measurements by electronic integration and by planimeter.

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(16) No traces of ortho-para′ and para-para′ linkages were detected. We have examined a number of claimed all-ortho novolacs manufactured according to the reported methods[17] and we have detected significant ortho-para′ peaks employing the ^{13}C method.[12]

(17) A. M. Partansky, *Am. Chem. Soc., Div. Org. Coat Plast. Chem., Pap.*, **27** (1), 115 (1967); D. A. Fraser, R. W. Hall, and A. L. J. Raum, *J. Appl. Chem.*, 676 (1957).

(18) Work is in progress to extend the synthesis and to explore the scope and limitations[19] of the reaction. For the present, successful syntheses of "ortho" di, tri, and tetranuclear phenol-acetaldehyde, phenol-benzaldehyde, and *p*-cresol-formaldehyde oligomers were achieved from phenoxymagnesium bromides and the respective aldehyde.

(19) Limitations are due to the inertia of the electron-withdrawing-substituted phenol (R_2 = NO_2, COR) as well as to the unselectivity of reactions involving some etheroaromatic aldehydes.

E. Dradi,* G. Casiraghi, G. Sartori, and G. Casnati

Istituto di Chimica Organica Dell'Università, Via M. D'Azeglio 85, 43100 Parma, Italy

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Formation of a New Crystal Form (α_p) of Poly(vinylidene fluoride) under Electric Field

Poly(vinylidene fluoride) (PVF_2) is known to have three crystal forms (α, β, and γ) reported up to now.[2] Recently the possibility of transforming the α form PVF_2 into a new crystal form has been considered in relation to the piezo- and pyroelectric properties of polarized PVF_2 films.[3,4] In this communication we present the evidence of another new crystal form of PVF_2 which is formed upon subjecting the α form PVF_2 to high electric field.

PVF_2 films were prepared by melting PVF_2 pellets of M_W = 120 000, obtained from Polyscience, in the laboratory press and then cooling rapidly to room temperature. These films were subsequently stretched by ca. four times at 155 °C and then annealed at 145 °C for 1 h at fixed lengths. X-ray diffraction[2] and infrared spectra[5] from these films show that the crystalline phase is predominantly of α form, the content of β form being less than 5%. Aluminum electrodes were vacuum deposited on both sides of the films and then these α-PVF_2 films were subjected to the field of 1500 kV/cm for 3 h at 24 °C. The aluminum electrodes were removed by dissolving in NaOH solutions afterwards.

The infrared spectra taken after the poling process did not show any change other than a minimal decrease in the α-form absorption[5] at 795 cm^{-1} and a little increase in the β-form absorption[5] at 840 cm^{-1}. Hence, the one-dimensional ordering of tg^+tg^- molecular conformations in the α-crystal form of PVF_2 remains unaffected[6] except for the formation of a minimal amount of β-crystal form.

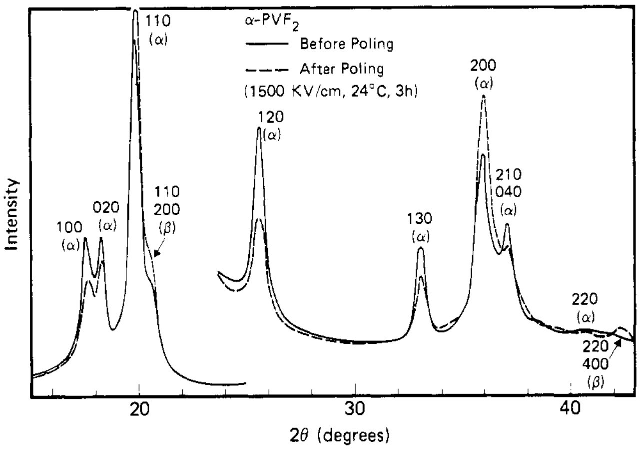

Figure 1. Tracings of X-ray diffraction intensities in the reflection mode from uniaxially oriented α form of PVF_2 before poling (solid line) and after poling with 1500 kV/cm for 3 h at 24 °C (dashed line). Indices of reflection for the peaks are assigned according to ref 2.

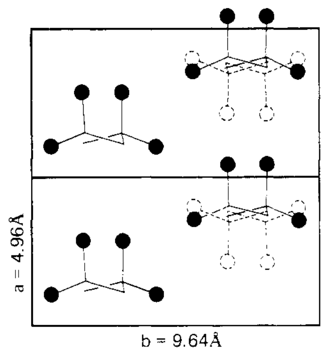

Figure 2. Crystal structure of the proposed α_p form of PVF_2 in the *ab* projection, fluorine atoms being shown by circles, compared with that of the α form; the second chain in the α form is shown by the dashed line. The atomic positions in the *c* coordinate for the α_p form remain the same as in the α form.[2]

Table I
Comparison of Calculated X-ray Intensity Form Factors for the α Form and the α_p Form of PVF_2 Crystals

reflections	form factors in rel units		reflections	form factors in rel units	
	α	α_p		α	α_p
100	76	0	120	49	0
020	74	74	130	45	56
110	133	205	200	103	158

On the other hand, the X-ray diffraction data measured with a conventional diffractometer in the reflection mode exhibited rather significant changes in intensity caused by the poling process as shown in Figure 1. Major changes to be noted are the increase in intensity at (110) and (200) reflections and a significant decrease of (100) and (120) reflection intensities. The contrasting changes at (100) and (200) reflections certainly rule out the orientation or disordering of crystallites as the major cause for the change in X-ray intensities. Also to be noted is the fact that the position of each observed peak remains unchanged within the experimental error. Therefore, only the symmetry of the unit cell seems to have undergone a major change due to the electric field, while the molecular conformations (tg^+tg^-) of α-PVF_2 chains in the unit cell and the dimensions of the unit cell remain the same as in the α form.[2]

A new crystal form, which is formed upon subjecting the α form PVF_2 to high electric field and is consistent with both the X-ray (Figure 1) and infrared results, is proposed in Figure 2. In this new form, designated α_p hitherfrom, the atomic coordinates for the first chain remain the same as in the α form, but the second chain is now related to the first one by the symmetry operation of screw axis [100] with translation component $a_0/2$. This results in the antiparallel alignment of the two chains along the *c* axis and the displacement of the second chain from the first one by ($a_0/2 + b_0/2$) in the *ab* projection. The projection of atomic coordinates of α_p form on the *bc* plane remains the same as in the α form[2] and, hence, is not shown here. The predicted X-ray intensity form factors at major reflections for this new α_p form are shown in Table I and compared with those for the α form. The observed increase

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in (110) and (200) reflections and decrease in (100) and (120) reflections are consistent with partial transformation of α to α_p form. The minor decrease in (020) and (130) reflections may arise from the preferential orientation of the a axis, which is the axis of molecular dipoles in the unit cell of α_p form, along the applied field.

This new α_p form should arise from the 180° rotation and $c_0/2$ translation along the c axis of every second molecular chain in the unit cell of α form such that the antiparallel dipolar alignment in the unit cell is changed to the parallel alignment due to the applied electric field (see Figure 2). This transformation is found to result in surprisingly little changes in major interatomic distances within the unit cell. In fact, the closest interatomic distances between fluorine atoms of adjacent chains change from 3.36 to 3.28 Å. Hence, the α_p form, once formed, is expected to be relatively stable.

This new α_p form of PVF_2 proposed above is highly polar, the dipole moment being ca. 1.3 D per monomer unit in contrast to the nonpolar character of the original α form. The fact that the nonpolar α form of PVF_2 can be transformed into the highly polar α_p form under high electric field has significant implications on the current investigations of the mechanisms of piezo- and pyroelectric behavior of polymers and PVF_2, in particular.[7] The piezo- and pyroelectric activities of the α_p form of PVF_2 and their implications will be discussed in a later publication.[8]

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(1) (a) IBM World Trade Postdoctoral Fellow. Institut für Organische Chemie, Universität Mainz, Mainz, West Germany. (b) While on a training assignment from the National Bureau of Standards, Washington, D.C.

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D. Naegele,[1a] D. Y. Yoon,* and M. G. Broadhurst[1b]
IBM Research Laboratory, San Jose, California 95193

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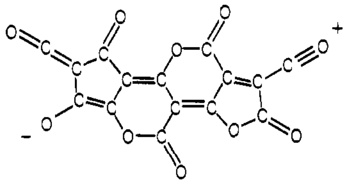
CORRECTIONS

A. W. Snow, H. Haubenstock, and N.-L. Yang: Poly(carbon suboxide). Characterization, Polymerization, and Radical Structure. Volume 11, Number 1, January–February 1978, page 77.

On page 77 the equation in the right column should be

$$\ln\,[\text{slope}] = n \ln\,[\text{M}] + \ln k$$

On page 84 in the second paragraph from the bottom, left column: the "charged resonance structure" referred to (Figure 13) has been omitted from the figure. The structure is



L. J. Mathias, W. D. Fuller, D. Nissen, and M. Goodman: Polydepsipeptides. 6. Synthesis of Sequential Polymers Containing Varying Ratios of L-Alanine and L-Lactic Acid. Volume 11, Number 3, May–June 1978, page 534.

The titles for Schemes I and II should read, respectively: "Synthetic Outline for Poly[(L-Ala)$_3$-L-Lac] and the Intermediate for Poly[(L-Ala)$_2$-L-Lac]" and "Synthetic Outline for Poly[(L-Ala)$_3$-(L-Lac)$_2$] and the Intermediate for Poly[(L-Ala)$_2$-(L-Lac)$_2$]".

All four structures a–d in Figure 1 should contain a –(C=O)– unit just before the right-hand parantheses.