Epitaxial crystallization of poly (vinylidene fluoride/vinyl fluoride) co-polymer

Epitaxial crystallization of polymers has been a subject of interest in this laboratory in recent years [1–4]. Here, we report results on the epitaxial crystallization of a co-polymer of vinyl fluoride (VF) and vinylidene fluoride (VF_2) from dilute (0.1 wt %) nitrobenzene solution on to (0 0 1) alkali-halide cleavage surfaces.

The co-polymer was synthesized by Scheinbeim* using a monomer feed ratio of 95/5 VF_2/VF. The intrinsic viscosity of the co-polymer was reported as $0.97\,\mathrm{dl\,g^{-1}}$ in dimethyl acetamide at 30° C. This compares with $[\eta] = 1.01\,\mathrm{dl\,g^{-1}}$ for commercial PVF_2 having a $M_w \simeq 2$ to 3×10^5.

Poly(vinylidene fluoride) (PVF_2) homopolymer exhibits at least three different polymorphic crystal structures, denoted forms I, II, and III by Hasegawa *et al.* [5]. The co-polymer (PVF_2/VF), however, crystallizes exclusively in form I, the structure of which has been determined to be a fully extended planar zigzag in an orthorhombic unit cell with $a = 8.58$ Å, $b = 4.91$ Å, and c (fibre axis) = 2.56 Å [5]. Since this particular crystal form displays piezoelectric properties [6, 7], this material is an interesting candidate for epitaxial crystallization. A highly oriented (i.e. epitaxial) film of form I crystals may possess enhanced piezoelectric properties.

Epitaxial films were produced on NaCl and KCl (0 0 1) surfaces using an isothermal immersion technique described elsewhere [1, 4]. All crystallizations were performed in thermostatted silicone oil baths maintained at the crystallization temperature ± 0.5° C. Samples were examined with a JEM-100B electron microscope operating at an accelerating voltage of 100 kV.

Substantial epitaxial growth on to NaCl and KCl from dilute nitrobenzene solution occurred in the temperature range 90 to 105° C. Typical micrographs are shown in Figs. 1a and 2a for the overgrowth obtained on NaCl and KCl respectively, at 95° C and 10 min crystallization time. Lamellar, rod-like crystals oriented in the substrate ⟨1 1 0⟩ and $\langle 1\,\bar{1}\,0\rangle$ directions are morphologically very similar to epitaxial overgrowths obtained with other crystalline polymers [1–3]. The ⟨1 1 0⟩ alignment of the lamellae was consistently more perfect on KCl than on NaCl. The simplest explanation for this phenomenon is that KCl forms a very flat, homogeneous surface upon cleavage, whereas NaCl has a high tendency to form cleavage steps in the ⟨1 0 0⟩ directions [8]. The crystallizing polymer preferentially nucleates at these defects, causing the resulting lamellae to deviate from perfect ⟨1 1 0⟩ orientation. If the cleavage step is large enough, ⟨1 0 0⟩ orientation of the lamellae may be observed. This ⟨1 0 0⟩ alignment was noted only on NaCl samples.

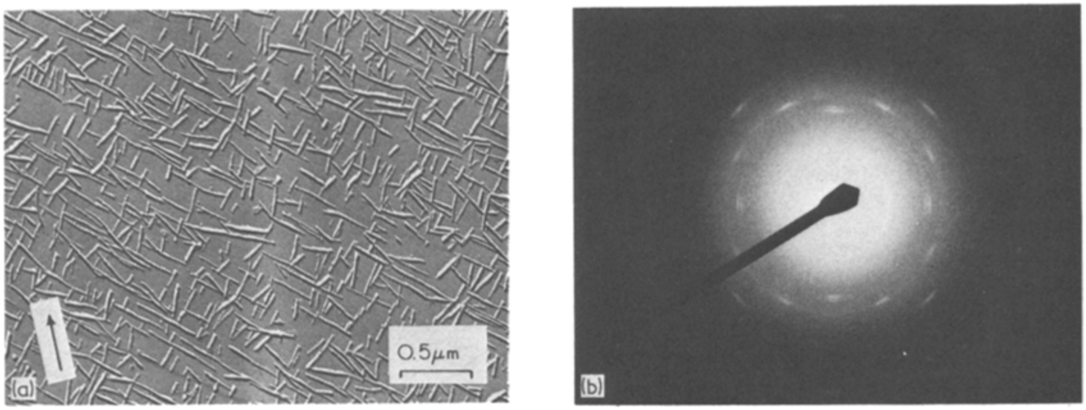

Figure 1 (a) Electron micrograph of PVF_2/VF co-polymer epitaxially crystallized on NaCl for 10 min at 95° C. Arrow points in substrate ⟨1 0 0⟩ direction. (b) Electron diffraction pattern obtained from the epitaxial overgrowth of the co-polymer on NaCl. Note the presence of reflections which do not index as $0kl$. (Refer also to Fig. 3.)

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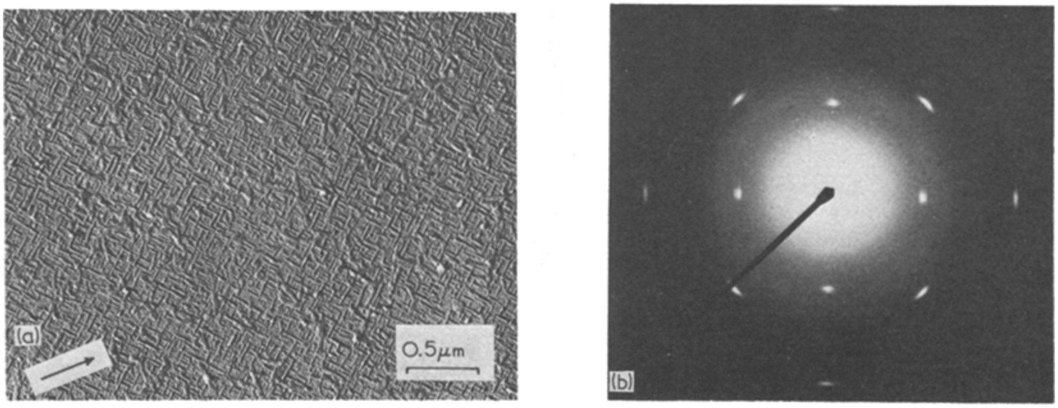
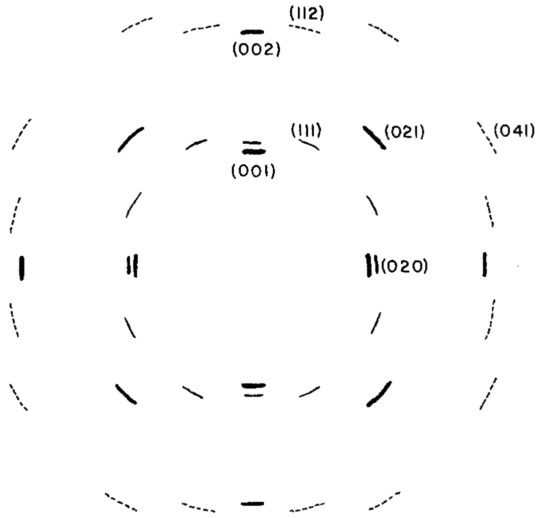


Figure 2(a) Electron micrograph of PVF_2/VF co-polymer epitaxially crystallized on KCl for 10 min at 95° C. Arrow points in substrate ⟨1 0 0⟩ direction. (b) Electron diffraction pattern obtained from the epitaxial overgrowth of the co-polymer on KCl. Here, only $0kl$ reflections are seen. (Refer also to Fig. 3.)



$d_{calc.}$	$d_{meas.}$	index
2.56 Å	2.56 Å	(001)
1.28	1.28	(002)
2.46	2.47	(020)
1.77	1.78	(021)
1.11	1.11	(041)
2.19	2.20	(111)*
1.23	1.24	(112)*

Figure 3 Indexing scheme for diffraction from the epitaxy. Unit cell: Orthorhombic; $a = 8.58$ Å, $b = 4.91$ Å, $c = 2.56$ Å. [5]. *Reflections which do not index as $0kl$ probably result from fallen over epitaxial crystals.

The presence of cleavage steps on NaCl samples may also explain the fact that PVF_2/VF has a lower nucleation density (lamellae/μm^2) on NaCl than on KCl. The polymer chains preferentially nucleate at cleavage steps and tend not to fill in the spaces in between. This results in long lamellae spaced relatively far apart, as seen in Fig. 1a. On KCl, however, there are few steps present, and crystal nuclei have an equal probability of initiating on any and all parts of the salt surface. The uniformity of the overgrowth and perfection of ⟨1 1 0⟩ orientation consistently observed on KCl lends support to this argument.

The width of the lamellae was relatively constant on both substrates, measuring roughly 200 Å at temperatures ranging from 90 to 105° C. At 90° C, a very thick mat of amorphous overgrowth was observed on top of the epitaxy, which prevented measurements of lamellae at this temperature. The crystal height was consistently less on KCl ($\leqslant 100$ Å) than on NaCl ($\simeq 200$ Å).

Several experiments were conducted at reduced crystallization times of 1 and 5 min to study the crystallization kinetics. On both substrates, the crystal height increased rapidly in the first 5 min of crystallization time, then proceeded more slowly. Approximately 40% of the height attained in 10 min was reached in 1 min; 75% of this height was reached in 5 min. The width of the lamellae did not vary with crystallization time. These results are in accordance with previous data obtained for epitaxial crystallization of polyethylene [1], and seem to be generally characteristic of solution epitaxial crystallization of polymers.

Selected-area electron diffraction clearly shows the presence of two chain orientations 90° apart (Figs. 1b and 2b). All diffraction patterns obtained indexed as form I, as shown in Fig. 3. All reflections in Fig. 2b index as $0kl$, indicating that the *bc* plane and thus the chain axis are both parallel to the substrate surface. "Extra" reflections, which do not index as $0kl$ were occasionally observed (e.g. in Fig. 1b), and probably result from "toppled over" epitaxial crystals which are still more or less oriented with respect to the substrate directions. Patterns containing these "extra" reflections in addition to the usual $0kl$ reflections were occasionally observed on KCl also. Similar electron diffraction patterns from thinner films (1 and 5 min crystallization times) showed that the same crystal structure (form I) persisted to within 30 Å of the substrate surface.

Acknowledgements

The authors appreciate the financial support of the National Science Foundation, grant number DMR 76-81768. We also appreciate helpful discussions with Scott Rickert concerning the initial experiments.

References

1. S. WELLINGHOFF, F. RYBNIKAR and E. BAER, *J. Macromol. Sci.* **B10** (1) (1974).
2. S. H. CARR, A. WALTON and E. BAER, *Biopolymers* **6** (1968) 469.
3. S. E. RICKERT and E. BAER, *J. Appl. Phys.* **47** (1976) 4304.
4. C. M. BALIK and A. J. HOPFINGER, *J. Polymer Sci.* **16** (1978) 1897.
5. R. HASEGAWA, Y. TAKAHASHI, Y. CHATANI and H. TADOKORO, *Polymer J.* **3** (1972) 600.
6. H. OHIGASHI, *J. Appl. Phys.* **47** (1976) 949.
7. K. NAKAMURA and Y. WADA, *J. Polymer Sci. A-2* **9** (1971) 161.
8. Harshaw Optical Crystals, catalog from Harshaw Chemical Co, Cleveland, Ohio (1967).

Received 27 September
and accepted 13 October 1978

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Computer calculations of heterogeneous equilibria in the system C–O–H–N–Si–Ar

In the development of ceramic materials for high-temperature applications there is a great need to establish phase equilibria in order to produce, process, and understand the properties in the service conditions. The understanding of the gas-phase reactions is more important than in the usual metallic systems since:

(1) the materials are usually made in a high surface area, fine powdered form by way of gas-phase reactions;

(2) the successful fabrication by hot-pressing or sintering is often made possible by the presence of a small amount of liquid that may be formed or consumed by gas-phase reactions;

(3) the materials are usually intended to be single phase but the service behaviour is dramatically influenced by the presence of minor amounts of residual grain-boundary phases;

(4) the service conditions are at high temperature and often in chemical environments much different with respect to temperature, pressure, and composition than those of fabrication;

(5) minor changes in the amounts of gas-phase species such as O_2, H_2, N_2, SiO, etc., can result in dramatic changes in the protective films responsible for high-temperature protection since the materials have many stable gas-phase molecular species and do not react only by evaporation.

In summary it is seldom instructive to deal only with the condensed phase equilibria as in the case of most metallic systems. In fabrication and service conditions there is always a chemically active