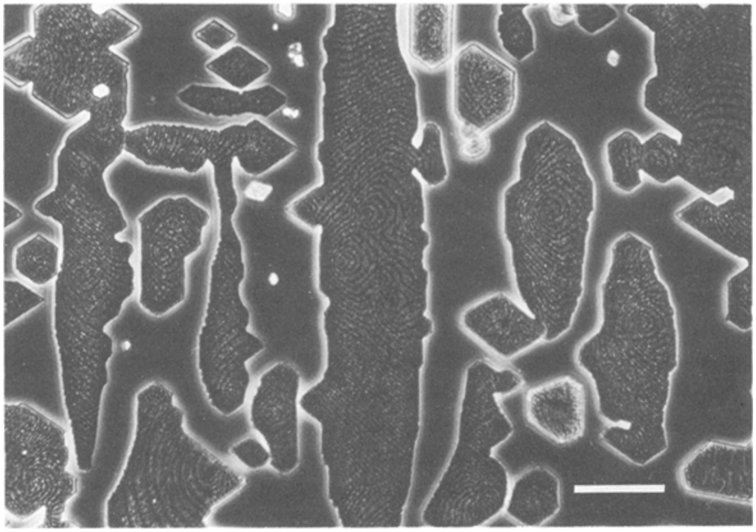

Figure 3 *p*-terphenyl dendritic crystals selenium-decorated at room temperature. Phase contrast optical micrograph; scale bar: 25 μm.

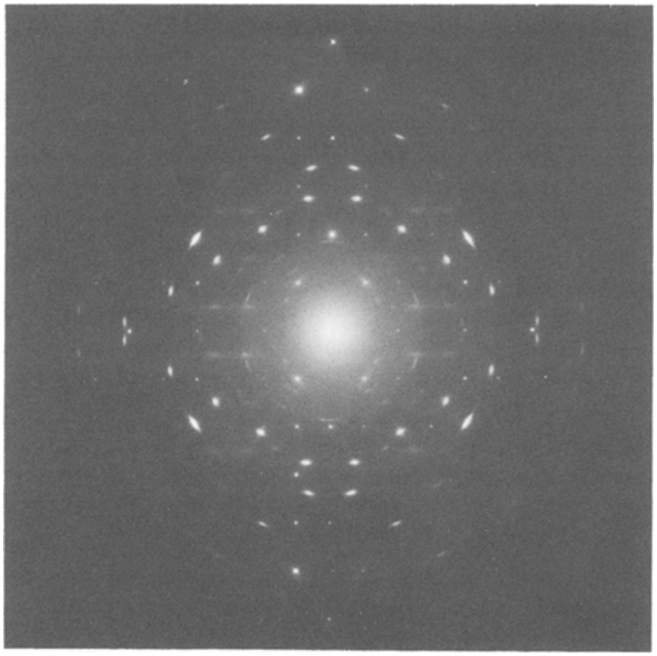

Figure 4 Selected area electron diffraction pattern of a selenium–p-quaterphenyl bicrystal.

since p-quaterphenyl possesses a good electron beam resistance and does not evaporate readily in the E.M column vacuum.

p-Terphenyl is less suited as a substrate for thin film studies. When it is not covered by a thick selenium film, it tends to sublimate at the crystallization temperatures used and therefore gives often rise to somewhat less specific, or even artifactual crystalline morphologies, which will not be further dwelt upon.

3.3. Orientation of the epitaxial overgrowth

3.3.1. Substrate structure

Fig. 4 shows a composite polymer/p-quaterphenyl diffraction pattern in which the p-quaterphenyl pattern part is characterized by a set of sharp spots and a series of diffuse (horizontal) bands.

The array of sharp diffraction spots corresponds to the *ab* section of the reciprocal net of the known monoclinic unit cell with $a = 0.805$ nm, $b = 0.555$ nm, $c = 1.781$ nm, $\beta = 95.8°$, $Z = 2$, (Table I) given by Toussaint [6].

Each diffuse band interesting the monoclinic a^* axis can be resolved on closer examination into two reflections indicating a doubling of the a and b parameters of the monoclinic unit cell. Similar diffuse bands and doubling of the unit cell parameters have already been observed for p-terphenyl single crystals, at somewhat lower temperatures [7]. They have been interpreted in terms of a triclinic unit cell resulting from the conversion of the planar aromatic molecular structure to a non planar one [7, 8], a phenomenon which apparently also occurs in p-quaterphenyl crystals.

Furthermore, as is the case with p-terphenyl

TABLE I Crystallographic data for some linear polyphenyls and condensed aromatic hydrocarbons

	a (nm)	b (nm)	c (nm)	β (degree)	Intermolecular distances along ⟨1 1 0⟩ (nm)	1 1 0 inter-row spacing (nm)
Biphenyl	0.804	0.551	0.939	94.5	0.494	0.463
p-Terphenyl	0 808	0.560	1.359	91.9	0.491	0.460
p-Quaterphenyl	0.805	0.555	1.781	95.8	0.489	0.457
p-Sexiphenyl	0.809	0.560	2.623	91.8	0.492	0.460
Naphthalene	0.8235	0.6003	0.8658	122.9	0.509	0.485
Anthracene	0.8562	0.6032	1.1184	124.7	0.524	0.493
Chrysene	0.8386	0.6196	2.520	116.2	0.521	0.498

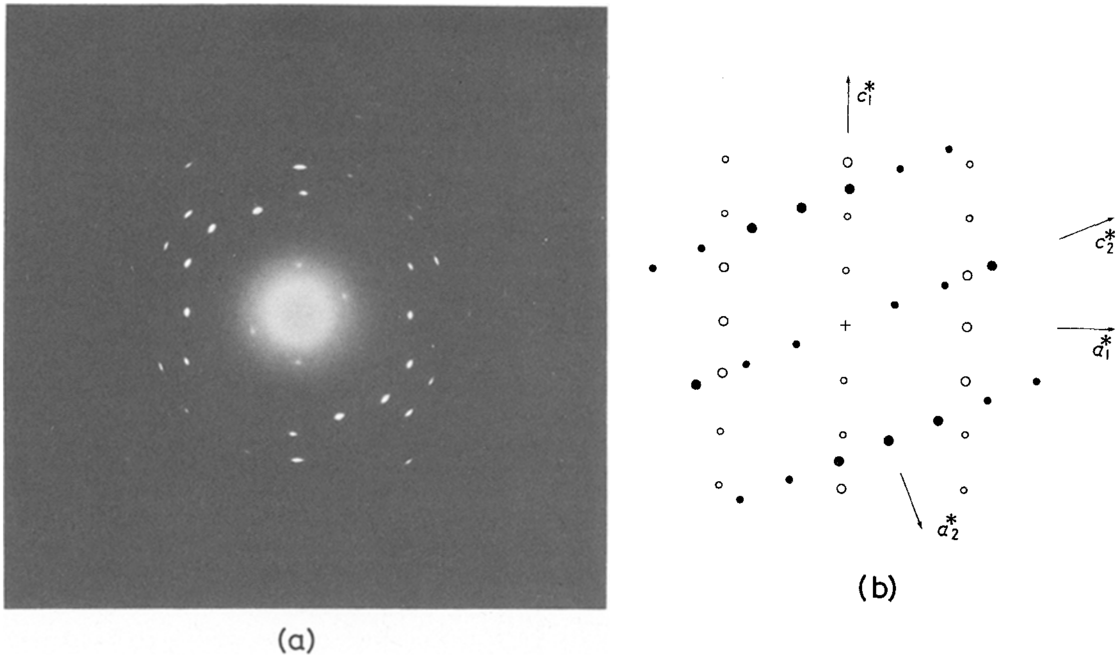

Figure 5 (a) Selected area electron diffraction pattern of an epitaxially grown selenium film after selective dissolution of the substrate. (b) Sketch of the pattern in (a) with indication of the crystallographic axes. Reflections of the two selenium domains oriented 70° apart have been drawn as open and filled circles.

[7], *p*-quaterphenyl experiences a phase transformation on irradiation by the electron beam: at room temperature the diffuse reflections gradually disappear up to the point where the diffraction pattern fits the structure of the pure monoclinic form. The transformation is irreversible.

In spite of the apparent complexity introduced by the existence, at room temperature, of a second crystalline form of the substrate, it is reasonable to analyse the crystallographic relationship between selenium and the various *p*-polyphenyls in terms of epitaxy and lattice matchings by considering the high temperature monoclinic form only. The following arguments can be put forth in favour of such an analysis:

(a) the molecular arrangement in the (0 0 1) contact plane is not drastically different in the two crystal modifications [8];

(b) for *p*-terphenyl, the transformation from the low temperature triclinic form to the monoclinic one, when thermally stimulated, is nearly completed at room temperature. Therefore only the pure monoclinic form should be taken into consideration, the more so that crystallization of selenium is usually performed at much higher temperatures ($T_c > T_{g,Se}$);

(c) finally, diffraction results clearly show that both *p*-ter and quaterphenyl promote identical orientations of the selenium crystals.

3.3.2. Epitaxial relationship and lattice matching

The selenium diffraction pattern obtained after selective dissolution of the substrate is shown in Fig. 5. It results from the superposition of two single crystal diffraction patterns rotated by ~ 70°, i.e. an angle identical to that determined microscopically (polarized light) on thick films.

By referencing the indexing to the normal hexagonal structure of selenium (with $a = 0.4355$ nm, $c = 0.4949$ nm, $Z = 3$ and space group $P3_121$ or $P3_221$ [9] each pattern corresponds to a rectangular net of hkl reflections with $h = k$. The forbidden $0 0 \cdot l$ reflections with $l = 1, 2, 4$ already observed by other authors [10, 11] are also present. Their existence is most probably linked to the very small thickness of the selenium crystals examined, although double diffraction has been proposed as an alternative explanation by Coughlin and Wunderlich [11].

As can be deduced from the diffraction patterns of Figs. 4 and 5, the selenium chains lie parallel to the (0 0 1) polyphenyl substrate surface, in [1 1 0] and [1 $\bar{1}$ 0] directions which are 70° apart. The selenium contact plane is the densely packed $(10\bar{1}0)$ plane. The epitaxial relationship between selenium and the *p*-polyphenyls can thus be summarized by:

$$(10\bar{1}0)_{\mathrm{Se}} \parallel (001)_{p\text{-polyphenyl}} \text{ and}$$

$$c_{\mathrm{Se}} \parallel \langle 110 \rangle_{p\text{-polyphenyl}}$$

This epitaxial relationship is very similar to that observed for polyethylene and various aliphatic polyesters crystallized on the same series of substrates. The similarity may look surprising in view of differences both in chain conformation and unit cell geometries of the inorganic and organic polymers. It appears to result from a fortuitous correspondence of the significant lattice parameters involved in the epitaxy. In particular, the chain axis distances are nearly identical (0.504 nm and 0.495 nm) although they correspond to that of a planar zigzag conformation in polyethylene and to the pitch of a three-fold helix in selenium, respectively.

Epitaxial growth can be analyzed in terms of a two-dimensional lattice matching between selenium and the series of *p*-polyphenyl substrates. As reported by Toussaint [6] and already discussed elsewhere [1, 2], the monoclinic uni cells of polyphenyls up to *p*-sexiphenyl belong to the same space group ($P2_1/a$, cf. Table I). The long axes of the hydrocarbon molecules are oriented roughly parallel to the *c* axis which therefore increases by about 0.42 nm on passing from a given polyphenyl to its next higher homologue, i.e. by increasing the molecular length by one C–C bond and one phenyl ring. The monoclinic angle stays almost constant. More importantly, the molecular packing is identical and, as apparent from Table I, the polyphenyls are isostructural in the (0 0 1) plane which is precisely the contact plane with selenium. The two substrate lattice periodicities involved in the epitaxy, namely the aromatic hydrocarbon intermolecular distance along ⟨1 1 0⟩ directions and the 1 1 0 inter-row distance (Table I), are therefore nearly constant for all the homologues.

The lattice misfits between the substrate and selenium in directions perpendicular and parallel to the chain axis are both very small. A quasi-perfect match is indeed achieved between the selenium helix pitch (0.495 nm) and the intermolecular distance along ⟨1 1 0⟩ (0.490 nm, Table I). In addition, the near 0.460 nm distance between the 1 1 0 molecular rows compares favourably with the 0.4355 nm interchain distance of selenium.

The most significant parameter appears to be the polymer interchain distance involved in the epitaxy. In this context, a comparison with the behaviour of polyethylene on similar and related substrates is of interest. The orthorhombic unit cell of polyethylene is characterized by two interchain distances: 0.445 nm in the {1 1 0} planes and 0.494 nm in the (1 0 0) plane. In addition polyethylene can exist in a monoclinic crystal modification characterized by three different interchain distances: 0.4045, 0.479 and 0.523 nm in (0 0 1), (1 0 0) and $(\bar{2}01)$ crystallographic planes, respectively. It was observed [1, 2] that, depending on the substrate lattice parameters, the epitaxial crystallization of polyethylene is realized with either {1 1 0} or (1 0 0) contact planes, the selection being dictated by the need to achieve the best lattice matching between polymer and substrate. Thus, {1 1 0} is the contact plane when *p*-terphenyl is used as a substrate (matching distances are 0.445 and 0.460 nm, respectively), while in crystallization on anthracene (and the other members of the related family of condensed aromatic hydrocarbons) the PE (1 0 0) plane becomes the plane of contact (matching of the PE 0.494 nm and substrate 0.495 nm periodicities, cf. Table I). Further work using a variety of similar and related organic substrates [12] indicates that when the substrate periodicities are increased to values close to 0.56 nm, it is the monoclinic modification of PE which is formed, the contact plane being $(\bar{2}01)$, i.e. the one which corresponds to the largest possible interchain distance in PE and to the lowest possible lattice mismatch. Observations along similar lines have already been made when using as substrates various salt crystals, in particular alkali halides [12, 13]. For NaCl for example, which has a lattice periodicity of 0.398 nm only, it is the (0 0 1) plane of the monoclinic form which becomes the contact plane [13], i.e. matching is achieved via the shortest possible PE interchain distance.

The fixed interchain distance of 0.435 nm (nearest neighbours) in polymeric selenium does not permit a similar versatility in behaviour. As a matter of fact, it restricts considerably the range of possible substrates for epitaxial crystallization. We observe that, since the 0.4355 nm distance is closest to the 0.445 nm interchain distance in {1 1 0} planes of orthorhombic PE, substrates suitable for epitaxial crystallization of selenium are those on which PE crystallizes with that (1 1 0) orthorhombic contact plane: this is precisely the case with the series of linear polyphenyls used in the present investigation. By comparison, the interchain lattice match is much less favourable for the parallel series of condensed aromatic hydrocarbons (nearly 12%, cf. Table I): it results indeed in a much poorer epitaxy.

Finally, these observations apply also to alkali halide crystals which can be used as substrates for the epitaxial growth of selenium. KBr which was found to be a suitable substrate for selenium [10], is known to induce the epitaxial crystallization of PE with a (1 1 0) contact plane [12]. It may be inferred that KCl for example, which is characterized by an even better lattice match with PE (0%) [13] should be also a very good substrate for the epitaxial crystallization of selenium.

4. Conclusion

Selenium has been evaporated onto (0 0 1) crystal surfaces of linear polyphenyls, namely *p*-terphenyl and *p*-quaterphenyl. On reheating from the glassy state to temperatures in the range 80 to 180° C, it polymerizes–crystallizes epitaxially, with the chain axis parallel to the substrate surface and oriented parallel to ⟨1 1 0⟩ directions of the latter. The epitaxial relationship ensures satisfactory lattice matching in directions parallel and normal to the selenium chain. This relationship is very similar to that found for polyethylene with {1 1 0} contact planes: substrates which induce this epitaxy should be suitable for selenium as well. The specific molecular orientation induced by epitaxial crystallization is ideal for further investigations, in particular on the lamellar character of polymeric selenium crystals [11, 14].

References

1. J. C. WITTMANN and B. LOTZ, *J. Polym. Sci. Polym. Phys. Ed.* **19** (1981) 1837.
2. *Idem, ibid.* **19** (1981) 1853.
3. R. G. CRYSTAL, *J. Polym. Sci. A2* **8** (1970) 2153.
4. G. A. BASSET, *Phil. Mag.* **3** (1958) 1042.
5. S. WOLPERT, A. WEITZ and B. WUNDERLICH, *J. Polym. Sci. A2* **9** (1971) 1887.
6. C. J. TOUSSAINT, *Acta Crystallogr.* **21** (1966) 1002.
7. W. JONES, J. M. THOMAS and J. O. WILLIAMS, *Mater. Res. Bull.* **10** (1975) 1031.
8. J. L. BAUDOUR, Y. DELUGEARD and H. CAILLEAU, *Acta Crystallogr.* **B32(1)** (1976) 150.
9. M. STRAUMANIS, *Z. Krist.* **102** (1940) 432.
10. O. S. HEAVENS and C. H. GRIFFITHS, *Acta Crystallogr.* **18** (1965) 532.
11. M. C. COUGHLIN and B. WUNDERLICH, *Kolloid Z. Z. Polymere* **250** (1972) 482.
12. B. LOTZ and J. C. WITTMANN, unpublished.
13. S. WELLINGHOFF, F. RYBNIKAR and E. BAER, *J. Macromol. Sci.-Phys.* **B10(1)** (1974) 1.
14. R. G. CRYSTAL, *J. Polym. Sci. A2* **8** (1970) 1775.

Received 26 July
and accepted 29 July 1983