Infra-red analysis of poly(vinylidene fluoride) thermoelectrets

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The copolymer poly(vinylidene fluoride)–poly(tetrafluoroethylene) studied by infra-red spectroscopy during its transformation into electrets, shows structural modifications of the copolymer due to the electrostatic field action. The dielectric used is a copolymer monoaxially oriented by stretching and the paper reports on the structural changes in the molecular arrangements, relative to the induced electrical properties. These results complete and confirm data obtained previously by Raman spectroscopy[1,7].

INTRODUCTION

PVF$_2$ exists in three crystalline forms α, β and γ (forms II, I and III). A number of workers[2–5] and principally Todokoro *et al.*[6] have characterized these three different conformations, particularly by X-ray, n.m.r. infra-red and Raman studies. The α-form is monoclinic[6], and is *trans–gauche–trans–gauche* prime as is found in poly(vinylidene chloride). The *tgtg'* arrangement results in a staggered orientation of the monomer dipole on successive groups, and this gives rise to a larger permanent dipole moment for individual molecules of the polymer. The configuration of the infra-red absorption bands in the region 400–600 cm^{-1} gives a method for characterizing the two phases α and β. *Figure 1* shows the infra-red spectrum in polarized radiation of a sample of PVF$_2$ (Kureha commercial) film stretched at 180°C and shows the presence of the two mixed phases α and β. The α-form is characterized by the absorption band 530 cm^{-1} in perpendicular light, and corresponds to the angular deformation vibration of the dipole group F–C–F. The β-form is orthorombic[6] and appears with the absorption band 510 cm^{-1} in perpendicular light. The mixing of the two phases α and β is shown by the 480 cm^{-1} band. When the polymer forms a complex of the two phases, the amount of each form can be estimated using the absorbance ratio D_{510}/D_{530}. The band 440 cm^{-1} in perpendicular light is characteristic of the γ-form. The form γ also has a monoclinic configuration[6] as has the α-form, of the unstretched polymer. The differences in vibrational spectrum between crystal forms β and γ, both consisting of essentially planar zig-zag chains, were interpreted[6] by the difference in relative heights of the chains in the unit cell.

Figure 2 represents the configuration of the molecule in the β-form. The copolymer also forms this same planar zig-zag configuration. The band assignment of infra-red spectra for the three fundamental forms have been described by Cessac, Curro Boerio and Koenig (see ref 5) and other workers[3–6], who also indicated the band assignment for the copolymers. *Table 1* gives the assignments of the 14 fundamental vibration modes. The (A_2) vibrations are not active in infra-red (only visible in Raman).

In the spectra of forms β and γ there appear many weak bands[6] which are not associated with optically active fundamentals of the regular crystal lattices of these forms.

EXPERIMENTAL

The copolymer PVF$_2$–PTFE provided by Pennwalt Co. (reference name: Kynar 7200) contained 25 to 30% of

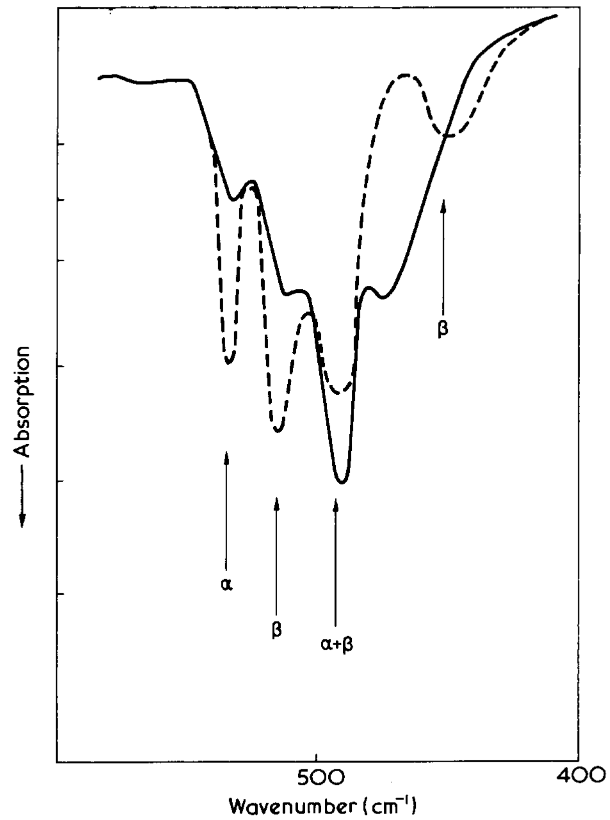

Figure 1 The infra-red spectrum of PVDF (stretched at 180°C) in the region 400–600 cm^{-1} shows the characteristic bands of α and β-configurations. ——, $E_{\|}$; – – – –, $E_{\perp}$

PTFE by wt, and had a crystallinity of 35% (by X-ray). It shows a planar zig-zag structure characteristic of the β-form. Its density was 1875 g/cm^3, and the thicknesses of the films used were 6 to 25 μm. The samples were monoaxially oriented by stretching to 400% in the direction of the plane of the film.

The spectrometers

The 1500–200 cm^{-1} infra-red spectra were recorded on two spectrometers (Perkin–Elmer 280, and spectromaster Grubb Parsons) to prevent errors due to the use of the apparatus or to the position of the sample. A Selenium polarizer was used. Since there is a polarization from the grating within the instrument used, and thus the spectrometer itself acts as a polarizer, the error due to this phenomenon was prevented by locating samples such that the direction of the stretching was oriented at 45° about the direction of the spectrometer optical axis; thus the two positions of the polarizer are 45° for the parallel radiations and 315° for the perpendicular radiations.

Formation of thermoelectrets

The classical method of poling was used[8]. The samples were heated at 80°C and the field intensity varied between 15 and 1700 kV/cm. Electrodes were made by bismuth evaporated in vacuum and the electrodes could be removed easily after the polarization of the sample to permit the optical measurements.

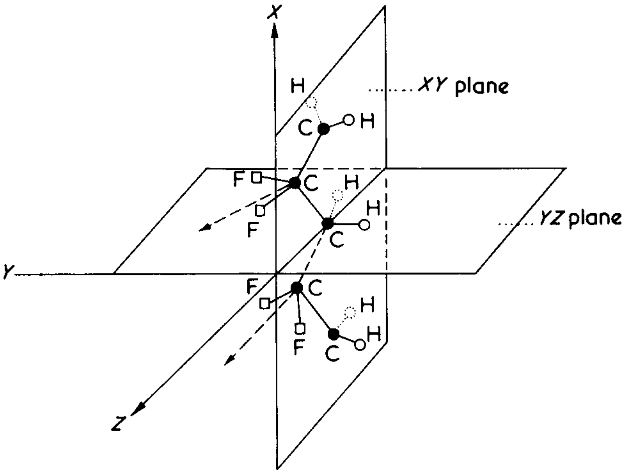

Figure 2 The planar zig-zag conformation of PVDF chain in the β-form configuration

RESULTS AND DISCUSSION

Figure 3 shows the spectra, in perpendicular light, of electrets polarized with electrostatic fields of 100 and 200 kV/cm, compared with the reference spectrum of a sample submitted only to the thermal treatment, not to the electrostatic field action. The most significant differences are: (a) a transmission percentage much more important for the electrets at practically all the frequencies of the spectrum; (b) a refining of the spectra with absorption bands stronger and sharper and a slight displacement to high frequencies; (c) an important increase in the absorption for the bands at 510 and 845 cm^{-1} relative to the movements of dipole: δ (CF$_2$) and γ*a* (CF$_2$); (d) between 550 and 700 cm^{-1} the refining of the spectra reveals the presence of new bands: a double band at 560–570 cm^{-1} and a band at 638 cm^{-1} corresponding to the very strong double band of PTFE in perpendicular light. *Figure 4* shows the spectra of PTFE in the region 1500–200 cm^{-1}. In *Figure 5* we note also new bands at 570, 560, 440, 405 cm^{-1} and between 300 and 200 cm^{-1}. All these differences indicate an increase in the degree of order of the polymer as a function of the electrostatic field intensity. This effect of reorganization seems to appear by the orientation of dipoles and an increase of the degree of crystallinity under field action. This last

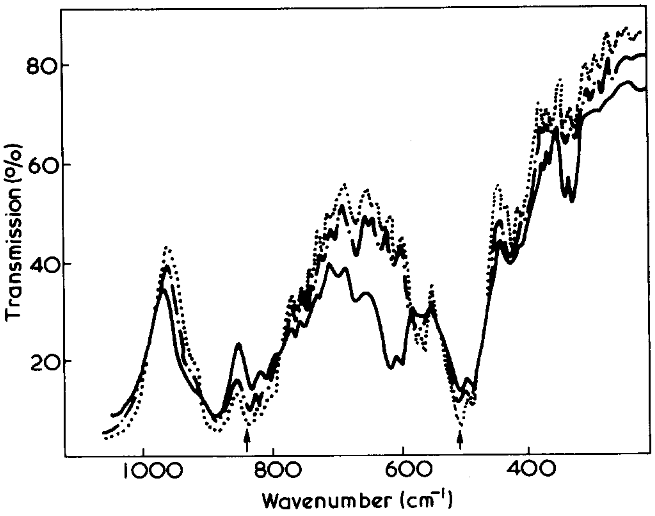

Figure 3 Infra-red spectra of PVDF–PTFE copolymer stretched 400% in perpendicular light, for reference and electrets samples. ———, Reference; — — — —, electrets E = 200 kV/cm; — · — · —, electrets E = 100 kV/cm

Table 1 14 Vibration modes of CH$_2$–CF$_2$ in i.r.

3 Fundamental modes of CF$_2$	(⊥) 1273 cm^{-1}:	Symmetrical valence vibrations	$\gamma s(CF_2) = A_1$
	(⊥) 1176 cm^{-1}:	Antisymmetrical valence vibrations	$\gamma a(CF_2) = B_2$
	(⊥) 508 cm^{-1}:	F–C–F deformation vibrations	$\delta\ (CF_2) = A_1$
3 Fundamental modes of CH$_2$	(⊥) 2980 cm^{-1}:	Symmetrical valence vibrations	$\gamma s(CH_2) = A_1$
	(⊥) 3022 cm^{-1}:	Antisymmetrical valence vibrations	$\gamma a(CH_2) = B_2$
	(⊥) 1428 cm^{-1}:	H–C–H deformation vibrations	$\delta\ (CH_2) = A_1$
2 Fundamental modes of CH$_2$–CF$_2$	(⊥) 1273 cm^{-1}:	Symmetrical vibrations of C–C	$\gamma s(CC) = A_1$
	(⊥) 884 cm^{-1}		
	(‖) 1071 cm^{-1}:	Antisymmetrical vibrations of C–C	$\gamma a(CC) = B_1$
	1398 cm^{-1}		
6 Movements of CH$_2$–CF$_2$ chain	(‖) 1071 cm^{-1}:	Wagging modes ‖ *Oxz* plane	$w\ (CF_2) = B_1$
	(‖) 1398 cm^{-1}:	Wagging modes ‖ *Oxz* plane	$w\ (CH_2) = B_1$
	(⊥) 442 cm^{-1}:	Rocking modes ‖ *Oyz* plane	$r\ (CF_2) = B_2$
	(⊥) 840 cm^{-1}:	Rocking modes ‖ *Oyz* plane	$r\ (CH_2) = B_2$
	inactive :	Twisting modes ∣ C_2	$t\ (CF_2) = A_2$
	:	Twisting modes ∣ C_2	$t\ (CH_2) = A_2$

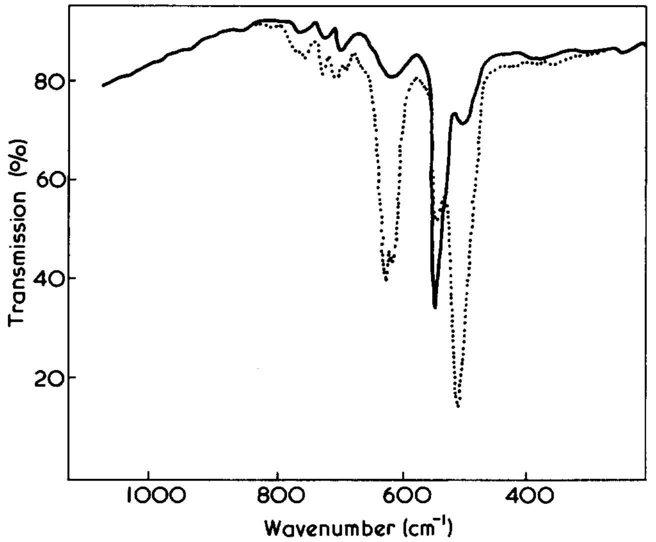

Figure 4 Infra-red spectra of PTFE. ———, $E_{\parallel}$; – – – –, $E_{\perp}$

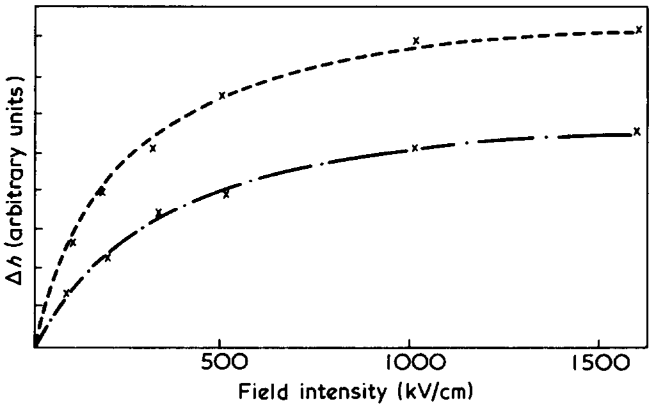

Figure 5 PVDF–PTFE copolymer: height variations in arbitrary units, for the two bands 840 and 510 cm^{-1} as a function of the poling field intensity. – – –, 840 cm^{-1} vibration band; — · — ·, 510 cm^{-1} vibration band

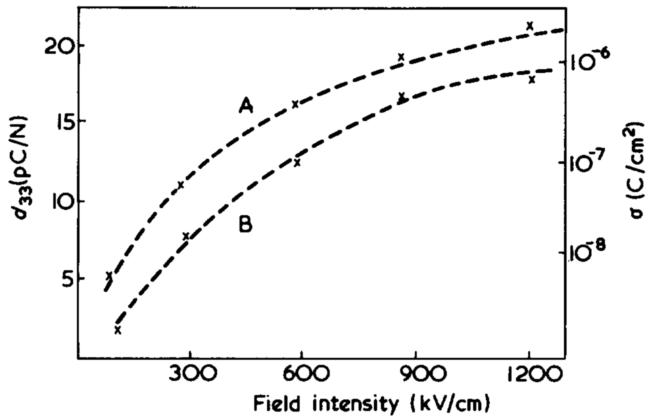

Figure 6 Variations of charge density (B) (C/cm^2) and the piezoelectric coefficient (*PC/N*) (A) as functions of field intensity: ●, charge density in C/cm^2; ○, piezoelectric coefficient in pC/N

hypothesis seems to be confirmed by Raman measurements presented in a previous paper[1] and by density measurements made by the gradient density column method*. The reference sample had a density 1.875 g/cm^3, but the same sample poled with an electrostatic field of 420 kV/cm had a density of 1.895 g/cm^3 (±0.005 g/cm^3). Regarding the movements of reorientation of dipoles under field action, we have shown in *Figure 5* the relative variations of height for the absorption bands 510 and 845 cm^{-1} as a function of field intensities between 200 and 1300 kV/cm. *Figure 6*, curve B gives the corresponding variations for the charge of the electrets poled with electrostatic field intensities between 200 and 1300 kV/cm, using blocking electrodes. *Figure 6*, curve A gives the corresponding variations of the piezoelectric coefficient d_{33} of these electrets. The d_{33} coefficient is measured by compression normal to the plane of the film[1]. The variations of the curves in *Figure 5* and *Figure 6* (curves A and B) are similar, this indicates a relation between the orientation of dipoles and piezoelectric coefficient of the copolymer.

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* Measurements carried out at the National Bureau of Standards, Washington D.C., USA (Dr T. Davis s group)