Evidence for a new crystal phase in conventionally poled samples of poly(vinylidene fluoride) in crystal form II

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INTRODUCTION

In studying the properties of poly(vinylidene fluoride) in crystal forms I (β) and II (α) we have found that oriented semicrystalline samples containing either crystal form, display significant piezoelectric and pyroelectric activity after poling (i.e. the application of an electric field, usually at an elevated temperature). In particular, we have prepared samples of uniaxially oriented PVDF in crystal form II which, when suitably poled, display a piezoelectric coefficient (d_{31}) as high as 10 pCN^{-1} and a pyroelectric coefficient of 15 $\mu Cm^{-2}K^{-1}$. These coefficients are about half of those obtained for uniaxially-oriented form I poled under the same conditions, though one must be careful to compare similarly oriented samples for this generalization to apply[1]. These results seemed to indicate that a large part of the piezoelectric and pyroelectric properties of PVDF was due to spurious effects involving trapped charges since the crystal form II is known to be centrosymmetric[2] and therefore not intrinsically piezoelectric or pyroelectric. Recently, however, Davis *et al.*[3] have suggested that a polar modification of crystal form II may be produced by poling a biaxially-oriented film which initially consists of a mixture of forms I and II. The suggested structure, which we shall denote IIp, is shown in *Figure 1*. It requires the rotations of half the chains in the antipolar form II to form a polar array of essentially the same lattice dimensions. This new phase could, of course, be intrinsically piezoelectric or pyroelectric and we have therefore compared the X-ray diffraction data of our uniaxially oriented samples of crystal form II before and after poling to determine whether such a conversion to form IIp has occurred.

EXPERIMENTAL

Oriented samples of crystal form II were produced by drawing 50 μm thick 'non-oriented' capacitor grade Kureha film to about 3.5:1 relaxed draw ratio at 160°C and then annealing for 18 h at constant length in an air oven at 120°C. Samples to be poled were provided with evaporated aluminium electrodes about 70–100 nm thick and the poling was performed at 130°C in oil using a field strength of 100 V/μm for 30 min. Subsequent to poling, the samples were heated to 75°C whilst measuring their pyroelectric response.

The density of the oriented and annealed samples was 1800 kgm^{-3} compared with 1769 kgm^{-3} for the starting material, indicating an increase in crystallinity from about 40 to 50%. X-ray diffraction studies before poling show that there is typically less than 5% form I in these predominantly form II samples[1].

The samples for the X-ray diffraction studies were prepared by sticking four layers of the drawn film together with PVA glue and cutting thin strips about 500 μm wide from the composite samples. Both poled and unpoled samples were of closely similar dimensions with the long axis of the strip parallel to the draw direction. For the results presented here, the aluminium electrodes were not removed prior to the X-ray investigations, but subsidiary studies have shown that similar results are obtained if the electrodes are removed from the sample using sodium hydroxide. The electrodes are responsible for the small peak at $2\theta \simeq 38.5°$ seen in the data for the poled sample.

The X-ray measurements were made 20 months after poling the samples. The apparatus used was a Siemens K-4 X-ray generator, equipped with a type F goniometer. All measurements were made with CuKα radiation. A 2θ scan of the zero order layer line was made both in reflection (scattering vector perpendicular to the plane of the film) and in transmission (scattering vector in the plane of the film) for both poled and unpoled samples. In addition, the meridional

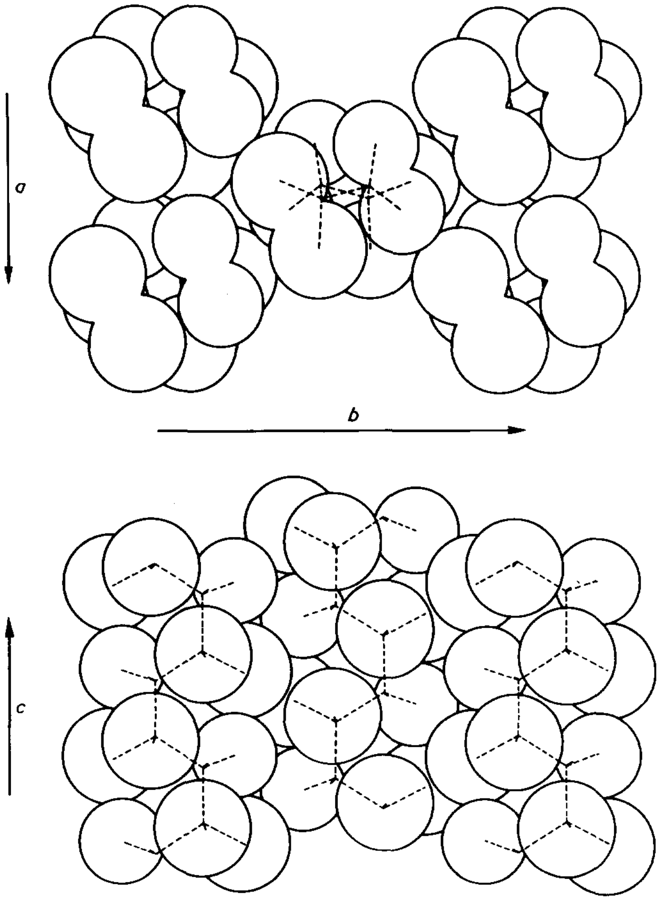

Figure 1 Proposed form IIp. (Large and small circles indicate fluorine and hydrogen atoms, respectively)

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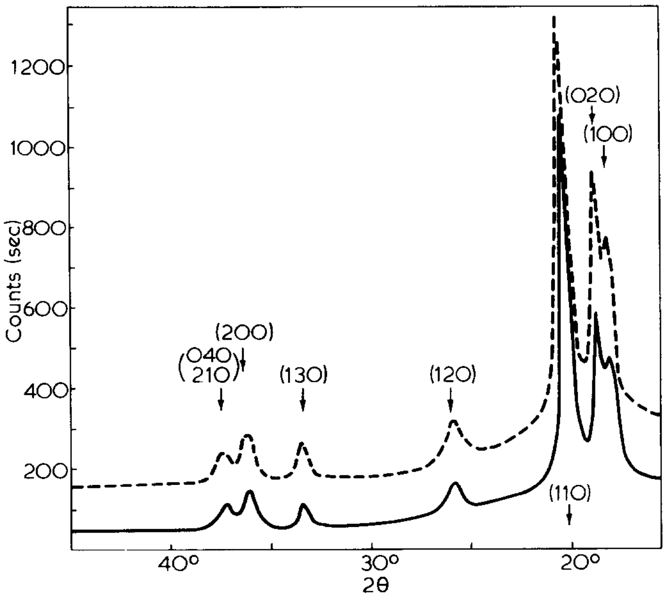

Figure 2 Equatorial scan, before poling, in reflection (solid line) and transmission (broken line shifted vertically by 100 cps)

Table 1 A comparison of structure factors for the equatorial reflections of PVDF in crystal forms II and IIp. (Assuming isotropic thermal parameters of 5 Å^2 for all atoms)

hkl	Form II	Form IIp	2θ(CuKα)
100	27	0	17.9
020	26	26	18.4
110	35	43	20.1
120	20	0	25.8
130	19	21	33.2
200	27	34	36.2
040	14	14	37.3
210	14	0	37.4

reflections were studied by rotating the sample by 90° from the transmission position and performing a 2θ scan with the scattering vector parallel to the draw direction.

RESULTS AND DISCUSSION

The equatorial scans before and after poling are shown in *Figures 2* and *3*. Considering first *Figure 2*, it should be noted that differences between the reflection and transmission data are caused by differential absorption effects due to the rectangular shape of the sample, and that the reflection scan is of inherently better resolution due to self-focussing effects. With this in mind, therefore, we consider the two runs as essentially the same prior to poling, indicative of a cylindrically symmetric distribution of crystal axes. The situation after poling is, however, quite different as shown in *Figure 3*. We first note that a new peak appears after poling at $2\theta = 20.8°$. It is reasonable to assign that to the (100) and (120) reflections of some additional crystal form I induced by the poling operation. The relative intensities of the form II reflections have changed, however, and the difference between the reflection and transmission scans now clearly indicates a degree of preferential alignment of the '*a*' and '*b*' axes which is particularly apparent in the (020) reflection at 18.4° and the (200) reflection at 36.2°. It is apparent that the '*a*' axes are preferentially aligned normal to the plane of the film whereas the '*b*' axes tend to lie in the plane of the film. Since this alignment has been produced by the application of an electric field we must agree with the suggestion[3] that we are now dealing with a polar crystal form with reflections at similar positions to those which occur in the non-polar form II. Structure factor calculations for the proposed form II (*Table 1*) show that in this form the (100) and (120) reflections are absent. The large overall reduction in the intensities of these reflections seen in our data therefore tend to confirm the proposed structure and show that the conversion II to IIp can occur to a significant extent under normal poling conditions.

The equatorial scans contain no information about the relative displacements of the chains parallel to *c*. We therefore need the meridional scans to determine the degree of translation of the chains on rotation from the II to the IIp structure. *Figure 4* shows the situation before poling. Note that although the form I reflections could not be detected in the equatorial scan prior to poling we can clearly see the

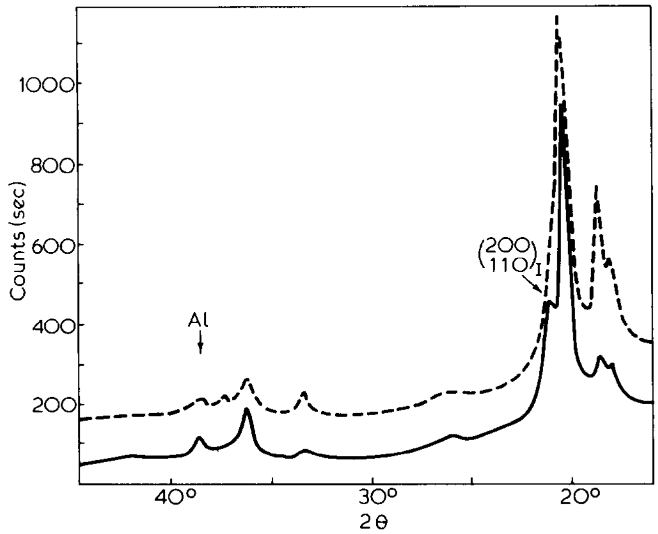

Figure 3 Equatorial scan, after poling, in reflection (solid line) and transmission (broken line shifted vertically by 100 cps)

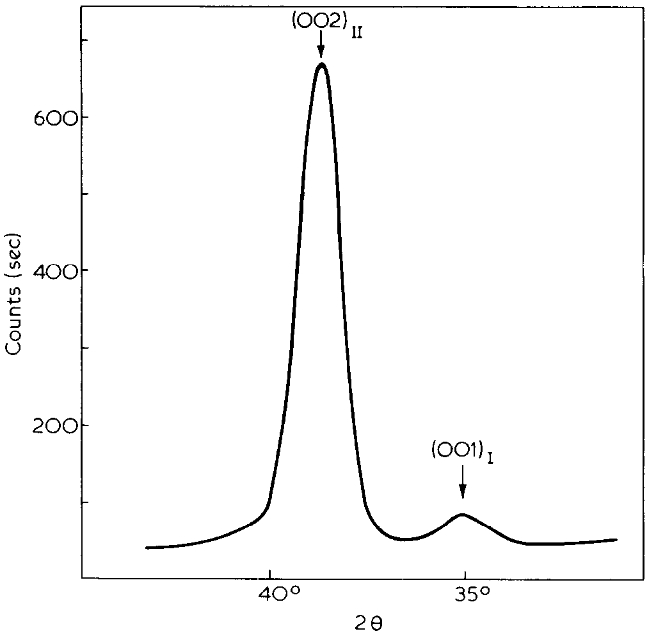

Figure 4 Meridional scan before poling

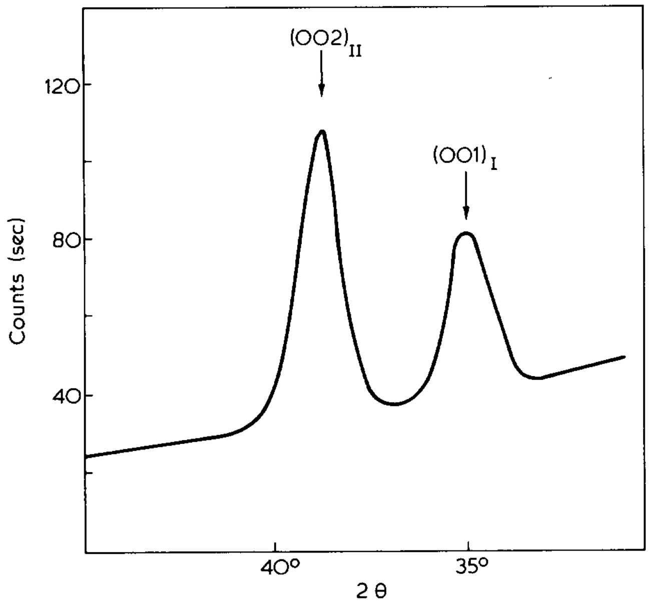

Figure 5 Meridional scan after poling

(001) reflection from form I in this scan and hence estimate the amount of phase I prior to poling. After poling, however, as shown in *Figure 5*, there is a drastic reduction in the form II (002) intensity without a corresponding increase in the form I (001) reflection. We therefore conclude that the reduction in the form II (002) intensity is due to a structure factor change and not due to a substantial degree of form II to form I conversion. A low structure factor for the (002) reflection of form IIp can be obtained either by raising the chain by 0.22*c* as it rotates or by lowering it by 0.28*c*. Rotation without translation, or with a translation of 0.5*c*, would leave the structure factor unchanged. We therefore conclude that the reduction in intensity of the (002) reflection on poling implies a translation of about *c*/4 on rotation.

If one assumes that the unit cell and the chain conformations do not change on rotation, then a shift of 0.22*c* on rotation to form the structure shown in *Figure 1* leads to closest interchain atomic contacts of 2.76 Å for fluorine–fluorine contacts, 2.78 Å for fluorine–hydrogen contacts and 2.73 Å for hydrogen–hydrogen contacts. These are all reasonable values; hence the proposed rotation and translation can be accommodated without a major change in the lattice parameters.

CONCLUSIONS

We have confirmed that a new polar modificaiton of PVDF exists and that it is present in conventionally poled samples of uniaxially oriented PVDF initially in crystal form II. It is possible, therefore, that the piezoelectric and pyroelectric activity of our initially form II samples arises as an intrinsic response of the non-centrosymmetric form IIp.

Alternatively, the crystal phase may act as an inert but polar 'filler' which produces internal fields in the amorphous phase. Piezoelectric and pyroelectric activity may then arise from the changes in dimension and permittivity of the amorphous phase with stress or temperature. The lower activity of form II samples compared with form I is then a natural consequence of the lower dipole moment of the polar form II and a general similarity of the behaviour of form I and form II samples is to be expected since the major effects are due to changes in the common amorphous phase.

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Some kinetic aspects of the radiation grafting of acrylic acid to nylon-6

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INTRODUCTION

γ-irradiation of nylon-6 (NY) immersed in aqueous acrylic acid (AA) induces grafting and homopolymerization[1]. The influence of reaction variables on both processes has been described previously[2–5] and the kinetics of the homopolymerization of AA discussed in detail[6]. We now attempt to provide a more quantitative description of the heterogeneous grafting reaction.

Previous kinetic analyses of other radiation grafting systems[7] have been basically similar to those applied to conventional, free radical, homogeneous homopolymerization. Recent theoretical treatments[8,9] have dealt with the influence of monomer diffusion on the rate of grafting and the molecular weight of the graft. Earlier results[3] for the present system indicated that monomer diffusion apparently plays no dominant role in the kinetics of grafting, but it should be emphasised that NY/AA is not a typical grafting system, since cupric chloride is always included as a retarder and the overall kinetics are consequently much affected by its presence.

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