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Perfectly alternating ethylene–carbon monoxide copolymers: structure and morphology of epitaxially grown crystals

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Epitaxial growth of the perfectly alternating ethylene–carbon monoxide copolymer (POK) has been successfully achieved using hydroquinone, first as a solvent in its liquid state, and then as a substrate in its crystallized form. Mono-oriented POK domains grow directly in the α crystal form. The polymer chain axis lies parallel to the substrate surface and each domain is composed of a stack of lamellae standing edgewise; the contact plane with the substrate is the crystallographically dense (100) plane.

(Keywords: alternating copolymer; crystals; morphology)

Introduction

Although copolymers of ethylene and carbon monoxide of formula $-(-CH_2-CH_2-CO-)_n-$ were synthesized in the 1950s[1–3], it is only since Drent *et al.*[4,5] developed a new polymerization method that it has been possible to produce perfectly alternating copolymers at such a rate that this polymerization technique might become technologically feasible. These *P*oly*o*lefin *k*etones are abbreviated as POK.

The improvement in the regularity of the chemical structure using organometallic catalyst systems leads to several interesting changes in physical properties, e.g. loss of solubility in common solvents, improved photostability, higher melting temperature ($T_m \approx 257°C$) and increased degree of crystallinity[6]. Moreover, Lommerts *et al.*[7] have recently demonstrated, by wide-angle X-ray diffraction on well oriented fibres, that the room temperature crystal structure (designated POK-α) of a 'perfect' polymer differs significantly from that (POK-β) reported earlier by Chatani *et al.*[8,9]. The latter was derived for radiation polymerized, and therefore probably less perfect, copolymers. Although in both cases the unit cell geometry is orthorhombic and the chain conformation is a planar zigzag, all the carbonyl groups in POK-α point in nearly the same direction; a more efficient chain packing results, i.e. a much denser crystal structure, with a unit cell cross-sectional area of 0.354 nm^2 *versus* 0.379 nm^2 for POK-β[7]. Subsequently, Lommerts and co-workers[10,11] showed that perfectly alternating copolymer fibres undergo a reversible α–β crystal–crystal transition on heating or cooling.

In the present work, we report the results of a structural analysis by electron microscopy and electron diffraction of epitaxially grown layers of this perfectly alternating ethylene–carbon monoxide copolymer. Mono-orientation of the copolymer crystalline lamellae was successfully achieved on hydroquinone, which acts both as a fairly good solvent in its liquid state ($T > T_m = 170°C$) and as a very efficient epitaxial substrate when recrystallized on cooling.

Experimental

The synthesis of two ethylene–carbon monoxide copolymers, differing in their molecular weight, has been described in detail elsewhere[6,7]. For the present investigation, a sample with a limiting viscosity number of 1.3 dl g^{-1} (*m*-cresol, 25°C) was chosen in view of its good solubility and ease of handling. The solvents hydroquinone and hexafluoroisopropanol (HFIP) were used as received. The latter is one of the very few solvents able to dissolve POK at room temperature[12]. Aromatic alcohols or analogues such as phenol or hydroquinone act as solvents above their melting temperature, i.e. at higher temperatures[13].

Epitaxial growth of the copolymer was achieved according to the procedure devised for hypo-eutectic polymer mixtures[14–16]. Starting from a very thin film deposited on a glass slide from dilute HFIP solutions, the copolymer is first co-melted (at $T \approx 200°C$ and for a short time) with an excess of hydroquinone. Large hydroquinone crystals grow between glass slide and coverslip on cooling the mixture; they act at lower temperatures as substrate for the crystallization of the copolymer that is still in solution. After complete crystallization, hydroquinone crystals are selectively dissolved in ethanol. The thin oriented POK layer remaining on the glass slides is backed with a carbon film, floated on water and picked up on copper grids for electron microscopy investigations, which were carried out using a STEM CM12 Philips instrument.

Results and discussion

The two-stage hypo-eutectic growth procedure, previously devised for other polymer/organic substrate pairs[14], can be successfully applied to the present system, despite the fact that perfectly alternating ethylene–carbon

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monoxide copolymers have a much higher melting temperature than hydroquinone (257°C compared to ≈170°C). Due to the relatively strong polymer/solvent interactions via hydrogen bond formation between phenolic compounds and the carbonyl groups of the polymer, the melting and crystallization temperatures of the latter are significantly depressed in solution. On cooling very dilute mixtures of the polymer in the solvent, hydroquinone crystals are formed well before the POK crystallization sets in. After complete solidification, the crystals of both components are highly intermingled, but wherever large and flat hydroquinone crystals have formed, highly ordered thin POK layers are left on the glass slides after selective dissolution of the hydroquinone.

In the optical microscope under polarized light, each large POK domain exhibits single crystal-like optical properties with well defined extinction positions; when rotated by an angle of 45° from these positions, each domain shows a high and uniform birefringence (*Figure 1*). These observations confirm that the favourable crystallographic interactions between hydroquinone and POK lead to a single orientation of the lamellar crystals of the copolymer.

Figure 1 Optical micrograph of a highly oriented and birefringent POK layer taken after selective dissolution of the hydroquinone substrate crystals. Crossed Nicols; scale bar = 50 μm

Since both size and thickness of the oriented domains are most appropriate for transmission electron microscopy, the orientation of the polymer crystal lattice was further characterized by electron diffraction. Surprisingly, the POK crystals were found to be extremely resistant to the incident electron beam; in this respect they are comparable to aromatic polymers known for their superior resistance. This property allowed an extensive series of rotation–tilt studies.

Figure 2a shows a diffraction pattern taken on the as-grown POK thin layer (0° tilt) and *Figure 3a* displays a pattern taken with the layer tilted by 38° around the meridian. All diffraction patterns, which were taken up to 50° tilt angles, can be indexed (see *Figures 2b* and *3b*) solely with the POK-α structure reported by Lommerts *et al.*[8] (orthorhombic unit cell, space group Pbnm; $a = 0.69_1$ nm, $b = 0.51_2$ nm and $c = 0.76_0$ nm). As sketched in *Figure 2b*, the pattern of an untilted sample with its prominent $00l$ (l = even) reflections on the meridian, represents a b^*–c^* section of the polymer reciprocal lattice. The tilted patterns fully corroborate this assignment; as expected from the known structure, a 38° tilt around the meridian brings the (110) planes (strongest $hk0$ reflections) into diffracting position (*Figure 3*).

These electron diffraction experiments thus demonstrate that the POK chains are aligned parallel to the hydroquinone substrate surface. This finding is in line with previous results on polymer epitaxy on organic substrates[15]. As a consequence, each epitaxially grown domain is made of a unique stack of parallel lamellae standing edgewise, and contacting the substrate surface through their crystallographically dense (100) or bc plane.

This peculiar morphology, characteristic of most, if not all, epitaxially grown polymer layers, can be revealed, for instance, by gold decoration (*Figure 4*). In this photomicrogaph, adjacent lamellae, outlined by parallel rows of tiny gold particles, are seen to extend over long distances ($\gg 1$ μm). Under the present crystallization conditions, their thickness, as approximated by the gold interrow distance, varies between 6 and 18 nm, with a

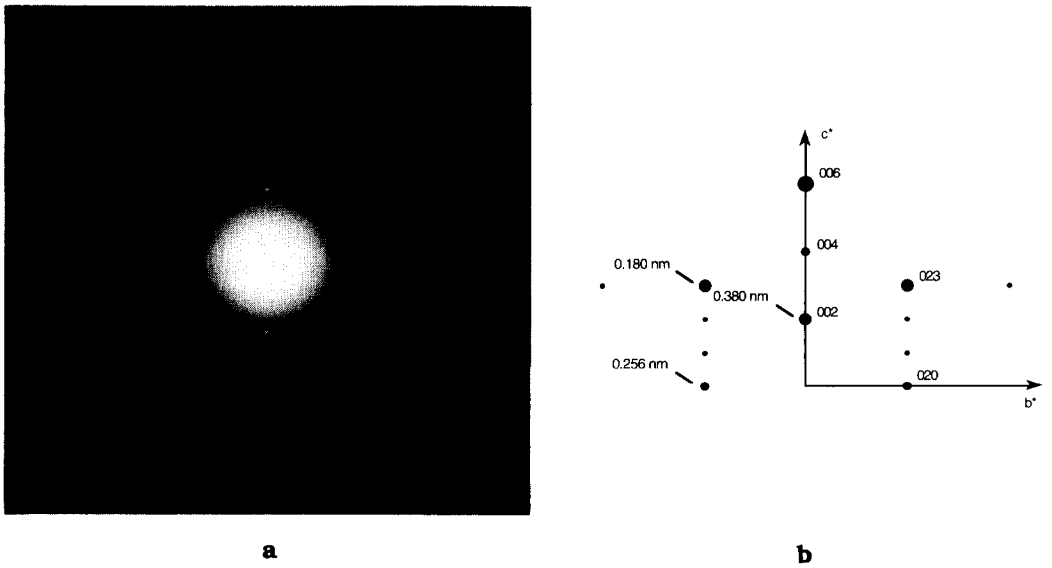
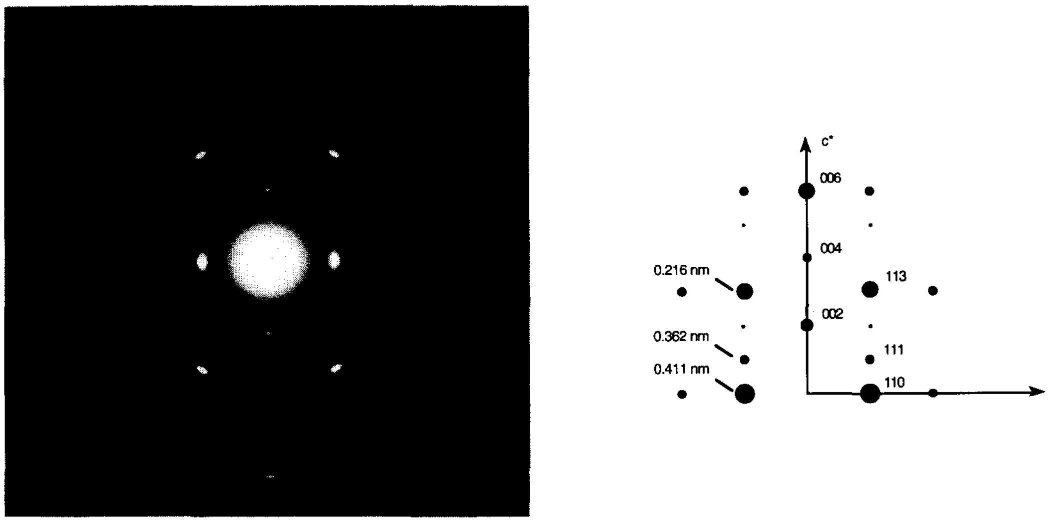


Figure 2 (a) Selected area electron diffraction pattern of an epitaxially grown POK layer. (b) Sketch of the $0kl$ diffraction pattern shown in (a) with the main indices (right-hand side) and the corresponding interplanar distances (left-hand side)



a **b**

Figure 3 Electron diffraction pattern (a) and indexed net (b) of an oriented POK layer tilted by 38° around the chain axis (meridian). Note the presence of the very strong (110) reflections on the equator

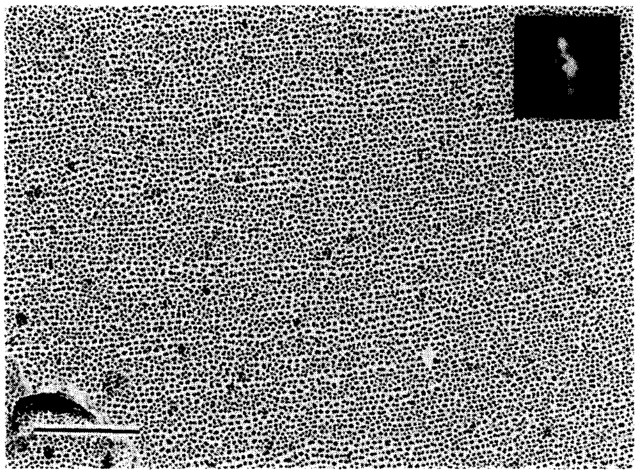


Figure 4 Edge-on lamellae revealed by gold decoration of the border region of an epitaxially grown POK domain and corresponding low angle electron diffraction (insert). Scale bar = 200 nm

mean value of 9 nm. As a consequence, the corresponding low-angle electron diffraction pattern displays only two, rather broad and diffuse reflections (see insert in *Figure 4*). This thickness variability may be linked to the rather broad POK crystallization temperature range observed with good solvents such as hydroquinone, as opposed to the much narrower temperature range obtained with poor solvents.

Several problems prevented the determination of the precise crystallographic relationship between the polymer chains and the substrate, and thus the analysis of the detailed orientation mechanism at hand. Several hydroquinone crystal modifications exist, and neither the crystal phase which forms on cooling the binary mixtures, nor the precise morphology and crystallographic nature of the exposed contact surface, are known. In addition, hydroquinone is not resistant to the electron microscope column vacuum because of its fairly high vapour pressure. Hence, no room temperature polymer/substrate composite electron diffraction pattern, often mandatory for an unequivocal determination of reciprocal orientations, can be obtained.

A final remark is in order. As will be reported in a forthcoming paper, POK lamellar single crystals formed from 'liquid' solvents ($T_m < 25°C$) undergo the same β to α solid–solid phase transition on cooling as well oriented fibres. In the present case, by contrast, diffraction evidence leaves little doubt that in the presence of the hydroquinone substrate, nucleation of the POK copolymer crystals occurs directly in the densely packed α form. This significant difference between the structure of epitaxially grown and solution-grown POK crystals may be attributed to a better matching of POK-α with the hydroquinone lattice.

Conclusion

We have shown that thin, mono-oriented layers of the perfectly alternating ethylene–carbon monoxide copolymer can be grown epitaxially on hydroquinone substrate crystals. Diffraction evidence clearly indicates that (i) the densely packed α phase is obtained, and (ii) the polymer contacting plane is (100), i.e. the chain axis lies parallel to the substrate surface. The unit cell dimensions derived from the electron diffraction patterns are in very good agreement with those reported by Lommerts *et al.*[7] for well oriented α-phase fibres.

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