Measurement of the Internal Electric Field in a Ferroelectric Copolymer of Vinylidene Fluoride and Trifluoroethylene Using Electrochromic Dyes

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ABSTRACT: This paper presents a measurement of the internal electric field induced by poling in a ferroelectric copolymer of 75 mol % vinylidene fluoride and 25 mol % trifluoroethylene (VDF–TrFE copolymer) using the electrochromism of dyes, 4-(dimethylamino)-4′-nitrostilbene (DANS) and 2-methyl-4-nitroaniline (MNA), dissolved in the copolymer. As a result of poling, the absorption intensity decreases, the peak position of the original band shifts to longer wavelength, and the width of the band slightly increases. These changes in the absorption spectra of DANS and MNA after removal of the poling field have been interpreted to assess the internal electric field E_i created by the oriented crystallite dipoles in the VDF–TrFE copolymer. E_i values were calculated from an analysis of the differential spectrum after and before poling, using theoretical expressions involving the first and second derivatives of the original spectrum. E_i values increase with increasing remanent polarization P_R, achieving a value of 3.4–3.9 MV/cm at P_R = 6.1 μC/cm^2 after poling at a maximum electric field of 1.15 MV/cm. In the process of thermal annealing after poling, E_i increases slightly in the vicinity of 80 °C and above this temperature gradually decreases until an abrupt decrease occurs near 135 °C corresponding to the total loss of polarization at the Curie temperature. Furthermore, a new absorption band arises and its intensity increases upon poling at higher electric field or upon thermal annealing after poling. This new absorption band is ascribed to that of a protonated species of the dye which implies that HF is generated upon poling and thermally dissociates into H^+ and F^-. The intensity ratio of the new to the original band increases with increasing annealing temperature up to 80 °C but decreases above 80 °C, suggesting that the generated HF is lost from the sample film above 80 °C. Therefore, the slight increase of E_i in the vicinity of 80 °C may be due to a loss of ionic countercharges at crystal–amorphous interfaces. Somewhat higher E_i and higher P_R are measured for a sample annealed prior to poling.

Introduction

Copolymers of vinylidene fluoride and trifluoroethylene (VDF–TrFE) have been of great interest because of their piezoelectric and pyroelectric properties and the existence of an observable ferroelectric to paraelectric transition.[1-7] In the ferroelectric phase, the orientation of the polar crystallites can be switched in an electric field and the crystallites remain preferentially oriented when the field is removed, thus giving rise to net polarization in the polymer film. Hill et al.[8] recently demonstrated that the electric field created by the preferentially oriented polar crystals can orient polar molecules which are dissolved in the amorphous region of the polymer. Using guest molecules which have nonlinear optical (NLO) properties, they showed that such poled copolymer films exhibit second-harmonic generation arising from the oriented NLO molecules.

In this work, we have measured the internal electric field using changes in the optical absorption spectra of electrochromic dyes dissolved in VDF–TrFE copolymers as a function of the remanent polarization. We have also investigated the stability of the internal electric field at elevated temperatures.

Experimental Section

The copolymer of 75 mol % vinylidene fluoride and 25 mol % trifluoroethylene was supplied by Atochem.[9] 4-(Dimethylamino)-4′-nitrostilbene (DANS) from Eastman Kodak Co.[9] was recrystallized from a mixture of acetone and tetrahydrofuran and dried at 90 °C. 2-Methyl-4-nitroaniline (MNA) from Aldrich Chemical Co.[9] was recrystallized from methanol. The structural formulas of these solute molecules are shown in Figure 1.

Polymer films were melt-pressed between 125-μm-thick films of Kapton[9] on a heated press to a thickness of 40–65 μm. The molten films were quenched into liquid nitrogen and in some cases were subsequently annealed. Crystallinity χ_c of the films was estimated from the density ρ as measured in a carbon tetrachloride–1,2-dibromoethane density gradient column. On the basis of data obtained in this laboratory for this copolymer, the density of the amorphous phase at 23 °C was taken as 1.735 g/cm^3 and that of the crystalline phase was 1.952 g/cm^3.

The solute probe molecules were introduced by soaking the polymer films in *n*-propyl alcohol solutions saturated with dye at the boiling point of the alcohol (97 °C) for 2 h followed by drying overnight at room temperature in vacuum. On the basis of optical absorption coefficients of the dyes in solution, the concentration of DANS in the copolymer was 1.1–1.2 mmol/L and that of the MNA was 6.5–8.0 mmol/L. Attempts were made to incorporate the dyes into the polymer by spin casting from a common solvent such as acetonitrile, but we found that the dyes precipitated as a separate phase as the solvent evaporated. Subsequent heating of the films to the melting temperature followed by quenching redissolved the dyes but caused partial isomerization of the DANS and significant loss of concentration of the MNA.

The polymer films were poled by applying several cycles of a sinusoidal voltage at a frequency of 0.05 Hz to 1.27-cm-diameter aluminum electrodes which had been evaporated onto opposing surfaces of the films. Poling current was monitored during application of the voltage and was used to calculate the remanent polarization, allowing for impedance losses.[10,11] Pyroelectric response was determined by measuring the current generated upon heating and cooling the poled film at a measured rate, usually about 2 °C/min in the vicinity of 25 °C. After poling and measuring the pyroelectric response, the aluminum electrodes were removed by immersing in 1 N NaOH for about 1 min in order to make the subsequent optical absorption measurements.

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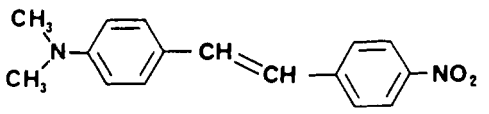
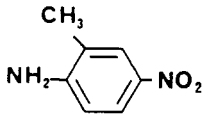


DANS



MNA

Figure 1. Structural formulas of dye molecules used in this study.

UV–visible spectra of the films were measured on a Model IF 552 Perkin-Elmer[9] spectrophotometer and recorded on a Model 3600 data station.[9] Data files were subsequently transferred to a PC for analysis.

Basis for Measurement of Internal Electric Field

A theory for electrochromic effects in liquid solutions was developed and published by Liptay and co-workers in a series of papers which are well summarized in a book chapter.[12] The theory was extended to macromolecules in solution by Yamaoka and Charney[13] and then applied to electrochromic molecules dissolved in a polymer matrix by Havinga and van Pelt.[14] Stated simply, optical absorption corresponds to energy transfer between an electronic ground state and an electronic excited state in a molecule. In the presence of an electric field the energy of each state is reduced by the product of the dipole moment μ, the field $\mathbf{E}$, and the cosine of the angle between the dipole and the field. The energy difference between the ground and excited states at a particular angular position is then altered by an amount proportional to the electric field and the difference in dipole moment between the two states. The angular distribution of dipoles with respect to the field is estimated from the Langevin function in terms of the dimensionless variable $\mu\mathbf{E}/(kT)$. Molecular parameters which enter the theory are the dipole moments of the ground state μ_g and the excited state μ_e and the angles between the dipole moments and a coordinate system within the molecule. For large values of μ, terms involving the polarizations of the two states are negligible.

The absorption spectra of the probe molecules are rather broad and the shifts in the peak maxima are small so that shifts are best determined by comparing large portions of the two spectra. For this purpose, it has been found convenient to express the spectrum in the presence of a field $A(\nu,E)$ as a Taylor series expansion of the unperturbed spectrum $A(\nu,0)$ with the wavenumber shift $\Delta\nu$ as the perturbation. Furthermore, according to Liptay[12] the absorption spectrum is practically identical to a Lorentzian line shape if expressed as absorbance divided by wavenumber. Following Havinga and van Pelt[14]

$$\frac{A(\nu,E)}{\nu} - \frac{A(\nu,0)}{\nu} = \frac{\delta A(\nu,0)}{\nu} + \langle\Delta\nu\rangle\frac{\partial}{\partial\nu}\frac{A(\nu,0)}{\nu} + \frac{1}{2}\langle(\Delta\nu)^2\rangle\frac{\partial^2}{\partial\nu^2}\frac{A(\nu,0)}{\nu} \quad (1)$$

The term involving δ accounts for a change in absorbance due to reorientation of the dye in the presence of the field. The reorientation can also be expected to be manifested in dichroic measurements, but such measurements were not performed in this work. Terms involving $\langle\Delta\nu\rangle$ and $\langle(\Delta\nu)^2\rangle$ describe field-induced shifts in the band and field-induced broadening of the band.[14] In the experimental procedure employed, the intensity of the absorbance (but not a shift in the spectrum) can be altered for reasons other than the presence of an electric field which will be discussed later. If we assume that the intensity of the absorbance is reduced uniformly by a factor f across all wavelengths in the absorption band and neglecting terms above $\langle(\Delta\nu)^2\rangle$, the poled spectrum can be expressed in terms of the unpoled spectrum by

$$\frac{A(\nu,E)}{(1-f)\nu} - \frac{A(\nu,0)}{\nu} = \frac{\delta A(\nu,0)}{\nu} + \langle\Delta\nu\rangle\frac{\partial}{\partial\nu}\frac{A(\nu,0)}{\nu} + \frac{1}{2}\langle(\Delta\nu)^2\rangle\frac{\partial^2}{\partial\nu^2}\frac{A(\nu,0)}{\nu} \quad (2)$$

The theoretical expressions for δ, $\langle\Delta\nu\rangle$, and $\langle(\Delta\nu)^2\rangle$ from the work of Havinga and van Pelt[14] and Yamaoka and Charney[13] are

$$\delta = -P(\cos\psi)\,G(u) \quad (3)$$

$$\langle\Delta\nu\rangle = 3|\mathbf{E}_i||\Delta\mu|\,G_1(u)/[hc\{1 - P(\cos\psi)\,G(u)\}] \quad (4)$$

$$\langle(\Delta\nu)^2\rangle = (|\mathbf{E}_i|^2|\Delta\mu|^2)[\{(2 - \cos^2\eta)H_1\} + H_2]/(5h^2c^2) \quad (5)$$

where $u = |\mu_g||\mathbf{E}_i|/kT$

$$G_1(u) = G(u)\,[(\cos\psi\cos\phi - 2\cos\eta)/u] + (1/2)u\,K(u)\sin^2\psi\cos\eta \quad (6)$$

$$G(u) = 1 - [3\coth(u)/u] + 3/u^2 \quad (7)$$

$$K(u) = 6/u^2 + 15/u^4 - [\coth(u)](1/u + 15/u^3) \approx -u^2/105 \quad (8)$$

$$H_1 = 15G(u)/[\{1 - P(\cos\psi)\,G(u)\}u^2] \quad (9)$$

$$H_2 = (1/2)G(u)\sin^2\psi\cos^2\eta + K(u)\,[2\cos\psi\cos\phi\cos\eta - 3\cos^2\psi\cos^2\eta - (1/2)\sin^2\psi\sin^2\eta] \quad (10)$$

$|\Delta\mu|$ is the magnitude of the difference between the dipole moments in the excited state and in the ground state ($=\mu_e - \mu_g$), ϕ is the angle between $\Delta\mu$ and μ_g, and η is the angle between $\Delta\mu$ and the transition moment, $\mathbf{m}$. $P(\cos\psi) = (3\cos^2\psi - 1)/2$, where ψ is the angle between the dipole moment in the ground state μ_g and the transition moment $\mathbf{m}$. $\mathbf{E}_i$ is the internal electric field, h is Planck's constant, c is the speed of light, k is Boltzmann's constant, and T is absolute temperature. (The term $15/u^2$ in the expression for $K(u)$ in ref 14 is a misprint. It should be $15/u^3$ as in eq 8.)

In the case of the DANS molecule, the dipole moments in the ground state and the excited state are essentially collinear so the angles η, ψ, and ϕ are close to zero.[15] Evaluating the trigonometric functions accordingly and recognizing that the H_2 term is negligible with respect to the H_1 term in eq 5, substitution of the expressions for δ, $\langle\Delta\nu\rangle$, and $\langle\Delta\nu^2\rangle$ in eq 2 results in

$$\frac{1}{1-f}\frac{A(\nu,E)}{\nu} - \frac{A(\nu,0)}{\nu} = -G(u)\frac{A(\nu,0)}{\nu} - \frac{3CG(u)}{1-G(u)}\frac{\partial}{\partial\nu}\frac{A(\nu,0)}{\nu} + 1.5C^2\frac{G(u)}{1-G(u)}\frac{\partial^2}{\partial\nu^2}\frac{A(\nu,0)}{\nu} \quad (11)$$

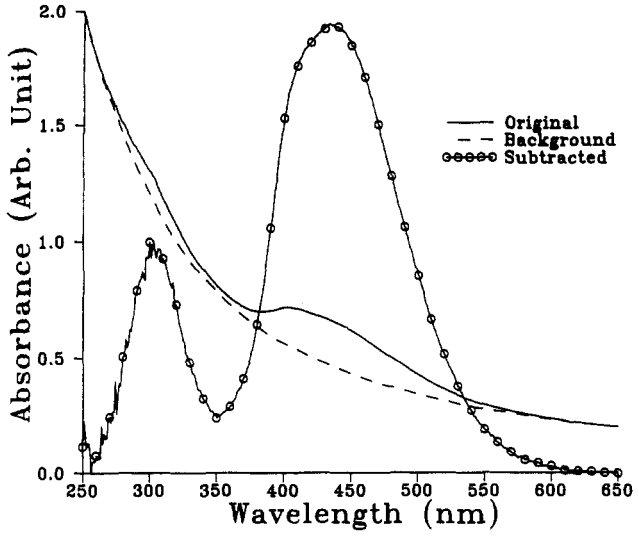


Figure 2. Typical absorption spectra for the systems investigated.

where $C = (kT|\Delta\mu|)/(hc|\mu_g|)$. Upon rearranging

$$\frac{1}{1-f}\frac{1}{1-G(u)}\frac{A(\nu,E)}{\nu} - \frac{A(\nu,0)}{\nu} = \frac{G(u)}{[1-G(u)]^2}\left[-3C\frac{\partial}{\partial\nu}\frac{A(\nu,0)}{\nu} + 1.5C^2\frac{\partial^2}{\partial\nu^2}\frac{A(\nu,0)}{\nu}\right] \quad (12)$$

Use of this equation for evaluating the internal electric field from the absorption spectra will be discussed after presenting typical experimental results.

Results

Typical optical absorption spectra for the systems investigated are shown in Figure 2. An apparent increase in absorbance with decreasing wavelength in the undyed copolymer film (background) is due to scattering losses caused by the presence of small crystallites in the semicrystalline copolymer. After soaking the polymer film in an alcohol solution of DANS as previously described, one obtains the spectrum shown by the solid line in the figure. The spectrum for DANS is then obtained by subtraction and is shown on an expanded scale in the figure. Poling can alter the background spectrum from that which was measured in the unpoled state, but it remains smooth over the range of wavelengths displayed in Figure 2. Multiplying the background absorbance by small amounts to allow for such changes before subtraction has negligible influence on the resultant dye spectrum. Note the presence of a small peak in the UV region around 300 nm in addition to the main peak at 435 nm before the application of a field.

The polymer film containing dye was then subjected to poling fields as previously described. Current as a function of applied electric field is shown in the upper portion of Figure 3, and the time integral of the current is shown in the lower portion of the figure. Remanent polarization is the value of polarization at zero applied field after the last cycle of poling. It is the polarization which creates the internal fields to which the probe molecules are subjected. Most of the polarization is developed within the first few cycles, but there is a gradual increase with the number of cycles. Usually 50 cycles at 0.05 Hz were applied at room temperature. Likewise, most of the polarization is developed at applied fields below 0.8 MV/cm, but there is a gradual increase as the maximum field is increased further. The large change in polarization near 0.5 MV/cm is due to the ferroelectric switching of dipoles within the crystalline phase of the copolymer.

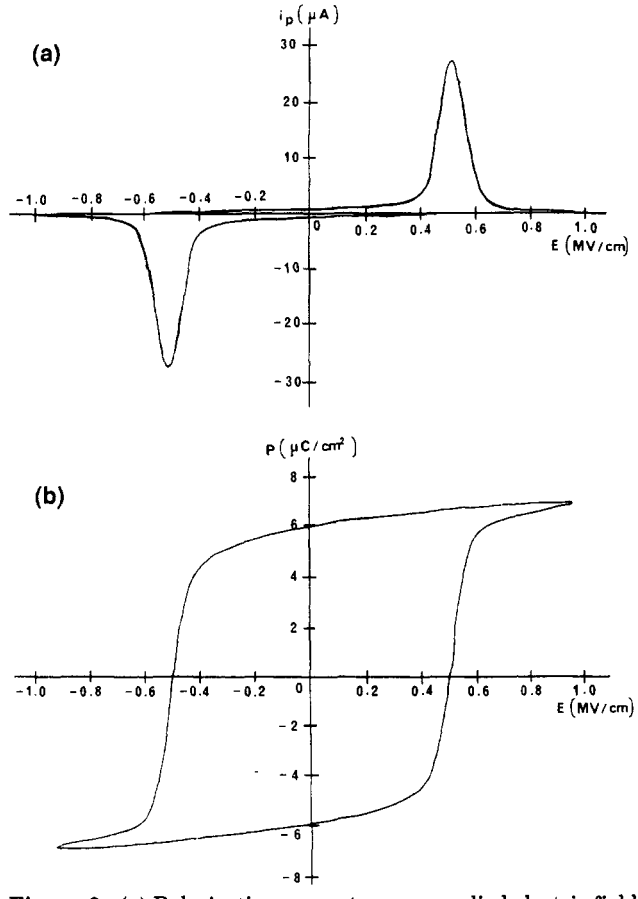


Figure 3. (a) Polarization current versus applied electric field. (b) Polarization charge (time integral of curve in Figure 3a versus applied field).

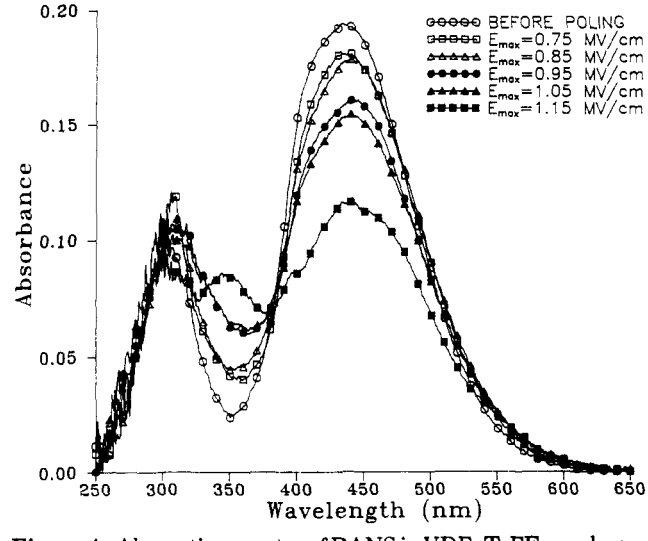


Figure 4. Absorption spectra of DANS in VDF–TrFE copolymer after poling at maximum fields indicated.

The effect of poling on the absorption spectrum of the dissolved DANS is shown in Figure 4 for a series of maximum applied fields E_{max} ranging from 0.75 to 1.15 MV/cm. These data were obtained on the same film which required the removal of the aluminum electrodes to record the spectrum and the redeposition of electrodes to pole at the next higher maximum field. It is apparent that the absorbance decreases and the maximum shifts slightly to longer wavelengths. Close inspection of the data reveals that the width of the band increases slightly as the poling

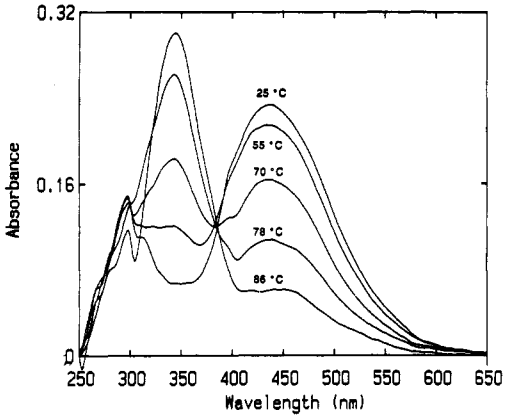


Figure 5. Absorption spectra of DANS in VDF–TrFE copolymer after being subjected to the indicated successively higher temperatures for 1 h after poling.

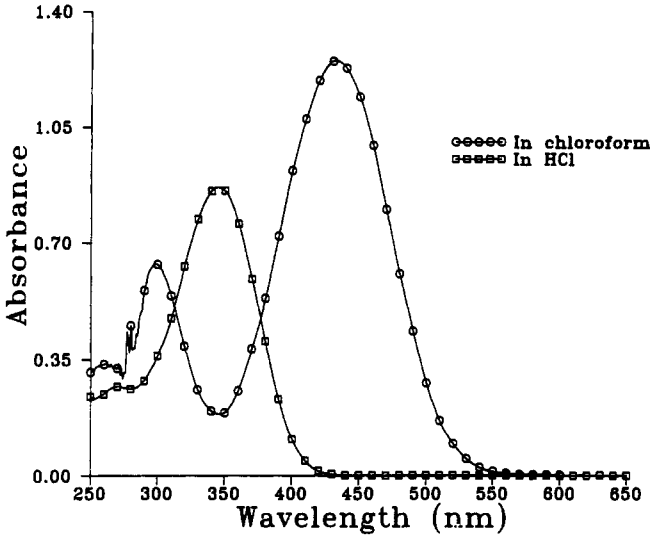


Figure 6. Absorption spectra of DANS in chloroform solution and in the presence of added HCl.

field is increased.

Furthermore, a new band near 345 nm develops after poling at the highest field in this set of experiments. We also found that thermal annealing of the sample film after poling at 1.0 MV/cm for 50 cycles gives rise to increased absorbance of this new band and decreased absorbance of the original band as shown in Figure 5. The development of this new band has been reproduced on several occasions. The absorption spectrum of protonated DANS in chloroform by adding HCl is shown in Figure 6, which is almost the same as the new absorption band after poling shown in Figures 4 and 5. The identification of the new absorption band in Figures 4 and 5 with that in Figure 6 in the presence of HCl implies that the poling produces H^+ to protonate the dye. The same type of protonated absorption spectrum is also obtained for an unpoled dyed film soaked in propyl alcohol with HCl. Recently, from a mass spectroscopic study,[16] the emission of HF gas has been reported when poling poly(vinylidene fluoride) (PVDF) film. Therefore, we assume that the poling liberates HF from the VDF–TrFE copolymer which dissociates into H^+ and F^- ions in the presence of small amounts of propyl alcohol remaining in the polymer bulk to protonate DANS.[17]

Decreases in absorbance at the original band position are expected due to orientation of dye molecules in the electric field which exists after poling.[8] However, as described above, the existence of the protonated species of DANS also causes a decrease in the absorbance at the

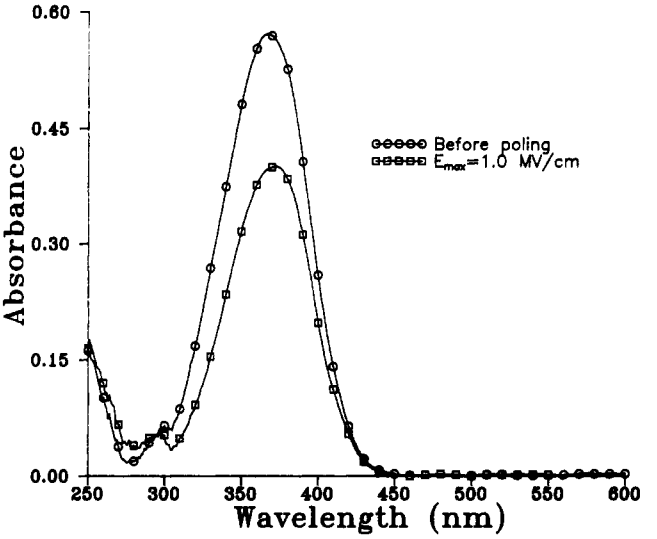


Figure 7. Absorption spectra of MNA in VDF–TrFE copolymer before and after poling for 50 cycles.

original peak position. Therefore, one must allow for the loss of some dye, which was done by introducing the factor $(1 - f)$ in eq 2.

Spectra for MNA in a copolymer film before and after poling at a maximum field of 1 MV/cm for 50 cycles are shown in Figure 7. In this case, we have not observed any new peaks; absorbance decreases upon poling, but the shift in peak maximum is smaller than in the case of DANS.

Data Analysis

In the absence of complications, the orientation-induced change in absorbance, δ, the shift in absorption spectra, $\langle \Delta\nu \rangle$, and the broadening of the peak, $\langle (\Delta\nu)^2 \rangle$ would be obtained from curves of absorbance divided by wavenumber according to eq 1. The difference in the absorbances divided by ν at several values of ν would be fit to the original spectrum and the first and second derivatives of the original curve at the corresponding wavenumbers. Coefficients obtained from such a fit are δ, $\langle \Delta\nu \rangle$, and $\langle (\Delta\nu)^2 \rangle / 2$. However, as mentioned previously, changes in absorbance are also caused by a decrease in the concentration of dye since some of it is transformed to a protonated species which does not absorb in the same region as the original and the background scattering of the semicrystalline polymer can change slightly as a result of poling. We have introduced the theoretical expressions involving electric fields, dipole moments, etc., of eqs 3–5 to arrive at eq 12. The spectrum after poling, now reduced from the original by factors f and $G(u)$, shifted by $\Delta\nu$, and broadened by $\langle (\Delta\nu)^2 \rangle / 2$, will cross the original spectrum at some value of wavenumber, ν_N, where $A(\nu_N,E)/[(1 - f)(1 - G(u))\nu_N] = A(\nu_N,0)/\nu_N$. At the point of intersection, the right-hand side of eq 12 will be equal to zero from which it can be deduced that $\partial\{A(\nu,0)/\nu\}/\partial\nu = (C/2)\,\partial^2\{A(\nu,0)/\nu\}/\partial\nu^2$. First and second derivatives of $A(\nu,0)/\nu$ were evaluated as a function of ν to determine the value ν_N for which the above relation was satisfied. A value of $(1 - f)(1 - G(u))$ was then chosen to make the spectra of the poled and unpoled samples intersect at ν_N, i.e., $A(\nu_N,E)/[(1 - f)(1 - G(u))\nu_N] = A(\nu_N,0)/\nu_N$. Having normalized the curves at ν_N, the differences in absorbance between the two spectra at several other values of ν were then determined, the derivatives were evaluated at the corresponding values of ν as required for eq 12, and the quantity $[G(u)/\{1 - G(u)\}^2]$ was evaluated from a linear least-squares fit. From $G(u)$ and eq 7, a value of u was obtained from

Table I
Values of E_i, P_R, and E_c for Films Subjected to E_{max} for 50 Cycles

E_{max}, MV/cm	E_i, MV/cm	P_R, μC/cm^2	E_c, MV/cm
0.65	0	1.3	0.46
0.75	2.5	3.7	0.48
0.85	2.7	5.0	0.51
0.95	2.8	5.7	0.52
1.05	3.2	6.0	0.54
1.15	3.4–3.9	6.1	0.55

which E_i was evaluated.

Discussion

The changes of absorption spectra after removal of the external electric field shown in Figure 4 have been interpreted to assess the internal electric field formed in VDF–TrFE copolymer, as reported by Hill et al.[8] As mentioned above, crystallites in VDF–TrFE copolymer preferentially form a β-phase which can be oriented in an electric field. Then the ordered crystallite dipoles locally form an internal electric field. Thus the dye molecule dispersed in the amorphous region would be subjected to the electric field, and the absorption spectrum is changed. The internal electric field helps to align dye molecules in the direction of the crystalline dipoles, resulting in a decrease in intensity of the absorption spectrum. Furthermore, the preferred orientation of dye molecules relative to completely random orientation gives rise to a broadening of the absorption band, and the internal electric field alters the energy levels of the dye molecules, which leads to the wavelength shift in the peak position. (See ref 15.)

Table I shows the internal electric field E_i calculated for μ_g = 7.4 D, μ_e = 24.8 D, and $\Delta\mu$ = 17.4 D.[18,19] For DANS, the angles ϕ, η, and ψ are zero or small enough that their cosines are nearly unity.[15] The remanent polarization P_R and the coercive field E_c from the hysteresis curves are listed for each E_{max}. The internal electric field is on the order of 10^6 V/cm and achieves a value of 3.4–3.9 MV/cm when P_R is 6.1 μC/cm^2 at E_{max} = 1.15 MV/cm, while the coercive field E_c is at most 0.55 MV/cm.

Higher maximum fields result in larger remanent polarizations, which is reflected in larger internal electric fields as shown in Figure 8. Since the dye molecules are presumed to reside solely in the amorphous region of the polymer, their spectral changes reflect the electric fields in this region. If subsequent to poling when the remanent polarization was measured, countercharges were to accumulate at the interfaces between crystallite and amorphous regions and thus compensate for polarization in the individual crystallites throughout the sample, one would expect to see no internal field between crystallites. Previous work on piezoelectric and pyroelectric response in PVDF concluded that there was very little countercharge at the crystal–amorphous interface,[20] and the data presented here support such a conclusion. The polarization which terminates at the polymer film surface is equivalent to a surface charge density of magnitude equal to P. This polarization charge will then produce an electric field within the amorphous regions of the copolymer where the dye resides. The electric field within such regions might be expected to be $P/\epsilon\epsilon_0$ where ϵ is the relative permittivity of the amorphous phase of the copolymer and ϵ_0 is the permittivity of vacuum.[21] The concept of internal field is often encountered in the context of being internal to a spherical assembly of oriented dipoles, in which case the field is $P/3\epsilon_0$.[22] However, in the case we are considering,

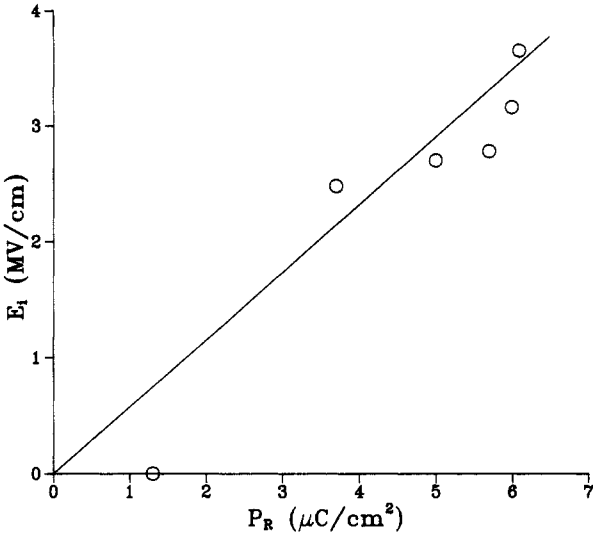


Figure 8. Internal electric field E_i vs remanent polarization P_R as deduced from DANS spectra. The line is drawn with a slope of $1/19.5\epsilon_0$ V·cm/C.

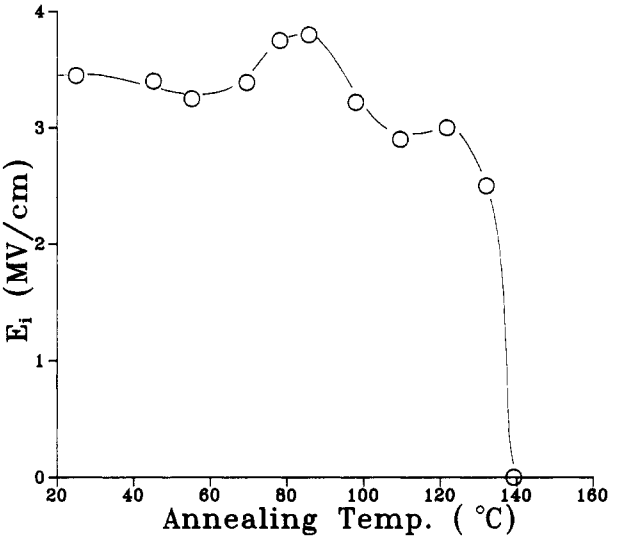


Figure 9. Internal electric field deduced from DANS spectra after annealing for 1 h at the indicated temperature.

we are interested in the field external to such an assembly of dipoles (the polar crystallites), and hence the field depends upon ϵ. In Figure 8, the electric field deduced from spectral shifts in DANS is plotted as a function of the remanent polarization imposed during electric field poling. The line drawn through the origin has a slope of $1/\epsilon\epsilon_0$ where ϵ = 19.5. Copolymers of vinylidene fluoride and trifluoroethylene near 75% VDF exhibit relative permittivities in the vicinity of 12–17 for the composite semicrystalline film.[23,24] The relative permittivity of the liquid phase of PVDF homopolymer at room temperature was estimated to be 12 from extrapolation of data above the melting point.[25] It is therefore not unreasonable to expect a value near 19.5 for the 75/25 copolymer used in this work.

The internal field in a melt-quenched film which had been poled for 50 cycles at a maximum field of 1 MV/cm and then annealed for 1 h each at successively higher temperatures is shown in Figure 9. The slight increase after heating to the vicinity of 80 °C was reproduced in two other samples. As described in the Results section, there are indications that HF is generated during the poling process which apparently protonates the dye giving rise to a new absorption band. Figure 10 shows the change of

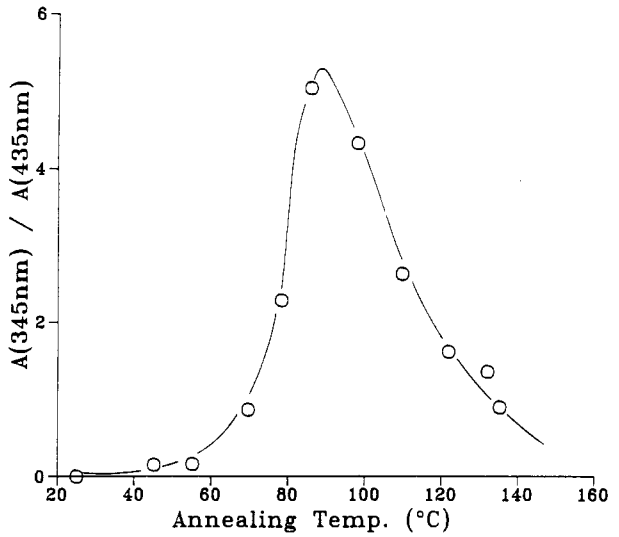


Figure 10. Ratio of the new absorbance at 345 nm to that of the original at 435 nm for DANS in poled films subjected to the indicated annealing temperatures for 1 h.

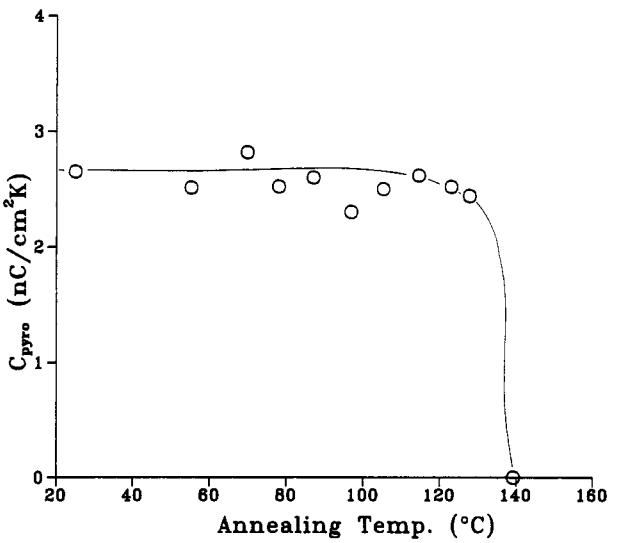


Figure 11. Pyroelectric coefficient C_{pyro} in poled VDF–TrFE copolymer as a function of annealing temperature after poling.

the ratio between absorbance of the new band $A(345\ nm)$ to that of the original one $A(435\ nm)$ when changing the annealing temperature (examples of spectra are shown in Figure 5). The annealing process leads to an increase of the new absorption band up to 80 °C, presumably due to the protonation. Such a change with annealing temperature suggests increased dissociation of the HF with increasing temperature. Although just the opposite should be expected for HF in aqueous solution,[26,27] data for HCl in polar organic solvents show that the dissociation increases with temperature in methanol but decreases with temperature in ethanol.[28] We are unaware of data for HF in a system similar to the one on which we are reporting. The absorbance ratio decreases upon increasing the annealing temperature above 80 °C, which implies the loss of HF and reversal to the nonprotonated original dye in the film. Such a loss of ionic countercharges at crystal–amorphous interfaces might be responsible for the increase in internal electric field in the vicinity of 80 °C. The decrease in E_i at temperatures above 90 °C is probably due to the gradual loss of polarization as one approaches the Curie temperature, and the abrupt decrease near 135 °C corresponds to the total loss of polarization at the Curie temperature. Measured values of the pyroelectric coefficient for the same sample after each treatment are shown in Figure 11 where the primary change is the sudden loss of activity at the Curie temperature.

Table II shows the comparison of values of E_i, P_R, E_c, ρ, and χ_c for a melt-quenched sample and those for a sample annealed at 135 °C for 1 h prior to poling. As a result of annealing, χ_c increases from 60 to 80%, P_R increases from 5.4 to 7.4 $\mu C/cm^2$, and E_i increases from 3.3 to 3.7 MV/cm. Annealing prior to poling results in an increase in the total amount of crystallite dipoles to be oriented, and this increase of dipoles leads to the higher polarization and thus higher internal electric field.

Table II
Comparison of Values of E_i, P_R, E_c, ρ, and χ_c for a Melt-Quenched Sample and for an Annealed Sample

sample	E_i, MV/cm	P_R, $\mu C/cm^2$	E_c, MV/cm	ρ, g/cm³	χ_c, %
melt-quenched sample	3.3	5.4	0.54	1.860	60
annealed sample[a]	3.7	7.4	0.54	1.904	80

[a] Annealed at 135 °C for 1 h prior to poling.

Conclusion

Poling gave rise to a decrease of absorption intensity of DANS and MNA dissolved in VDF–TrFE copolymer, a shift of its peak position, and a slight broadening of its width. These changes in the absorption spectra of DANS and MNA after removal of the poling field have been interpreted to assess the internal electric field E_i created by the alignment of the oriented crystallite dipoles in VDF–TrFE copolymer. E_i values were calculated from analysis of the differential spectrum before and after poling, using theoretical expressions for changes in the original spectrum. E_i is on the order of 10^6 V/cm, increases with increasing P_R, and achieves a value of 3.4–3.9 MV/cm when P_R is 6.1 $\mu C/cm^2$ at E_{max} = 1.15 MV/cm, while the coercive field E_c is at most 0.55 MV/cm.

In the process of thermal annealing after poling, E_i increases slightly in the vicinity of 80 °C and above this temperature gradually decreases until an abrupt decrease occurs near 135 °C corresponding to the total loss of polarization at the Curie temperature. A new absorption band arises upon poling, and its intensity increases when thermally annealed at higher temperature after poling. This new absorption band is ascribed to that of a protonated species of dye which implies that HF is generated upon poling and thermally dissociates into H^+ and F^-. The intensity ratio of the new band to that of the original band increases with increasing annealing temperature up to 80 °C but decreases above 80 °C, suggesting that the generated HF is lost from the sample film above 80 °C. The slight increase of E_i in the vicinity of 80 °C may be due to loss of ionic countercharges at crystal–amorphous interfaces. Increases of crystallinity give rise to increases of P_R and E_i.

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Registry No. DANS, 4584-57-0; MNA, 99-52-5; (vinylidene fluoride)(trifluoroethylene) (copolymer), 28960-88-5.