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Effects of dye doping on ferroelectricity in vinylidene fluoride and trifluoroethylene copolymers

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The effects of dye doping on ferroelectricity in vinylidene fluoride and trifluoroethylene copolymers have been investigated mainly through dielectric and switching measurements. Large dielectric relaxation, which cannot be explained by dipole fluctuations of individual chain molecules around their axes, was observed in the dye-doped copolymer films. With increasing dye content in copolymers, the relaxation times increase, and the dielectric relaxation strength becomes large. However, the switching times and the switching curve are nearly independent of dye content. These results can be explained if we assume that dye is doped into noncrystalline regions but not into crystalline regions, and forms a long and slender phase boundary in which the dye content is high.

1. Introduction

Ferroelectric polymer research began in 1980 [1, 2]. At that time, polyvinylidene fluoride attracted attention because of its high piezoelectricity [3, 4]. The fact that polymers exhibit ferroelectricity became widely known after it was observed in a copolymer of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) [5–7]. Since that breakthrough, research on ferroelectricity of polymers has been promoted because it is considered to be an important characteristic of polymers. Thus far, over one thousand papers have been published, and several hundred patent applications have been submitted [1, 2, 8]. Ferroelectricity is also important from the aspect of industrial applications of copolymer films such as their use as optical memory elements [8, 9]. As the coercive field of VDF/TrFE copolymers is extremely large (over 40 MV m^{-1}), it is necessary to fabricate them into thin films [10, 11] for use as optical memory elements.

To construct a multibit memory using ferroelectrics, the polarity of polarization at selected points on a medium has to be controlled [9]. In general, for writing and reading polarity we must control the temperature of films using laser power. For memory devices, the most important characteristics include recording density, writing and reading speed, and sensitivity [9]. In order to increase the read/write density and reduce the laser power required for writing and reading, dye can be doped into VDF/TrFE copolymer films in order to make the ferroelectric layer suitable for light absorption [9]. The physical parameter dependence of the optical memory characteristics must be examined if the films are intended for use as optical memory elements. In this paper, the effects of dye doping on the dielectric and switching characteristics of ferroelectric VDF/TrFE copolymers are examined.

2. Experimental procedure

The samples used were VDF/TrFE copolymers with the composition of 65/35 mol % Daikin Kogyo Co., Ltd, Japan; (abbreviated to VDF(65)/TrFE(35) copolymer). Films 0.5 μm thick were fabricated using a spin-coating technique [11]. A 3 wt % dimethylformamide solution with 5 wt % dye (Mitui Toatsu Dyes, Ltd, PA1006) was added dropwise on to one surface of a glass plate on which an aluminium electrode had been previously deposited. The chemical structure of the dye used here is shown in Fig. 1. The glass plate had been rinsed thoroughly. After spinning in a spin coater, a rectangular electrode ($4 \times 4\ \text{mm}^2$ in area) was deposited on the other surface of the glass plate. Before measurements, the sample was heat treated at 145 °C for 2 h in order to increase its crystallinity [10, 11].

The experimental equipment used to measure switching transients was described previously [11]. The complex permittivity was measured in the 10 mHz–1 MHz frequency range.

3. Results

Fig. 2 shows the frequency spectra of the complex permittivity $\varepsilon^* = \varepsilon' - j\varepsilon''$ for a VDF(65)/TrFE(35) copolymer sample doped with 5 wt % dye. At 100 °C, a large relaxation was observed. With decreasing temperature, the spectra shift to the low-frequency region. An attempt was made to reproduce the observed frequency spectra using the equation

$$\varepsilon^* = \varepsilon_{in} + \frac{\Delta\varepsilon_1}{(1 + j\omega\tau_1)^{\beta_1}} + \frac{\Delta\varepsilon_2}{(1 + j\omega\tau_2)^{\beta_2}} + \left(\frac{\sigma}{j\omega}\right)^{\gamma} \tag{1}$$

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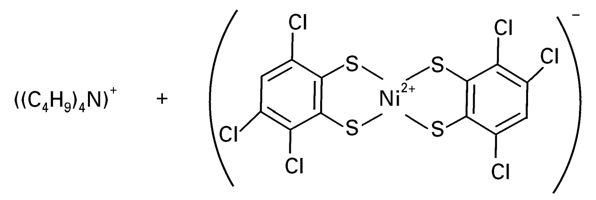

Figure 1 The Chemical structure of the dye.

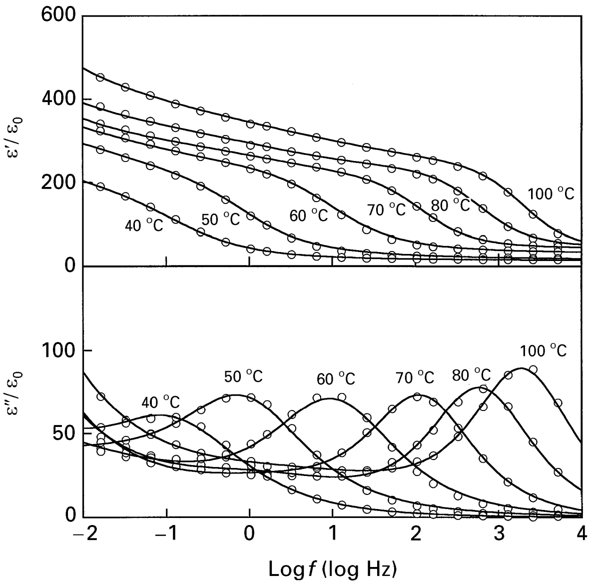

Figure 2 Frequency spectra (○) of the complex permittivity of 5 wt % dyed VDF/TrFE copolymer. (——) Calculated data.

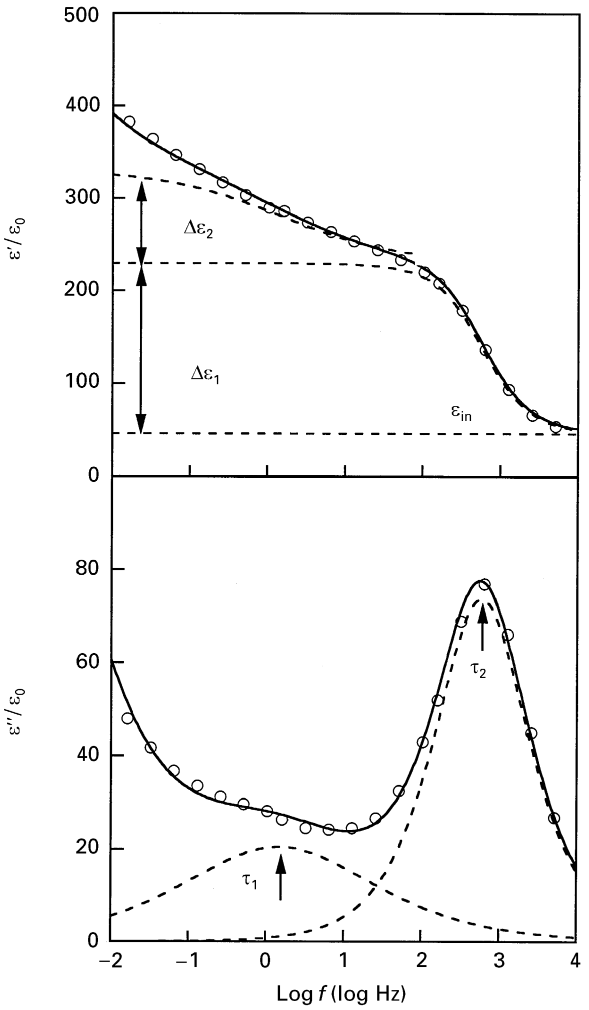

Figure 3 Comparison of (○) observed and (——) fitted frequency spectra of the permittivity at 80 °C of 5 wt % dyed VDF/TrFE copolymer.

where, ε_{in} is the instantaneous permittivity, $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ are dielectric relaxation strengths, τ_1 and τ_2 are relaxation times, σ is d.c. conductivity, β_1 and β_2 are parameters expressing the distribution of the relaxation times, and γ is a conductivity parameter. Subscript 1 corresponds to the relaxation process in the high-frequency region, and subscript 2 to the low-frequency relaxation process. Using the least squares method, the constants, ε_{in}, $\Delta\varepsilon_1$, $\Delta\varepsilon_2$, τ_1, τ_2, σ and γ in Equation 1 were determined. Fig. 3 shows a typical example of the results. The experimental data obtained at 80 °C, are shown to be reasonably well reproduced by Equation 1, represented by the solid lines. The dashed lines correspond to each term in Equation 1. The two relaxation processes must be included in Equation 1 because the increase of the spectra cannot be explained only in terms of the conductivity in the low-frequency region. In Fig. 2, the data calculated from Equation 1 at each temperature are also represented. Using the same method, the constants (for example, $\Delta\varepsilon_1$, $\Delta\varepsilon_2$, τ_1, τ_2 of VDF/TrFE copolymer with various dye doping concentrations) in Equation 1 can be determined. As a result, the transition map shown in Fig. 4 is obtained. The constants of the relaxation process in the low-frequency region cannot be ascertained, because the two relaxation processes cannot be separated at low temperature. It should be noted that the relaxation strength, $\Delta\varepsilon_1$, in the high-frequency region reaches over 250 with increasing dye content. The gradients of $\Delta\varepsilon_1$, $\Delta\varepsilon_2$, τ_1 and τ_2 against temperature change at the Curie point.

Typical results for the sample with 5 wt% dye doping under various values of applied field strength, E, ranging from 55–100 MV m^{-1} at 20 °C are shown in Fig. 5, where the electric displacement, D, and its derivative $\partial D/\partial \log t$ are plotted against the logarithm of time, t. The amount of reversed polarization is nearly independent of E. Switching times become faster with increasing applied field. Fig. 6 shows the results obtained at 20 °C and 82 MV m^{-1} with respect to the reverse direction and the forward direction to that of the reversed polarization which was created in a sample by applying the same field. The difference between the solid and dashed lines is due to the contribution from the switching process, because the contribution from the relaxation process and conductivity is common to both curves. It was also found that the shapes of switching curves of dyed VDF/TrFE copolymers are almost the same as the results of undyed VDF/TrFE copolymers shown in Fig. 6. In general, for ferroelectric polymers, the switching time, τ_s, is defined as the time at which $\partial D/\partial \log t$ becomes maximum [1, 2, 11]. Fig. 7 shows plots of $\log \tau_s$ of dyed and undyed VDF/TrFE copolymers against the

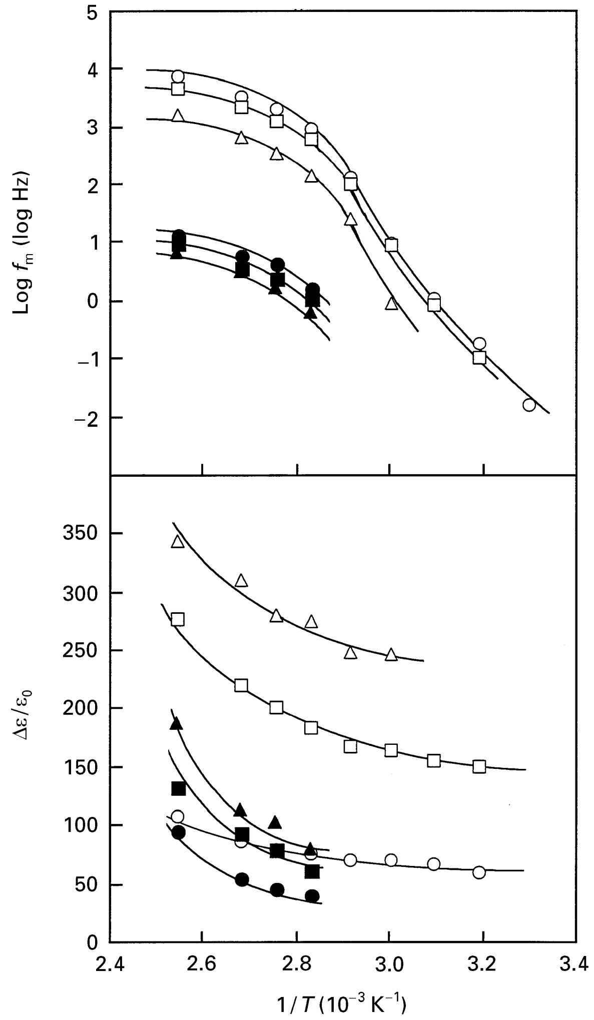

Figure 4 A transition map of VDF/TrFE copolymer doped with dye undergoing two relaxation processes. Dye content: (○, ●) 2%, (□, ■) 5%, (△, ▲) 10%. (●, ■, ▲) Low-frequency region, (○, □, △) high-frequency region.

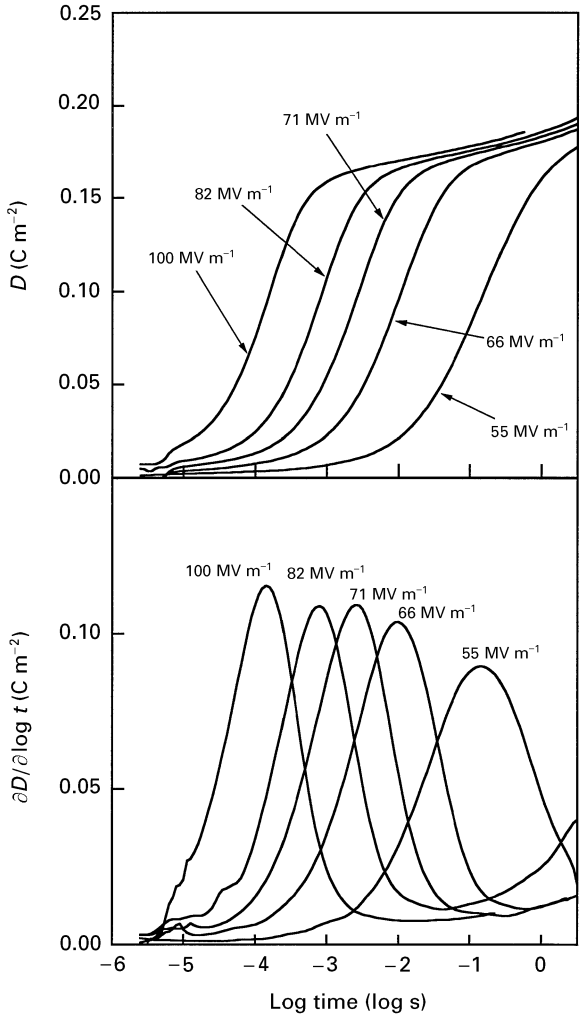

Figure 5 Typical switching characteristics of VDF/TrFE copolymer with 5 wt % dye doping plotted in terms of D and its derivative $\partial D/\partial \log t$ against $\log t$ at 20 °C.

inverse of the applied field. The linear relationship can be described by an exponential law [11]

$$\tau_s = \tau_{s0} \exp\left(\frac{E_a}{E}\right) \tag{2}$$

where, τ_{s0} is the switching time in an infinite field and E_a is the activation field. As described above, no difference could be found in switching characteristics between dyed and undyed VDF/TrFE copolymers.

4. Discussion

The relaxation strength of VDF/TrFE copolymer with 5 wt % dye doping in the high-frequency range is larger than 150. Such a large strength may arise from interfacial polarization which is caused by the accumulation of space charge at phase boundaries in composite materials. An expression can now be derived for complex permittivity, ε^*, assuming a two-phase system with spherical dispersions [12]. If the dielectric constant of a medium, ε_m, and that of spheroidal dispersions, ε_d, are unequal, and the volume fraction, q, of spheroidal dispersions is very small, the following equation is obtained.

$$(\varepsilon^* - \varepsilon_m) \Big/ \left[\varepsilon_m + \frac{(\varepsilon^* - \varepsilon_m)}{N}\right] = q(\varepsilon_d - \varepsilon_m) \Big/ \left[\varepsilon_m + \frac{(\varepsilon_d - \varepsilon_m)}{N}\right] \tag{3}$$

where N is a parameter related to the axial ratio of the spheroidal dispersions. When the dispersions are spherical, $N = 3$. Using $\varepsilon_m = \varepsilon_b + \sigma_b/j\omega$, $\varepsilon_d = \varepsilon_s + \sigma_s/j\omega$, the expression for ε^* can be obtained.

$$\varepsilon^* = \varepsilon_{in} + \frac{\Delta\varepsilon}{1 + j\omega\tau} + \frac{\sigma}{j\omega} \tag{4}$$

$$\varepsilon_{in} = \varepsilon_b\left(1 + \frac{NqA}{N\varepsilon_b + A}\right) \tag{5}$$

$$\Delta\varepsilon = Nq\left[\frac{A(A\sigma_b - B\varepsilon_b)}{(N\sigma_b + B)(N\varepsilon_b + A)} + \frac{B(B\varepsilon_b - A\sigma_b)}{(N\sigma_b + B)^2}\right] \tag{6}$$

$$\tau = \frac{N\varepsilon_b + A}{N\sigma_b + B} \tag{7}$$

$$\sigma = \sigma_b\left(1 + \frac{NqB}{N\sigma_b + B}\right) \tag{8}$$

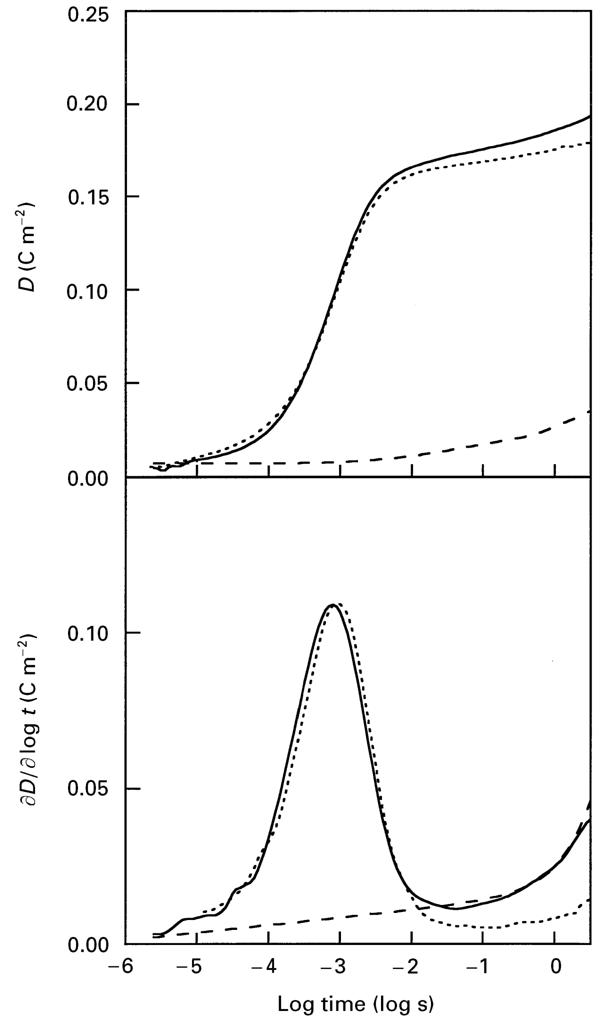

Figure 6 Plots of D and $\partial D/\partial \log t$ after the application of 82 MV m^{-1} to dyed VDF/TrFE copolymers in the (——) reverse and (- - -) forward directions and (···) undyed VDF/TrFE copolymers in the reverse direction. at 20 °C.

$$A = \varepsilon_s - \varepsilon_b \quad (9)$$

$$B = \sigma_s - \sigma_b \quad (10)$$

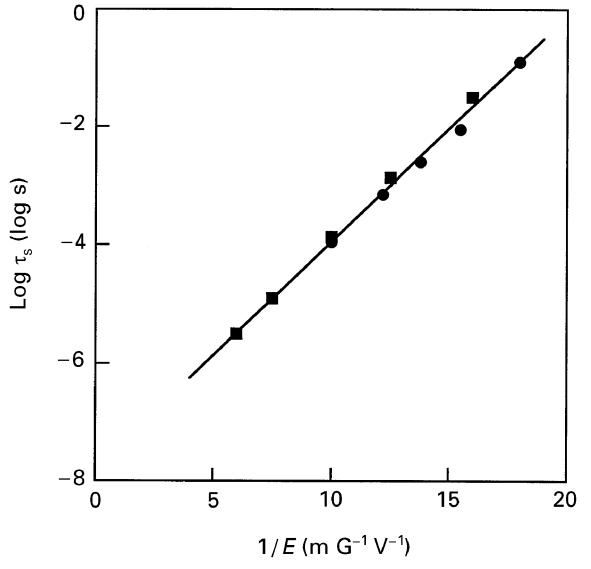

Figure 7 Plots of the logarithm of switching time, τ_s, against the reciprocal field. 1/E. (■) VDF/TrFE, (●) dyed VDF/TrFE.

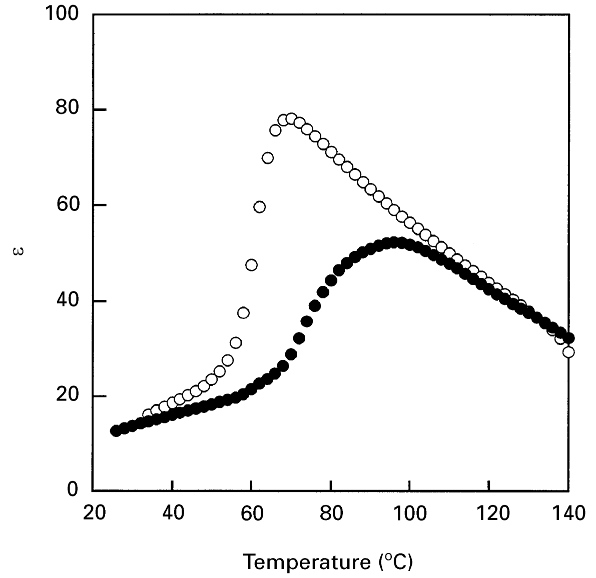

Figure 8 Temperature spectra of dielectric constant with ferroelectric transition on (○) cooling and (●) heating for VDF/TrFE copolymer.

Because of the high crystallinity and the lamellar structure of the crystalline regions of VDF/TrFE copolymer [10, 13], a two-phase system with spheroidal dispersions for non-crystalline regions can be considered [14]. On the other hand, the switching characteristics, for example, the shape of the switching curve and the switching time, are independent of the dye content. These results suggest that dye doping does not directly affect the crystalline region. On the basis of these results, we can speculate that dyed VDF/TrFE copolymer is an inhomogenous system consisting of a highly conductive phase, in which the dye content is high, dispersed in a less conductive matrix in which the dye content is low, because the conductivity of the dye [8], shown in Fig. 1, is larger than that of pure VDF/TrFE copolymer [1]. Based on these speculations, it is assumed that the dielectric constant of the medium is that of crystalline regions shown in Fig. 8 [15], and the dielectric constant, ε, of spheroidal dispersions is that of non-crystalline regions, which is almost constant above the glass point [15]. On the basis of these assumptions, using the least squares method, N can be obtained from the data shown in Fig. 4. As a result, a large $N \gg 3$ is obtained at each temperature. In other words, for the case of long spheroidal dispersions, N is much greater than 3. Consequently, it can be speculated that dye doping is distributed and extended along non-crystalline regions. This discrepancy indicates the need for future investigation on the effects of dye doping on a nanometre scale, such as in the interface layer between crystalline and non-crystalline regions.

5. Conclusion

VDF/TrFE copolymer with dye doping shows large dielectric relaxation which cannot be explained by dipole fluctuations of individual chain molecules around their axes, and switching characteristics the same as those of undyed VDF/TrFE copolymer. These results infer the existence of non-crystalline regions containing dye, and that the dye does not affect crystalline regions. Taking into consideration the structure of VDF/TrFE copolymer, it is assumed that dyed VDF/TrFE copolymer is an inhomogeneous system consisting of a highly conductive phase comprised of non-crystalline regions containing dye. This assumption of long spheroidal dispersions in the medium was found to enable explanation of the large relaxation.

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