Epitaxial crystallization of isotactic polypropylene on alkali halide surfaces

Polymer epitaxy from dilute solution was first reported by Willems [1] and Fischer [2] in 1957 for crystallization of polyethylene from xylene on NaCl. Wellinghoff *et al.* [3] in 1974 were the first to report a metastable crystal induced by an epitaxial deposition. Polyethylene was isothermally crystallized from a dilute xylene solution in thin regions near a (1 0 0) NaCl surface, and electron diffraction indicated the presence of the metastable monoclinic crystalline structure of polyethylene. This form could be transformed to the usual orthorhombic structure by annealing or melt recrystallization on the substrate. Lattice matching between the intermolecular spacings of the metastable form and the ⟨1 1 0⟩ spacing on the salt was proposed to explain this observation.

Isotactic polypropylene was an interesting candidate for further investigation in this area in that three polymorphic forms are known, with structure differences not primarily involving changes in lateral spacings. Koutsky *et al* [4] originally crystallized this polymer epitaxially on alkali halides in 1967, but few details of the morphology or the resulting crystal structure were presented.

Isotactic polypropylene ($M_v = 280{,}000$), dissolved at 185° C to 0.1 wt% nitrobenzene was crystallized from 1 to 10 min on several different alkali halides. By cooling very slowly, the onset of precipitation from solution was measured to be at 150° C. Successful epitaxial deposition was achieved at 160° C. A mixed solvent system consisting of 35% mesitylene and 65% nitrobenzene was used in order to crystallize from a clear solution below 150° C. The precipitation from this mixed solvent solution occurred at 110° C. Substantial epitaxial growth was observed only at 140° C from this system.

The experimental technique of preheating the alkali halide substrate to ensure isothermal conditions, and of cleaving the substrate to expose two fresh (1 0 0) faces to the solution, have been described in detail by the authors [3, 5]. The resulting polymer film was removed from the substrate by dissolution of the salts in water, after being coated with platinum, gold, or carbon. Subsequently, the film was placed on an electron microscope grid for examination using a JEOL Jem 100B 100 kV electron microscope in transmission and diffraction modes.

A typical diffraction pattern taken from regions of epitaxial growth at 160° C clearly shows the two ⟨1 1 0⟩ perpendicular orientation of growth on the substrate (Fig. 1a). Such a pattern cannot be indexed as the normal monoclinic form (usually designated as the α form) of isotactic polypropylene. However, it will index as the unusual triclinic (γ form) using the unit cell proposed by Morrow and Newman [6]. The indexing of the pattern reveals the presence of some reflections which have not been reported previously (Table I). This type of pattern was observed from all epitaxial crystallization on (1 0 0) faces on NaCl, KCl, NaF, and KBr single crystals. Recrystallization of the polymer on these substrates after melting produced a mixture of monoclinic and hexagonal (β form) spherulites when quenched to room temperature. Annealing of the epitaxial crystal at 175° C for 1 h on the substrate produced a mixture of triclinic and monoclinic diffraction. This temperature thus caused a melting of some of the triclinic form and subsequent recrystallization in the monoclinic form upon removal from the oven. This melting temperature is believed to be the highest reported for γ form polypropylene, and is probably caused by the stabilizing influence of the substrate. A similar transformation from triclinic to monoclinic was observed in those samples which were annealed off the substrate at 145° C for 1 h. This technique of studying structure changes using diffraction did not permit us to prove definitively whether the transformation was a crystal–crystal or a crystal–melt–crystal type transiton, although the temperature seen suggests a crystal–crystal transition, based on DTA studies made by Kardos *et al* [7]. It was found that no γ melting occurred below 150° C

TABLE I List of triclinic reflections observed from crystals grown for 5 min on potassium chloride.

d_{observed}(Å)	$(h\,k\,l)^*$	Intensity
6.37	1 0 0	Strong
4.16	1 0 1	Strong
3.22	2 0 0	Medium
3.06	$\bar{2}$ 0 1†	Weak
2.09	3 0 0†	Medium

*Indexed using Morrow and Newman's unit cell [6]
† Previously unobserved reflections

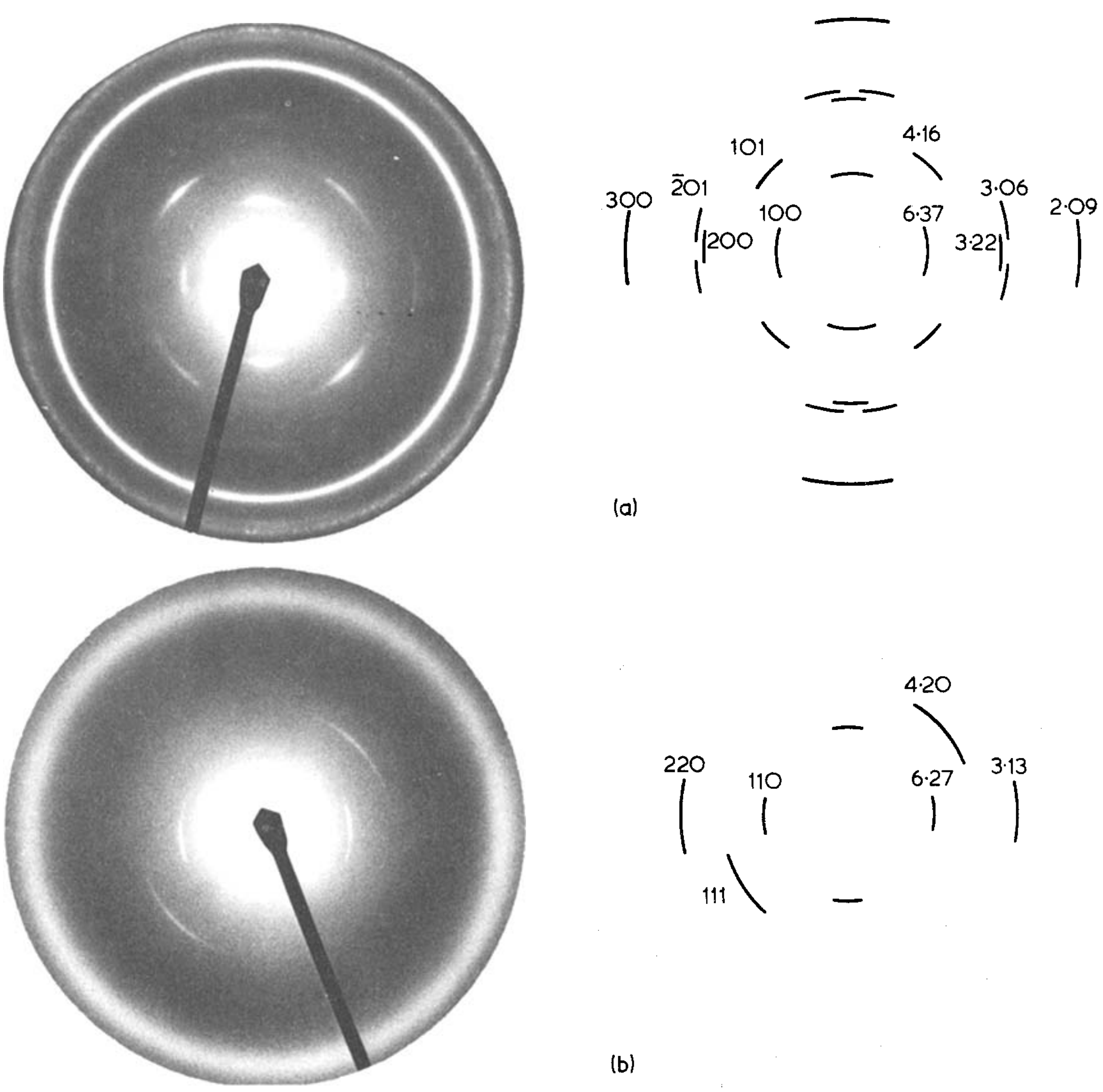

Figure 1 (*a*) Electron diffraction pattern resulting from crystals epitaxially grown from a 0.1 wt% polypropylene solution crystallized isothermally at 160° C for 5 min on potassium chloride. Triclinic ($h\,0\,1$) reflections and gold calibration rings are visible. (*b*) Electron diffraction pattern resulting from crystals epitaxially grown from a 0.1 wt% polypropylene solution crystallized isothermally at 140° C for 5 min on potassium chloride. Monoclinic ($h\,k\,l$) reflections (where $h = k$) and platinum calibration rings are visible.

for their pressure crystallized samples, but a γ to α transition did occur in the region at 145 to 150° C. The epitaxially induced crystals grown at 140° C on KCl yielded patterns in which only monclinic reflections were observed (Fig. 1b). These patterns did not show the number of reflections visible in the triclinic patterns, indicating a lower degree of crystal perfection coupled with a lower nucleation density, as will be shown later.

The crystallization of iostactic polypropylene on alkali halides yielded significant amounts of epitaxial growth at 160° C only on NaCl and KCl (Fig. 2). These crystals showed average dimensions which did not change appreciably with increasing crystallization times (Table II). Only nucleation density increased with time, with 5 to 10 min growth yielding meshlike mats of epitaxial crystals (Fig. 3). These mats are completely filled in with

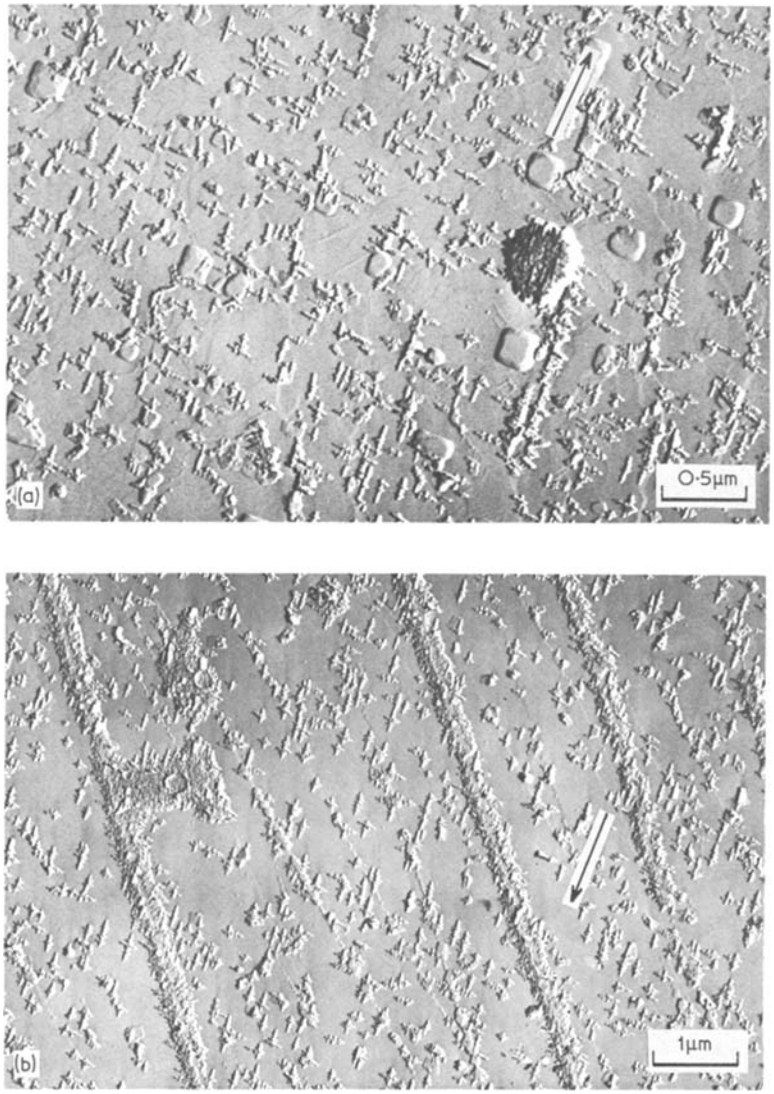

Figure 2 (*a*)) Electron micrograph of crystals grown from a 0.1 wt% isotactic polypropylene solution in nitrobenzene crystallized isothermally at 160° C for 1 min on sodium chloride, showing good nucleation of bidirectional epitaxial growth oriented in ⟨1 1 0⟩ directions. (Arrow pointing in the sodium chloride [1 1 0] direction; 45° shadow angle), (*b*) Electron micrograph of epitaxial growth on potassium chloride under similar conditions as in Fig. 2a. Note the presence of (1 0 0) steps in the surface which act as nucleation sites for initial epitaxial crystallization.

crystals, owing to the unique morphology of each crystal. The rodlike epitaxial crystals grown on NaCl and KCl exhibited branching normal to the parent crystals. The growth directions strictly corresponded to the substrates' ⟨1 1 0⟩ directions (Fig. 4). This morphology is unique to polypropylene epitaxy. Various mechanisms for formation of similar structure have been proposed by Khoury [8]. These include various twinning mechanisms and an epitaxial growth of branch molecules on the parent crystals' fold planes. Growth on NaF and KBr was mcuh more sparse and was poorly oriented in both ⟨1 0 0⟩ and ⟨1 1 0⟩ directions of the surface. In addition, no branch crystals were observed. The area of coverage was the only time dependent quantity (after the first minute) for crystallization on these substrates.

Attempts to crystallize on alkali halides at 130° C from a cloudy nitrobenzene solution did not yield observable epitaxial growth, but use of the mixed solvent system described earlier allowed solution crystallization at 140° C. The rodlike crystals obtained were not branched and were poorly oriented (Table II). This growth was probably enhanced by nucleation on cleavage step planes.

Turner-Jones *et al* [9] in 1964 described the differences between the α and γ forms of isotactic

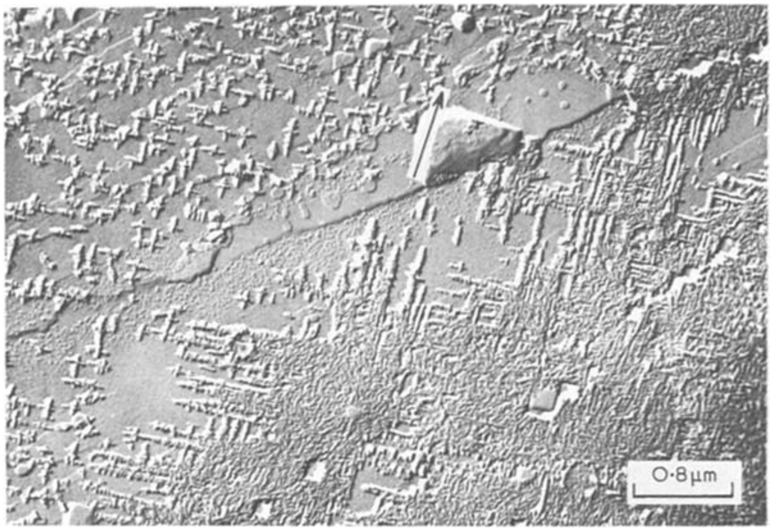

Figure 3 Electron micrograph of epitaxial growth on sodium chloride under similar conditions as in Fig. 2a, with a crystallization time of 5 min. A dense meshlike epitaxial growth edge with crystals oriented in usual ⟨1 1 0⟩ directions is clearly visible.

polypropylene; their main conclusion concerning the monoclinic structure was that it exhibited a low degree of crystal perfection due to a substantial amount of disorder found within the polymer chain (i.e. anticlinic chains). Since a polypropylene chain can be either a left or right handed 3_1 helix, it is probably that, in the α form, a disordering of a chain with similar sense (i.e. isoclinic) to an anticlinic chain may occur randomly in a chain segment between folds. This supposition is supported by Mencik [10], who predicted at 45% "disordering" to exist in the monoclinic chain type.

In contrast, triclinic polypropylene exhibits a high degree of crystal perfection [9]. Turner-Jones *et al.* speculated that blocks of isoclinic chains existed within the γ form. This is supported by the observation of the γ form only under conditions of slow crystallization rate [6, 7, 9]. The form has been most easily observed in slow cooling low molecular weight polymer from the melt [6] and by slow cooling normal material from the melt under very high pressure [7]. Our results can be explained on a similar kinetic reasoning, although the γ form has not been previously solution crystallized with a normal molecular weight. The epitaxial substrate allows crystallization above the solution precipitation temperature. At temperatures near the equilibrium melting point of the polymer, the rate of crystallization is slow enough to allow the formation of perfect crystals. One could speculate that these "perfect" crystals are really composed of isoclinic chains. At 140° C, crystallization rates are dramatically increased and the result is formation of the usual α crystal form.

The observed nucleation density of epitaxial crystals on the various substrates could be related

TABLE II Average crystal dimensions resulting from 1 min crystallization of isotactic polypropylene on alkali halides.

T_c^*(° C)	Substrate	Length/ Width	Height (Å)	Density (no. μm^{-2})
160 ± 1	NaF	12.5 ± 3	123 ± 20	7 ± 5
160 ± 1	NaCl	8.3 ± 3	70 ± 20	40 ± 10
160 ± 1	KCl	9.0 ± 3	80 ± 20	50 ± 10
160 ± 1	KBr	13.0 ± 3	125 ± 20	8 ± 5
140 ± 1	KCl	18.0 ± 3	184 ± 20	11 ± 5

*T_c ≡ Temperature of the crystallization.

Figure 4 Enlarged view of section of epitaxial growth shown in Fig. 2a, showing bidirectional morphology of each crystal. (Arrow pointing in the sodium chloride [1 1 0] direction; 45° shadow angle).

to lattice matching. Since the [0 1 0] triclinic dimension (parallel to the substrate) is 21.4 Å, with five chains equally spaced along that dimension, a spacing of 4.3 Å would be most favourable according to lattice matching rules. Of all the alkali halide substrates, NaCl and KCl, with [1 1 0] spacings of 4.0 and 4.5 Å, respectively, should yield the maximum growth. This is precisely what is observed.

It can be concluded that isotactic polypropylene crystallized epitaxially in the unusual triclinic crystal form on alkali halides at 160° C. Epitaxial growth at 140° C produced monoclinic epitaxial crystals. The alkali halide substrate permitted crystallization at a high enough temperature to form the γ structure using very slow crystallization rates. Epitaxially grown crystals on NaCl and KCl at 160° C exhibited branch growth with an unusual morphology, and the nucleation density was definitely influenced by a matching of polymer to substrate dimensions.

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Fracture of brittle materials in uniaxial compression

It is well known that brittle materials are often used as structural materials in compression, rather than in tension, since tension gives rise to catastrophic failures. In this paper a theory is proposed for the mechanism of failure of a brittle material in uniaxial compression.

The strength and direction of the propagation of an inclined crack (see Fig. 1) in a brittle material, under a uniaxial loading system, have been carried out [1, 2] using strain energy density concepts. The axial stress, σ, required to propagate an inclined crack (see Fig. 1) is given by

$$\sigma^2 a = \frac{2}{\pi} K_{\mathrm{IC}}{}^2 \mathrm{U}(\beta), \tag{1}$$

where K_{IC} is the critical stress intensity factor, a is the semi-crack length and $\mathrm{U}(\beta)$ is a function of crack angle, β, which has two values corresponding to tensile and compressive loadings.

Under a tensile loading system, propagation of a single crack leads to total failure, since the subsequent crack path runs normal to the applied stress. Therefore the strength in tension has been studied [3, 4] using the "weakest link concept". This study assumed that the probability density, $f(a)$, of the semi-crack length is well fitted by

$$f(a) = \frac{c^{n-1} a^{-n} e^{-c/a}}{(n-2)!} \quad \text{for } a > 0, \tag{2}$$

where c/n is the mode of the distribution and n determines the rate at which the density tends to zero with increase in crack size. It is then shown that the distribution of strengths (tensile) is closely fitted by a Weibull distribution [5] for sufficiently large volumes and that the Weibull modulus, m, is related to n which is a property of the flaw size distribution, by the expression

$$m = 2n - 2 \tag{3}$$

In the case of uniaxial compression the subsequent crack path does not grow catastrophically,