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Field-Induced Conformation Transition and Dipole Orientation in Poly(Vinylidene Fluoride)

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SUMMARY

The poling of biaxially stretched poly(vinylidene fluoride) (PVDF) films which have been metallized on both sides results at the poling temperature of 115 °C and the poling field of 400 MV/m in almost complete conformational change from T-G-T-$\bar{G}$ to the trans conformation as well as in a residual polarization of at least 11×10^{-2} C/m^2. The transition temperature T_f of the field-induced conformation transformation in the crystalline regions is found to be $T_f = 75$ °C. The thermally stimulated decrease of polarization proceeds gradually and is not characterized by a defined Curie point.

INTRODUCTION

The effect of high electric fields, called poling, on polyvinylidene fluoride (PVDF) films causes residual polarization. On subjecting the films to changes of stress and temperature the polarization varies, thus indicating piezoelectricity or pyroelectricity, respectively. Therefore, PVDF films can obviously be applied in many fields including microphones, earphones, hydrophones, heat sensors and keyboards. Many of these feasibilities are on the verge of commercial exploitation. Commercial PVDF films contain the α- as well as the β-modification within the crystalline regions. In the α-phase the backbone has T-G-T-$\bar{G}$ conformation and within the unit cell the CF_2 dipole moments of adjacent chains cancel each other. Therefore, the α-modification is considered to be non-polar and does not contribute to piezoelectricity and pyroelectricity. The highest values of polarization in PVDF are reached by the β-modification in which the macromolecules are arran-

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ged in planar zig-zag conformation (trans conformation). Thus, the ß-phase of PVDF shows the highest values of piezoelectric and pyroelectric coefficients (DAVIES et al. 1978).
In untreated PVDF samples the polar structural regions have uniform alignement in submicroscopic dimensions only. However, an appropriate poling treatment allows to align the dipole moments of differently oriented structural regions into the preferred direction of the external electric field. Further, the polarization process will be combined with a field-induced conversion of the nonpolar α-modification into the polar ß-modification if the poling conditions are appropriately established (FUKADA and FURUKAWA, 1981). Particulary, the effects of high temperature and high field strength on the field-induced conformational changes and the orientation of CF_2 dipols as indicated by IR spectroscopic measurements were the objects of our investigations. As observed by ENNS and SIMHA (1977) a premelting transition occurs in PVDF within 60 to 100 °C which was assigned to the mobility of polymer chains around the c-axis. This should result in a more efficient polarization process by poling beyond this temperature range.

POLING EXPERIMENTS

The investigations were carried out with commercial PVDF films (Kureha Co., Japan). The thickness of the biaxially stretched films was 12 µm. Prior to poling experiments the films were coated on both sides with copper layers, which were removed after poling in order to allow structural investigations to be carried out with unmetallized samples. In the poling experiments extremely high field strengths E_P were applied (up to 400 MV/m) at poling temperatures T_P far above 100 °C for the first time. The poling voltage was switched off as soon as the sample was cooled down to less than 50 °C. The poling period reached 10 s at a maximum.

INFRARED MEASUREMENTS

The spectra were recorded at room temperature with the IR spectrophotometer IR-12 (Beckman). In the initial PVDF sample films the molecules were highly oriented with the chain axis preferably parallel (T-G-T-$\bar{G}$ fraction) and perpendicular (trans fraction) to the machine direction of the film (DANZ, 1982). Therefore the IR investigations were carried out by polarized light. The film was arranged thus, that its machine direction was the same as that of the slit of the spectrometer. In the IR-spectrum of PVDF the conformations of the chains are represented by corresponding conformational bands. The relationships to the crystalline α- and β-modifications are based on the T-G-T-$\bar{G}$ and the trans conformations. Further, the conformational changes in the amorphous regions are also reflected by the IR spectra.

Based on the assignements of the bands by KOBAYASHI et al. (1975) the conformational state of PVDF can be determined by IR spectroscopic absorbance values of the conformational bands. Thus, the trans fraction of the initial sample films was found to be 35 % (DANZ, 1982).

The field-induced conformational changes were determined quantitatively by evaluating the decrease of intensity of the band at 616 cm^{-1} (T-G-T-$\bar{G}$ conformation) in dependence on the poling temperature and the field strength. The band at 616 cm^{-1} is found to be highly π-dichroitic, the σ fraction being lower than 5 %. Therefore, the absorbance $A_{616}(\parallel)$ (parallel polarized light) proves invariant with respect to the rotation of molecular groups around the chain axis, thus allowing to record the conformational changes only.

FIELD-INDUCED CONFORMATIONAL CHANGES

After poling at T_P = 115 °C (E_P = 400 MV/m) the T-G-T-$\bar{G}$ conformational bands disappear completely (e.g. the bands at 535, 489, 795 and 976 cm^{-1}) or the intensity is strongly reduced (e.g. the bands at 616, 766 and 1 290 cm^{-1}). Contrarily, the intensities of the ß bands (e.g. at 445 and 473 cm^{-1}) increase considerably, exept that of the band at 510 cm^{-1}. These changes, apart from that of the band at 510 cm^{-1}, suggest efficient transformation from the non-polar α- to the polar β-modification. The temperature dependence of the field-induced conformational changes is shown in Fig. 1. The absorbance values $A^{P}_{616}(\parallel)$ of the poled sample were normalized to that of

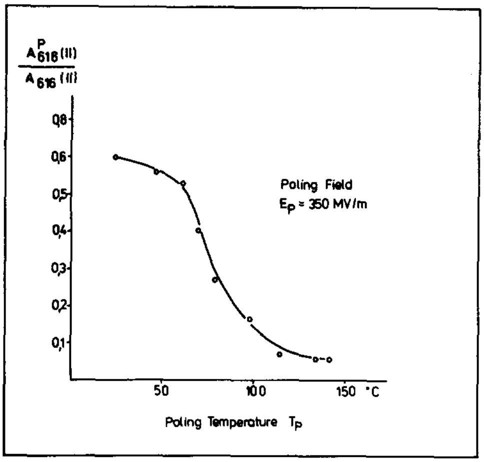

Fig. 1 Temperature - dependence of the decrease in the T-G-T-$\overline{G}$ conformation in PVDF as observed by the change of the corresponding conformation band at 616 cm^{-1}

the untreated. The ratio $A^P_{616}(\parallel)/A_{616}(\parallel)$ represents the relative decrease of the T-G-T-$\overline{G}$ fraction. As seen in Fig. 1 the poling temperature T_P affects distinctly the conformational changes. Although considerable changes occur already at room temperature ($A^P_{616}(\parallel)/A_{616}(\parallel)$ = 0,6) the T-G-T-$\overline{G}$ fraction is strongly reduced only above 100 °C. Based on the temperature dependence of the field-induced conformational changes the transition temperature T_f is found to be T_f = 75 °C, if the value of the highest slope of the curve is considered. This means, the conformational changes at the temperatures taken into consideration become sufficiently strong only if the polymer chains are able to move around the c-axis in the crystalline regions. On the other hand, below T_g no conformational changes were observed. Thus, the temperature-dependence of the conformational changes suggests that these changes proceed predominantly in the amorphous regions at room temperature and in the crystalline regions at the temperatures considered.

The dependence of the conformational changes on the electric field at T_P = 115 °C is demonstrated in Fig. 2. Below 100 MV/m no changes are observed, while a linear increase occurs between 100 and 300 MV/m and saturation is reached above 300 MV/m. If the conformational fractions in the untreated film are known, the conformational changes can be determined quantitatively. At room temperature the ß fraction amounts to 60 % (E_P = 350 MV/m) and above 100 °C the ß fraction reaches 95 %.

CHARACTERIZATION OF THE STATE OF POLARIZATION

The component P_r^Z of the residual polarization normal to the surface of the film is expressed by

$$P_r^Z = P_o \quad <\cos\delta> \qquad (1)$$

where

P_o - Total polarization

δ - Angle between an individual CF_2 dipole and the direction of the poling field, averaged over the time

$<\cos\delta>$ - Average over the dipoles in the volume

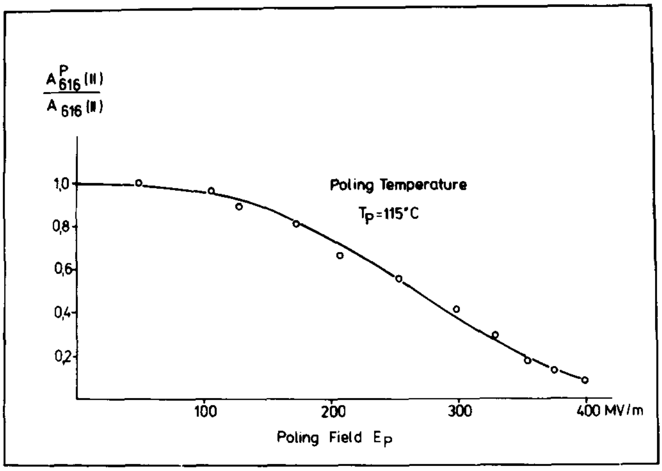

Fig. 2 Decrease of the T-G-T-$\overline{G}$ conformation in dependence on the poling field E_P

Preferred orientation of the CF_2 dipoles in the direction of the electric field, i.e. normal to the plane of the film, by the poling process causes P_r^Z values proportional to $<\cos\delta>$.

The state of polarization was investigated by means of the orientation bands at 510 and 445 cm^{-1}. These bands are assigned to CF_2 bending and CF_2 rocking modes respectively. The directions of these transition moments are normal to each other, and also normal to the chain axis, if the molecules of PVDF are highly oriented. The direction of the transition moment of the CF_2 bending vibration is equal to that of the dipole moment of the corresponding CF_2 group, while the transition moment of the CF_2 rocking mode is arranged normal to the dipole moment. For the absorbances A_{510} and A_{445} follow (DECHANT, 1972)

$$A_{510} \alpha < \sin^2 \delta > \tag{2}$$

and $$A_{445} \alpha < \cos^2 \delta > \tag{3}$$

As the orientation of the CF_2 dipoles in the direction of the external electric field increases A_{510} decreases and A_{445} increases. Contrarily, a desorientation of CF_2 dipoles will be reflected by decreasing A_{445} and increasing A_{510}. The absorbance of the trans conformational band at 510 cm^{-1} remains unchanged by the poling treatment (T_P = 115 °C, E_P = 400 MV/m). By this band no conformational changes are revealed because a certain amount of CF_2 groups corresponding to the transformed T-G-T-$\bar{G}$ fraction is directed normal to the surface of the film and thus does not contribute to the absorbance A_{510}. On the other hand, this allows to suggest residual polarization the value of which will be as high as the transformed α fraction.

Based on the polarization of a PVDF single crystal ($P_r = 22x10^{-2}$ C/m^2) (BROADHURST and DAVIS, 1980) and supposing efficient conformational changes, the average residual polarization P_r^Z is found to be about $11x10^{-2}$ C/m^2, thus reaching a value surmounting the usual average polarization values.

THERMALLY STIMULATED DECREASE OF POLARIZATION

The thermally stimulated desorientation of CF_2 dipoles will be reflected by decreasing absorbance A_{445}^T or increasing A_{510}^T after annealing the poled sample at the temperature T. The desorientation of dipoles results in turning the transition moment of CF_2 rocking mode out of the plane of the film, while the transition moment of CF_2 bending mode will be arranged in direction of the plane. The change of P_r^Z by thermal treatment was investigated by storing the poled sample (E_P = 400 MV/m, T_P = 115 °C) for 1 h at the required temperature T and then recording the bands at 445 and 510 cm^{-1} at room temperature. Fig. 3 demonstrates the normalized absor-

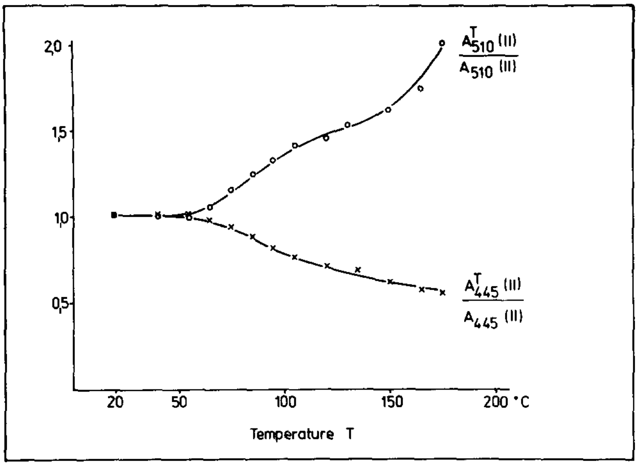

Fig. 3 Temperature - dependence of the normalized absorptions of the bands at 445 and 510 cm^{-1} of poled (E_P = 400 MV/m, T_P = 130 °C) and subsequently stored samples as measured at room temperature

bance values ($A^T(\parallel)/A(\parallel)$) in dependence on the storing temperature T. Small decrease of $A^T_{445}(\parallel)/A_{445}(\parallel)$ starts above 60 °C simultaneously with an increase of $A^T_{510}(\parallel)/A_{510}(\parallel)$. These effects grow stronger at 75 °C. Above 110 °C the desorientation of the CF_2 groups is observed to slow down as expressed by the lower increase of $A^T_{510}(\parallel)/A_{510}(\parallel)$ and the lower decrease of $A^T_{445}(\parallel)/A_{445}(\parallel)$. The strong increase of $A^T_{510}(\parallel)/A_{510}(\parallel)$ above 150 °C cannot be assigned only to stronger dipole orientation because a small increase of the thickness of the sample by annealing within this range of temperature, which would result in an increase of the apparent absorbance, cannot be excluded. Similar results were obtained with the absorbances $A^T_{510}(\perp)/A_{510}(\perp)$ and $A^T_{445}(\perp)/A_{445}(\perp)$. The dependence of these absorbances on the storing temperature T proved the thermally stimulated decrease of polarization in PVDF to proceed gradually and to be not characterized by a defined Curie point.

In the range of temperature around 80 °C the decrease of polarization is accelerated and proceeds gradually above 110 °C up to the melting point. The gradual decrease of polarization within a wide temperature range suggests a distribution of crystallite size on the state of polarization.

REFERENCES

BROADHURST, M.G. and DAVIS, G.T.: Top. Appl. Phys. 33, 285 (1980)

DANZ, R.: Acta Polymerica 33, 1 (1982)

DAVIES, G.R., KILLEY, A., RUSHWORTH, A. and SINGH, H.: Org. Coat. Plast. Chem. 38, 257 (1978)

DECHANT, J.: Ultrarotspektroskopische Untersuchungen an Polymeren, Berlin: Akademie Verlag 1972

ENNS, J.B. and SIMHA, R.: J. Macrom. Sci., B: Phys. 13, 11 (1977)

FUKADA, E. and FURUKAWA, T.: Ultrasonics No. 1, 31 (1981)

KOBAYASHI, M., TASHIRO, K. and TADOKORO, H.: Macromolecules 8, 158 (1975)

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