Crystallization of the β phase of poly(vinylidene fluoride) from the melt

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The purpose of this report is to describe the first conclusive evidence for crystallization of poly(vinylidene fluoride from the melt at atmospheric pressure in the polar β phase. This phase is the one that has attracted the widest interest among the four known polymorphs of PVF_2 because of its extensive piezoelectric and pyroelectric applications.

The unit cell of the β-form is orthorhombic[1] with dimensions $a = 8.58$ Å, $b = 4.91$ Å, and $c = 2.56$ Å; the molecular chains adopt a slightly distorted all-*trans* conformation[1]. The β-phase may be grown from solution[2], but, as regards crystallization from the melt, it has only been obtained at elevated pressures[3], or from copolymers of PVF_2 with other fluorocarbons (e.g. trifluoro- or tetrafluoroethylene)[4]. In the latter case, however, Lando and coworkers[4,5] have shown that the β unit cell is adopted only because the chains lack the choice of other conformations as a result of major steric conflicts attributable to the copolymer segments. The only reported crystallization of pure PVF_2 from the melt in the β phase at atmospheric pressure was described by Prest and Luca[6] on the basis of infra-red spectroscopy. However, Lovinger[7] later found that electron diffraction patterns from such crystals are consistent with the γ rather than the β polymorph; this conclusion has recently been confirmed by Morra and Stein[8]. Attribution of the β phase to these γ spherulites in the study of Prest and Luca[6] is perfectly understandable because, at that time, β and γ conformations were considered to be identical[1].

Crystallization of β-PVF_2 from the melt at atmospheric pressure has now been achieved by epitaxial growth on the (001) surface of potassium bromide. KBr single crystals, obtained from the International Crystal Co., Elizabeth, NJ, were cleaved and used as substrates for the deposition of PVF_2 (Kynar 821 of Pennwalt Corporation) at 180°C from 0.1% solution in dimethylformamide. The coherent molten films of PVF_2 obtained after evaporation of the solvent were then crystallized isothermally at ~165°C. Following shadowing with Pt/C and coating with carbon in a vacuum evaporator, the films were isolated by dissolution of the substrate, and examined in the transmission and diffraction modes of a Jeol 100-CX electron microscope.

The typical morphology in thin regions of such films is seen in *Figure 1*; it consists of lamellar crystals standing on edge and aligned in the two ⟨110⟩ directions of the KBr substrate. This type of epitaxial alignment is common for polymers crystallized on alkali halides[9,10] and has also been observed during solution-crystallization of a PVF_2 copolymer[11]. Although close lattice matching is not a necessary prerequisite for epitaxial crystallization, there is good matching in the case of β-PVF_2 on $(001)_{KBr}$: the difference between $b_{\beta\text{-}PVF_2}$ and $[110]_{KBr}$ is 5.6%, while that between $2c_{\beta\text{-}PVF_2}$ and $[110]_{KBr}$ is 4.3%. In thicker areas, platelets (lying flat on the substrate) and spherulites were obtained, typical of those described by Lovinger and Keith[7,12]. Clearly, these must have nucleated away from the surface and are thus free from any epitaxial influences of the substrate; their electron diffraction patterns are those of the γ and α forms that are normally grown at these temperatures[7,12].

Electron diffraction from the epitaxially grown crystals of *Figure 1* yields the pattern shown in *Figure 2*. The reflections are seen to lie in two orthogonal reciprocal lattice grids, in agreement with the morphological evidence (*Figure 1*); they all may be indexed as $0kl$, signifying that the bc plane of the unit cell has grown parallel to the substrate and that the a-axis is normal to the film surface.

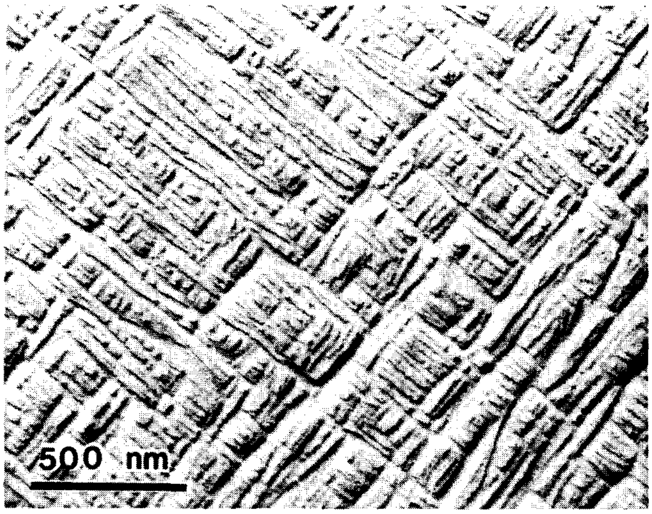

Figure 1 Typical morphology of β-crystals grown epitaxially from the melt on KBr

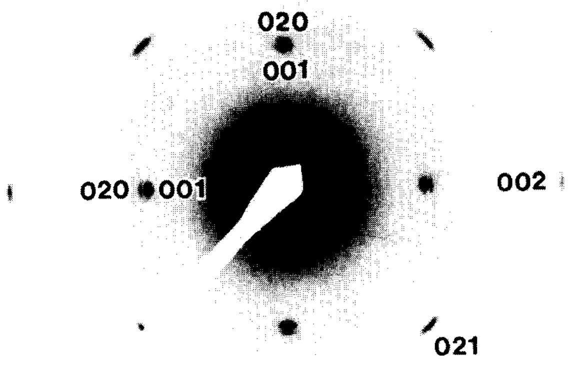

Figure 2 Electron diffraction pattern from the β-crystals of *Figure 1* (rotated ~45° with respect to the field)

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Further, the relative orientation of the diffraction pattern with respect to the field is such that the molecular chains must either be parallel or perpendicular to the long axes of these crystals; the latter is assumed here, implying that the dipole vectors are then parallel to these long axes. The (200) planes are among the most densely packed in β-PVF$_2$; in common with the situation in other polymers[13], it is these densely packed planes that are nucleated by the substrate.

From *Figure 1*, *b* appears to be the preferred growth direction of these essentially two-dimensional crystals of β-PVF$_2$; this agrees with the radial growth direction of polyethylene with which β-PVF$_2$ shares a great similarity in unit-cell structure. However, if such were the case also in three-dimensional crystals, β-PVF$_2$ would differ from the α and γ polymorphs, since there the dipole vectors are normal to the radial growth direction[7]. However, it is probable that the preferred growth direction in three-dimensional crystals of the β phase is *a*, which happens to be restricted by the thinness of the sample; this would then make the radial orientation of unit cells and dipole vectors consistent among the α-, β-, and γ-polymorphs of PVF$_2$ (note that the *a*- and *b*-axial designations are reversed in β-PVF$_2$ from their assignments in the α and γ forms).

Investigations of the morphology and temperature-dependence of melt-grown β crystals are continuing.

REFERENCES

1 Hasegawa, R., Takahashi, Y., Chatani, Y. and Tadokoro, H. *Polym. J.* 1972, **3**, 600
2 Miller, R. L. and Raisoni, J. *J. Polym. Sci.* (*Polym. Phys. Edn*) 1976, **14**, 2325
3 Scheinbeim, J., Nakafuku, C., Newman, B. A. and Pae, K. D. *J. Appl. Phys.* 1979, **50**, 4399.
4 Lando, J. B. and Doll, W. W. *J. Macromol. Sci.* (*B*) 1968, **2**, 205
5 Farmer, B. L., Hopfinger, A. J. and Lando, J. B. *J. Appl. Phys.* 1972, **43**, 4293
6 Prest, W. M. Jr, and Luca, D. J. *J. Appl. Phys.* 1975, **46**, 4136
7 Lovinger, A. J. *J. Polym. Sci.* (*Polym. Phys. Edn*) 1980, **18**, 793
8 Morra, B. S. and Stein, R. S. *J. Polym. Sci.* (*Polym. Phys. Edn*) in press
9 Willems, J. and Willems, I. *Experientia* 1957, **13**, 465
10 Fischer, E. W. *Kolloid Z.* 1958, **159**, 108
11 Balik, C. M., Farmer, R. and Baer, E. *J. Mater. Sci.* 1979, **14**, 1511
12 Lovinger, A. J. and Keith, H. D. *Macromolecules* 1979, **12**, 919
13 Lovinger, A. J. *Polym. Prepr.* 1980, **21**, 253

Proton n.m.r. relaxation and molecular motion of liquid n-paraffin $C_{32}H_{66}$ as studied by isotopic dilution

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INTRODUCTION

The proton spin-lattice relaxation time, T_1, gives useful information about the molecular motion of macromolecules[1]. However, there is some difficulty in understanding the mechanism of T_1 of macromolecules in concentrated solution and melt because of the effects of chain entangling. The isotopic dilution technique[2-11] is useful to overcome such problems, because it eliminates the proton–proton dipolar interaction on neighbouring polymer chains thus enabling the determination of the intramolecular and intermolecular T_1's by dilution of a molecule considered with a fully-deuterated analogue.

We have successfully applied this technique to the understanding of the mechanism of molecular motion of polyethylene (PE)[10,11]. In molten PE the molecular motion which contributes to intramolecular T_1, is in the extreme narrow region, $\omega\tau_c \ll 1$, however, the molecular motion contributing to intermolecular T_1 is in the slow motional region, $\omega\tau_c > 1$, where ω is the resonance frequency and τ_c is the correlation time. The intermolecular T_1 was influenced by the effect of chain entangling. In order to clarify this effect, liquid n-paraffin may be compared with PE, because the effect of chain entangling depends considerably on the chain length of the molecule considered.

The purpose of this work is to separate the observed proton T_1 of liquid n-paraffin, n-$C_{32}H_{66}$, into intra- and intermolecular contributions by the isotopic dilution technique, and to discuss the molecular motion of this molecule as compared with molten PE which we have reported in a previous paper[10].

ISOTOPIC DILUTION TECHNIQUE

The observed proton spin-lattice relaxation rate, $(1/T_1)_{\text{obs}}$, is given by the sum of the following terms.

$$\left(\frac{1}{T_1}\right)_{\text{obs}} = \left(\frac{1}{T_1}\right)_{\text{intra}} + \left(\frac{1}{T_1}\right)_{\text{inter}} \qquad (1)$$

where $(1/T_1)_{\text{intra}}$ and $(1/T_1)_{\text{inter}}$ are the intra- and intermolecular relaxation rates respectively. The intramolecular relaxation depends on the segmental motions of the molecule whereas the intermolecular relaxation depends on the relative translational motions of different molecules. The general expressions for these contributions are given by Gutowsky and Woessner[12] as

$$\left(\frac{1}{T_{1_i}}\right)_{\text{intra}} = \frac{2\pi\hbar^2\gamma^2\eta a}{3kT}\left(3\gamma_i^2\sum_j r_{ij}^{-6} + 2\sum_f^{*}\gamma_f^2 r_{if}^{-6}\right) \qquad (2a)$$

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