mensional space group when projected along the *c* axis. From the systematic absence of the diffraction spots along the *b* axis, it is very likely that a twofold screw axis is present along the b^* axis, as is seen in the case of dextran.[7] The growth face of the crystal is {100} which is parallel to the longitudinal direction of the crystal.

The X-ray powder pattern of the CTP single crystal is identical with that of the oriented CTP sample which was annealed in an autoclave at 205 °C in the presence of water. No change of ^1H NMR spectra was noticed during the CTP single-crystal preparation, which proves that the CTP single crystal is chemically identical with the initial CTP sample.

Acknowledgment. We are greatly indebted to Dr. Henri D. Chanzy, C.N.R.S., Grenoble, France, for his invaluable suggestion and discussion on the crystallization procedure.

Registry No. CTP, 39320-19-9.

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Ferroelectric Properties of Form I Perdeuteriated Poly(vinylidene fluoride)

In a recent paper,[1] two of us (R.E.C. and J.M.K.) reported the synthesis of perdeuteriated poly(vinylidene fluoride), d-PVF_2, which contained fewer chemical defects compared to the commercially available protonated PVF_2, H-PVF_2. The low level of chemical defects, which include head-to-head and tail-to-tail (H–H, T–T) linkages from reversed-monomer units, internal unsaturations, branching, and cross-links, was suggested as being the reason for the high melting point and high density (or crystallinity) observed in D-PVF_2.[1]

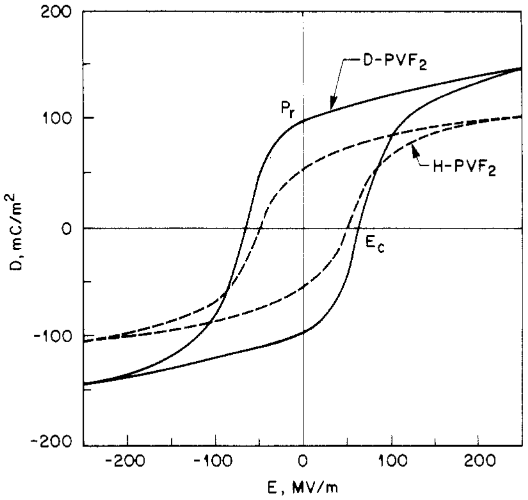

Figure 1. Comparison of *D–E* hysteresis curves obtained under a signal frequency of 0.01 Hz at room temperature from the deuteriated and protonated form I PVF_2 films.

Since the ferroelectricity of PVF_2 originates in the polar form I crystals, the reduced chemical defects in the deuteriated polymer can be expected to have important bearings on ferroelectric properties. For example, in a related study[2] on copolymers of vinylidene fluoride and tetrafluoroethylene, TFE, the Curie temperature was found to decrease with increasing fraction of TFE (which is equivalent to introducing extra head-to-head defects into the H-PVF_2 molecules). However, while these copolymers crystallize naturally into the polar phase I, the natural form of PVF_2 crystals is nonpolar (form II); therefore, to render it ferroelectric, the polymer is usually mechanically stretched to convert the crystals to the polar form I. In this solid-state phase transformation, the final crystal structure can be expected to be highly sensitive to chain defects because of the severe lattice distortion involved in stretching. In fact, it has long been suspected that the presence of chemical defects in the commercial resins may be responsible for the low crystallinity (<50 vol %) observed in the uniaxially oriented films regardless of their preparation conditions. For this reason, the deuteriated polymer offers a unique opportunity for probing the effects of chemical defects on the stress-induced phase transformation and the ferroelectric properties of the resulting samples. In this paper, we describe the highlights of a study made on the *D–E* (i.e., electric displacement vs. electric field) hysteresis behavior and other properties of D-PVF_2 and compare them with those of H-PVF_2.

Deuteriated PVF_2 was synthesized according to the procedure described in ref 1. Films of D-PVF_2 were prepared by casting them from a solution in dimethyl formamide. As with protonated PVF_2, these films contained only the nonpolar form II crystals. To convert them to the polar form I crystals, the films were uniaxially stretched at 70 °C to 4 times the original length and then annealed at 120 °C for 2 h in the stretched state. Complete conversion of crystal form was confirmed by X-ray diffraction patterns. Final thicknesses of the films were about 10 μm. Samples of H-PVF_2 were uniaxially oriented 7-μm-thick unpoled films supplied by Kureha Chemical Co. They were used without further treatments.

The *D–E* hysteresis curves were obtained by measuring the current responses across the film thickness while the film was being subjected a triangular or saw-tooth pattern electric field *E* with a frequency of 0.001 Hz. The current was then computer integrated to yield polarization *P* or displacement *D*. The contribution from dc conductivity was removed by numerical subtraction on the assumption that the dc conductivity is independent of *E*. Sample temperature, which was varied between −100 and 200 °C, was controlled to within 1 °C by using a thermostat. Linear dielectric relaxation was measured by using an impedance analyzer (Hewlett-Packard 4192A). Thermal properties were measured by differential scanning calorimetry, DSC (Perkin-Elmer DSC-4), the scanning rate being 40 °C/min to avoid crystal transformation during the heating measurements.

Typical *D–E* data of D-PVF_2 and H-PVF_2, measured under a field amplitude of 250 MV/m at room tempera-

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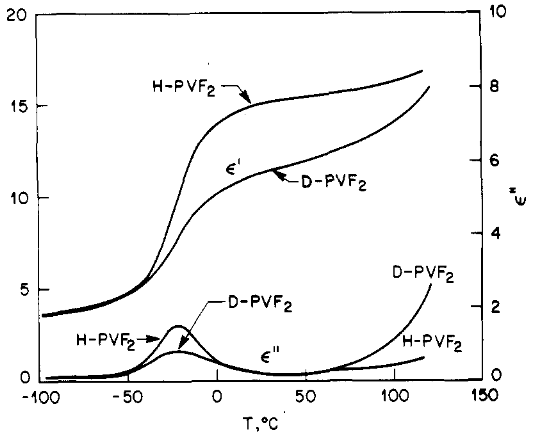

Figure 2. Temperature dependence of dielectric data obtained at 1 kHz for the form I D-PVF$_2$ and H-PVF$_2$ films.

ture, are shown in Figure 1. A clear hysteresis behavior characteristic of a ferroelectric is seen in each sample. Of particular interest is the unusually large remanent polarization P_r in D-PVF$_2$ (≈100 mC/m^2) which is about 80% higher than the corresponding value in H-PVF$_2$ (≈55 mC/m^2). To our knowledge, this is the highest P_r value ever reported for PVF$_2$. The other ferroelectric polymers which show such high values (90–110 mC/m^2) are the copolymers of vinylidene fluoride and trifluoroethylene having VF$_2$ contents of 65 to 82 mol %.[3] However, unlike the copolymers whose Curie temperatures, T_c, are in the range 90–140 °C,[3] the homopolymer is thermally much more stable and does not lose its polarization until the temperature reaches the melting point, ca. 180 °C. Since the P_r value of form I single crystals of H-PVF$_2$ is estimated to be 127 mC/m,[2,4] the above result indicates that our D-PVF$_2$ should have a high crystalline content (ca. 80%) as well as a high degree of net dipole orientation along the surface normal of the film. The significance of the high P_r value can be seen by noting that several important properties such as the apparent piezoelectric e_{31} coefficient,[5] the electrochemical coupling coefficient k_t,[3] and the pyroelectric p_3 coefficient[6] are all directly proportional to P_r.

Another feature in Figure 1 is the coercive field E_c which is slightly higher in D-PVF$_2$ (≈65 mV/m) than in H-PVF$_2$ (≈50 mV/m). The reason for this is not clear although it is tempting to speculate that the higher coercive field is associated with the improved crystalline order in the sample.

The linear dielectric data obtained at the frequency of 1 kHz and a heating rate of 2 °C/min are shown in Figure 2 as a function of temperature. While both D-PVF$_2$ and H-PVF$_2$ display a sharp rise in ϵ' and a peak in ϵ'' in the temperature region of −50 to 0 °C, their intensities are much smaller in the former than in the latter. These results, which indicate participation of a smaller number of dipoles in the amorphous region of D-PVF$_2$, are consistent with the observation made earlier that the D-PVF$_2$ sample has a higher degree of crystallinity.

To further confirm that the D-PVF$_2$ sample does have greater crystallinity and crystalline order, both the deuteriated and protonated samples were subjected to DSC measurements and some of the results are shown in Figure 3. It can be seen that not only are the melting point, T_m, and the heat of fusion higher for D-PVF$_2$ but the melting peak is sharper. This result clearly indicates that the D-PVF$_2$ sample is much more readily transformed into a well-ordered structure in the solid state stretching. This is understandable since the transformation entails a massive chain movement (draw ratio 4) in which the majority of crystal chain segments must break off from the form II structure and realign themselves into the polar form I. Thus the chemical defects, particularly the branches and cross-links which are presumably more abundunt in H-PVF$_2$, are expected to place additional restraints on the movement and hinder the recrystallization process. The lower T_m observed in the H-PVF$_2$ sample is probably a manifestation of this severely constrained recrystallization process.

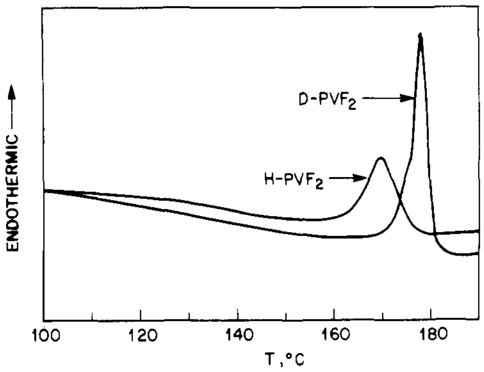

Figure 3. Thermograms of form I D-PVF$_2$ and H-PVF$_2$ films measured at a heating rate of 40 °C/min.

From the melting peaks in Figure 3, the heat of fusion is found to be about 60% greater in D-PVF$_2$ (13.9 cal/g) than in H-PVF$_2$ (8.7 cal/g). A simple estimate of crystallinity based on the heat of fusion data and the strengths of main loss peaks of the dielectric measurements in Figure 2 (assuming a two-phase model) shows that the volume fraction of form I crystals is about 0.7 in the D-PVF$_2$ sample and 0.45 in the H-PVF$_2$ sample. In this connection, we note that the difference in the H–H,T–T defect level between D-PVF$_2$ and its protonated analogue is very small (2.8% vs. 3.8%); perhaps too small to have any sizable effect as observed here. Instead, it is more likely that the observed changes resulted from a combined effect of H–H,T–T defects, cross-links, and chain branching. The last factor should be particularly important here since transfer reactions leading to branching or disproportionation are less frequent with deuteriation than with protons, as described in ref 1.

From the above data for the heats of fusion and crystalline fractions, the heat of fusion for the form I crystal is estimated to be about 19 to 20 cal/g. For comparison, a value of about 19 cal/g has been measured by Nakagawa and Ishida[7] for the form II crystal having a lamellar thickness of 25 nm.

In summary, we found the remanent polarization of D-PVF$_2$ to be nearly twice as much as that of H-PVF$_2$. The cause for this has been ascribed to fewer chemical defects in D-PVF$_2$, which gives rise to greater crystallinity and more perfect crystalline order.

Acknowledgment. We are grateful to A. J. Lovinger for the X-ray determination of the form I crystal structure and to S. Tasaka for preparing the uniaxially oriented D-PVF$_2$ sample.

Registry No. D–PVF$_2$, 91606-88-1; H-PVF$_2$, 24937-79-9.

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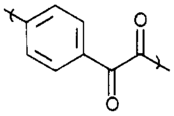
Synthesis of Conductive Polymers. Lewis Acid Doping of Terephthalaldehyde Polymers

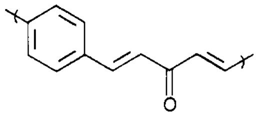
With the exception of polyaniline, which must be doped with aqueous acid,[1] all the conducting polymers reported to date have required doping with redox agents, e.g., I_2 and AsF_5 (p-type dopants) or sodium naphthalide (n-type dopant), to achieve semiconductivity.

We now report three polymers that show enhancements in conductivity on treatment with BF_3 etherate and H_2SO_4, both Lewis acids, as well as with AsF_5.

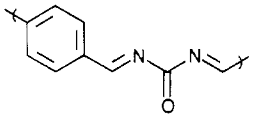
The three polymers that we report are prepared by the condensation of terephthalaldehyde with itself (I), acetone (II), and urea (III). Although polymers I and II are known,[2,3] their data have not been reported. We have synthesized these polymers in an effort to explore new conductive polymer systems. We had hoped that the higher oxidation states of these polymers might impart intrinsic conduction to them or, at least, that they might be convertible into conductors by the application of acidic reagents. Chien and Babu[4] have reported copolymers of acetylene and carbon monoxide which conduct at high levels on p-type doping. They protonated their polymer with methanolic HCl but did not report the conductivity of the resulting adduct.



I



II



III

Polymerization. We have polymerized terephthalaldehyde (Aldrich) to the yellow polybenzoin by a benzoin-type condensation, T_m 200–220 °C (lit. 170–200 °C[2]); IR (KBr pellet cm^{-1}) 3500 (br, OH str), 1700 (s, singlet, C=O str).

We could not oxidize the polybenzoin to I according to the published procedure.[2] Even $CuSO_4$/pyridine/air oxidation proved ineffective. We oxidized the polymer in 90% yield by refluxing it with a large excess of HNO_3/H_2O (1/4 mixture) for 72 h when we observed the disappearance of hydroxyl group absorption in the IR spectrum: IR (KBr pellet cm^{-1}) 1650 (s, sharp, C=O str), 1180 (s, singlet, C=O bend). This polymer is insoluble in practically all common organic solvents.

We prepared polymer II, a yellow powder, in 55% conversion by known methods[3,5] using acetone distilled over K_2CO_3; IR (KBr pellet cm^{-1}) 3500 (br, OH str), 1653 (s, singlet, C=O str), 1600 (s, singlet, C=C Ar str). We ascribe the OH band to the hydroxyl group of the simple aldol adduct, even though the fully conjugated system was reported[3] as the product of this reaction. The occurrence of a doublet at δ 4.75 and a triplet at δ 5.5 in the ^1H NMR spectrum (DMSO-d_6) further supports the presence of some initial aldol polymer.

Table I
Conductivities of Polymers with Various Types of Dopants

	conductivity, S/cm					
polymer	undoped	AsF_5[a]	AsF_3/ AsF_5[b]	BF_3 etherate[c]	BF_3 etherate[d]	H_2SO_4
I	10^{-13}	10^{-13}	10^{-6}	10^{-8}	10^{-8}	10^{-13}
II	10^{-13} [e]	10^{-7}	10^{-8}	10^{-6}	10^{-8}	10^{-6}
III	10^{-13}	10^{-8}	10^{-7}	10^{-6}	10^{-8}	10^{-7}
$-(CH_2CH_2)-$	10^{-13}	10^{-13}	10^{-13}	10^{-13}	10^{-13}	10^{-13}

[a] 400 Torr. [b] 400 Torr AsF_5, equilibrium vapor pressure of AsF_3 at 25 °C. [c] Ca. 2 Torr, equilibrium vapor pressure at 25 °C. [d] Equilibrium vapor pressure of BF_3 etherate at −196 °C (ca. 0 Torr). [e] This value was obtained on the undehydrated precursor to II.

Attempts to dehydrate this polymer with P_2O_5/H_2SO_4 failed; however, BF_3 etherate caused rapid dehydration as shown by loss of the OH band and the change in color to brown. This polymer is insoluble in all solvents.

We prepared polymer III by refluxing equimolar quantities (0.025 mol) of urea (Aldrich) and terephthalaldehyde in 25 mL of DMF (Aldrich, dried over molecular sieve). The solution turned yellow after 10 min. After 1 h of reflux we poured the solution into 100 mL of methanol. The precipitated polymer was redissolved in 20 mL DMF and reprecipitated by methanol. The DSC scan shows no transitions up to 450 °C. After the second precipitation, the polymer dissolves in DMF with great difficulty, owing either to a change in the morphology of the polymer or to an increase in the molecular weight during workup. IR (KBr pellet cm^{-1}) 1656 (s, singlet, C=O str), 1625 (s, singlet, CH=N); ^1H NMR (DMSO-d_6) δ 10.38 (CH=N) and 8.28 (C_6H_4). We have not been able to determine the molecular weight of these polymers by conventional methods owing to their insolubility in all common organic solvents. However, we are pursuing other means to determine molecular weights.

Electrical Conductivity. We measured electrical conductivity by using the standard two-probe method with a Keithley bridge and exposing the pressed pellets to AsF_5, BF_3 etherate, H_2SO_4, and AsF_3/AsF_5. The apparatus has been described elsewhere.[8] Conductivity data are summarized in Table I.

BF_3 Doping. We measured the conductivity of these polymers exposed to BF_3 etherate in the following manner: BF_3 etherate was transferred to the doping chamber under Ar, and the chamber was cooled to liquid nitrogen temperature. The pellet mounted on the probes was inserted in a current of Ar. The chamber was evacuated for 15 min while cooling with liquid nitrogen. BF_3 etherate was allowed to warm to room temperature by removing the liquid N_2 bath. As soon as BF_3 etherate reached room temperature the conductivity increased. Polymer I exhibited a smaller conductivity enhancement than II and III.

We could not make a pellet of dehydrated brown polymer II, so we exposed the pressed pellet of yellow polymer (the undehydrated precursor to II) to BF_3 etherate vapor. As soon as the pellet came in contact with the vapor its color changed from yellow to brown, and its conductivity increased from 10^{-11} to 10^{-8} S/cm and finally to a maximum value of 10^{-6} S/cm. After 30 min we cooled the

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