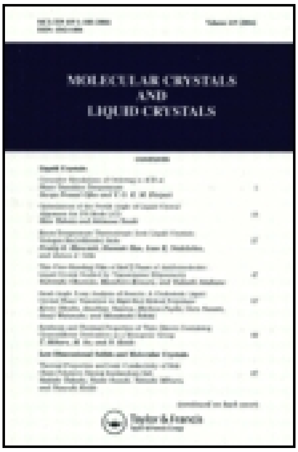

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Field-Induced Structural Changes and Dipole Orientation in Poly(Vinylidene) Fluoride

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FIELD-INDUCED STRUCTURAL CHANGES AND DIPOLE ORIENTATION IN POLY(VINYLIDENE)FLUORIDE

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Abstract Infrared spectra of ß-PVDF films under the influence of an electric field were registered for 13 cycles of field strength. Butterfly-shaped hysteresis curves due to dipole orientation changes were obtained for the absorbances as well as for the frequencies of the bands at 445 and 510 cm^{-1}. Investigations of α-PVDF show considerable changes in the spectra after polarization at field strengths of 180 MV/m to 320 MV/m. The absorbance decreases of the bands 218 cm^{-1} and 616 cm^{-1} were discussed in terms of a conformation conversion and of an alignment of the CF_2-dipoles in α-PVDF.

INTRODUCTION

The process of electric polarization of poly(vinylidene)fluoride (PVDF) is accompanied by an alignment of the CF_2-dipoles and structural changes at various levels in dependence on electric field strength and polarization temperature [1]. Infrared spectroscopy can be used to investigate the orientation of the CF_2-dipoles and its field-induced conformation changes. For studies of the dipole orientation the all-trans conformation of ß-PVDF may be most suitable, since no field-induced conformation changes occur in this case. Electric polarization at room temperature of α-PVDF results in a field-induced conversion of the nonpolar α- into the polar piezoelectric α_p-modification and in an alignment of the CF_2-dipoles towards the field direction as proved by x-ray investigations [1,2].

No significant changes were found in the infrared spectra under the given polarization conditions[3]. The purpose of this paper is to study by infrared spectroscopy the field-induced hysteresis of the dipole orientation in ß-PVDF and the electric polarization in α-PVDF.

EXPERIMENTAL

Dipole orientation hysteresis was studied using uniaxially drawn ß-PVDF films (α-content < 5 %, thickness 8 μm to 10 μm)[4,5]. Thin carbon layers (25 nm) were evaporated onto the films to form highly IR-transparent electrodes (transmittance > 90 %) for in-situ experiments [5]. The high voltage was applied in up to 13 cycles with maximum field strengths varying between ± 240 MV/m in one cycle. Absorbances were measured at distances of 1 cm^{-1}, and the maxima positions of the bands were obtained with a resolution of 0.1 cm^{-1}.

PVDF samples used in the experiments on α-PVDF were unoriented, commercial films (40 μm thick) manufactured by Bemberg-Folien GmbH, FRG (resin Solef 1008, Solvay & Cie., Belgium). Aluminium electrodes were evaporated onto both sides of the films prior to poling. The metallized PVDF films were polarized using electric fields from 50 MV/m to 320 MV/m at room temperature (polarization time 40 s). The infrared spectra of the PVDF films were recorded before and after the polarization process by the Bruker-Fourier-spectrometer IF 5 113 V in the region of 150 to 1000 cm^{-1}.

FIELD-INDUCED HYSTERESIS OF DIPOLE ORIENTATION

The ß-bands at 510 cm^{-1} (CF_2-bending) and 445 cm^{-1} (CF_2-rocking) depend on dipole orientation ($A_{510} \sim \sin^2\Phi$, $A_{445} \sim \cos^2\Phi$, Φ-angle between field and dipole moment)[4]. Under the influence of the electric field the intensity of the 510 cm^{-1} band decreases considerably, whereas the intensity of the 445 cm^{-1} band strongly increases. These changes are only partially removed when the field is switched off (Fig. 1).

Increasing the field strength in opposite polarity causes the absorbances to approach their original values, but without reaching them. When the field strength is further increased to its maximum and then decreased to zero again, the absorbance values measured during first field application are more or less reproduced. Repeating this procedure leads to butterfly-shaped hysteresis curves for the absorbances of these two orientation-sensitive absorption bands. Figure 2 shows the absorbance values A_{445} measured at maximum field strength to increase to a certain extent with increasing cycle number (510 cm^{-1}: decreasing values). Taking the bending band as example, Figure 3 reveals that the frequencies of the bands depend on the applied field strength. During the first cycle a hysteresis-like relation between wave number and field strength develops, which remains essentially unchanged during subsequent cycles.

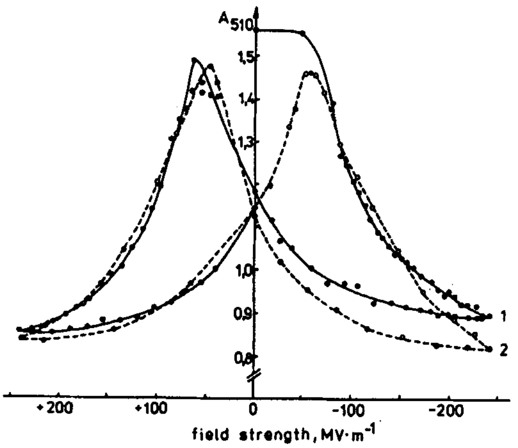

FIGURE 1 Absorbance of the CF_2-bending band in dependence on applied field for the first two poling cycles.

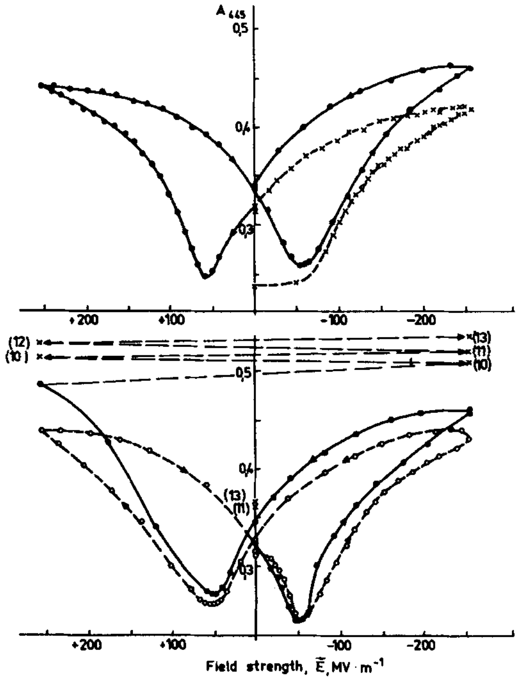

FIGURE 2 Absorbance of the CF_2-rocking band as a function of field strength for several poling cycles. Points with numbers in parentheses refer to cycle numbers.

ELECTRIC POLARIZATION IN α-PVDF

The strong absorption bands observed at 218, 288, 355, 410 and 616 cm^{-1} are assigned to the α-modification (tgtg'-conformation) of PVDF, whereas bands of the ß-form (tt-conformation) at 372 and 445 cm^{-1} are very weak. Thus the used films exist mainly in the α-modification. Applying the electric field leads to a decrease of the α-bands and to a small increase of the ß-bands. Furthermore we observed a shift of the CCC-bending band at 218 cm^{-1} to 215 cm^{-1} and a new band at 208 cm^{-1} (Figure 4). A significant decrease of the band at 218 cm^{-1} begins at a field strength of 180 MV/m, whereas below 120 MV/m no changes occur. At higher field strengths (250 MV/m, 320 MV/m) a strong intensity decrease as well as a distinct frequency shift of this band is observed; the new band at 208 cm^{-1} occurs clearly. To compare the field dependence of the two α-bands at 218 cm^{-1} and 616 cm^{-1}, respectively, we also measured the absorbance decrease of the latter, which is related to the field-induced reduction of the gauche conformation. Fig. 5 shows the absorbances A^P_{218} and A^P_{616}, related to the respective values of the unpoled films, in dependence on the polarization field strength. Obviously the ratio A^P_{218}/A_{218} decreases stronger than A^P_{616}/A_{616} indicating different polarization processes.

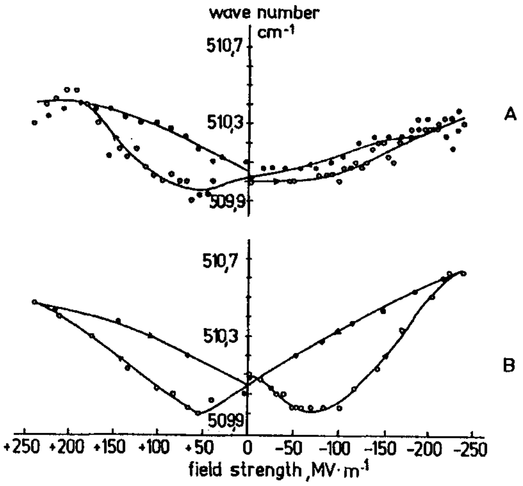

FIGURE 3 Wave number of the absorption maximum of the CF$_2$-bending vibration in dependence on the field being applied. A: first cycle, B: second cycle.

DISCUSSION

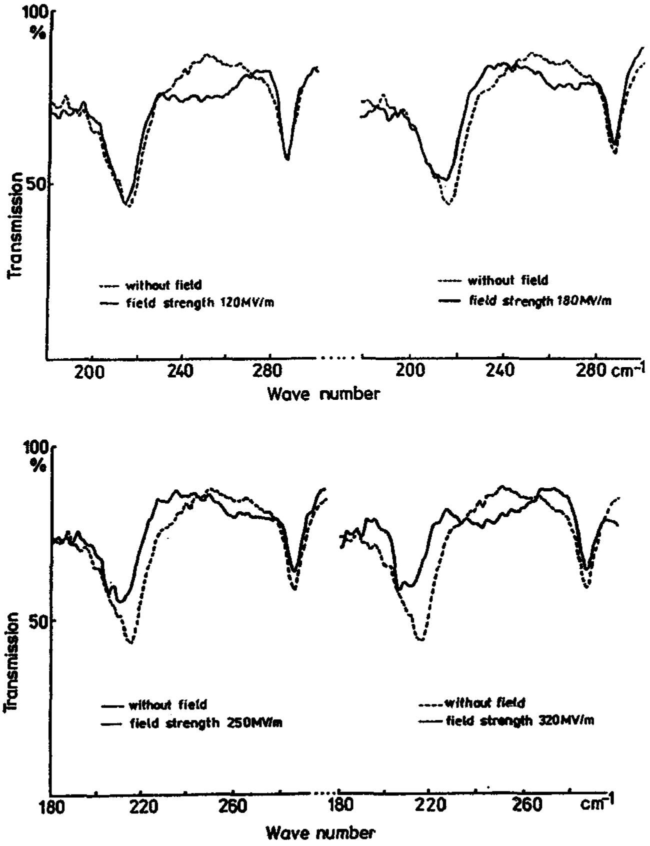

FIGURE 4 IR-spectra before and after the electric polarisation of α-PVDF.

Due to their dependence on $< \sin^2 \phi >$ and $< \cos^2 \phi >$, respectively, the absorbances A_{510} and A_{445} can be interpreted as a measure for the mean dipole orientation. Thus the butterfly-shaped hysteresis curves reflect immediately the ferroelectric character of the field-induced dipole orientation changes. After alignment at increasing field strengths the dipoles remain in partially stable positions at decreasing field strength; thus a certain opposite field is needed to cancel largely this preferential orientation, before new alignment occurs at higher field strength. After first electric polarization, the original orientation distribution is never reproduced. Intensity changes at high field strengths with increasing cycle number may be due to field-induced structural transitions[6]. According to model calculations the field-induced frequency increase is due to strong dipole alignment in field direction, whereas a frequency decrease may reveal opposite directions of dipoles and field strength[7]. The different decrease of the absorbance ratios

A^p_{218}/A_{218} and A^p_{616}/A_{616} reveals two processes: the field-induced gauche-trans-transition and a field-induced alignment of the CF_2-dipoles in the α_p-modification. The behaviour of the absorbance A_{616} reflects the gauche-trans-transition only[6], whereas the absorbance A_{218} includes both a dipole alignment effect and the gauche-trans-conversion.
The new band at 208 cm^{-1} is assigned to the α_p-modification.

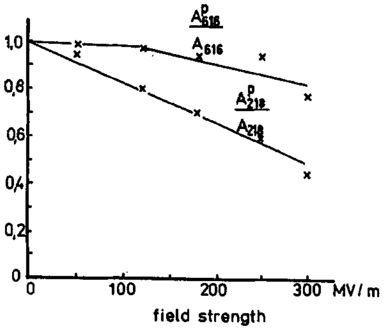

FIGURE 5 Absorbances A^P_{218} and A^P_{616}, related to the respective values A_{218} and A_{616} of the unpoled films, in dependence on the polarization field strength.

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