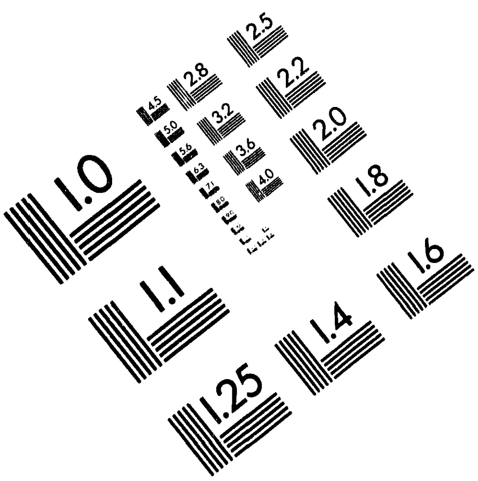

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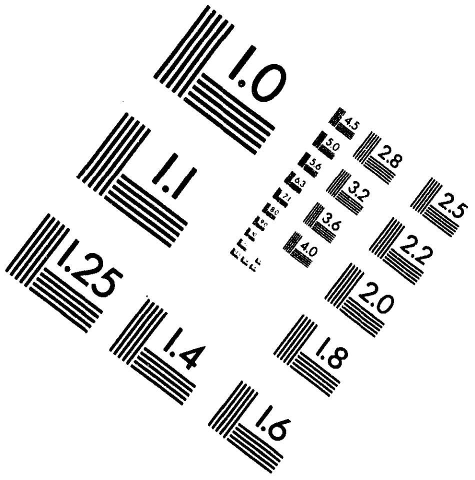

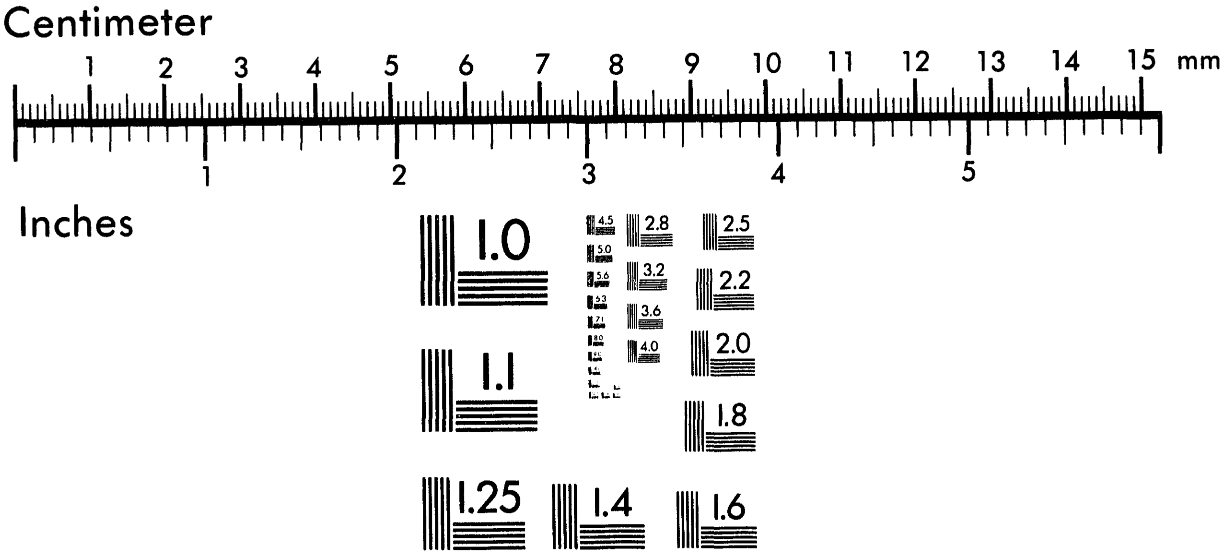

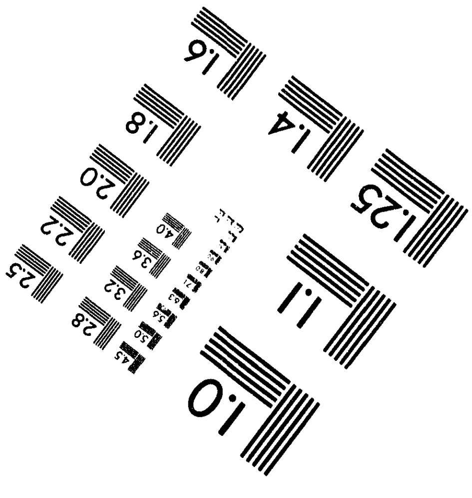

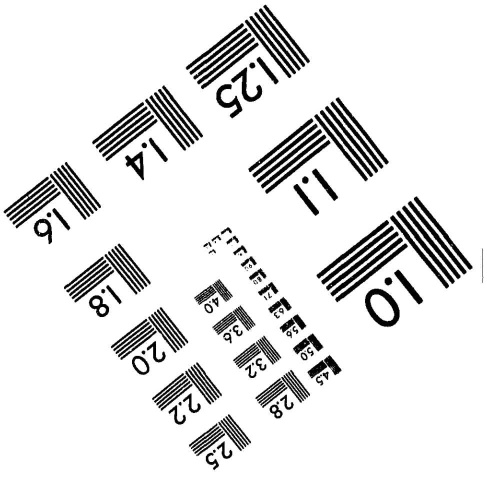

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THE ROLE OF HIGH PRESSURE IN THE STUDY AND APPLICATIONS OF THE FERROELECTRIC POLYMER POLYVINYLIDENE FLUORIDE AND ITS COPOLYMERS

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Abstract

The effects of frequency, temperature and hydrostatic pressure on the dielectric properties, molecular relaxations, and phase transitions of PVDF and a copolymer with 30 mol% trifluoroethylene will be discussed. Pressure causes large slowing down of the β molecular relaxations as well as large increases in the ferroelectric transition temperatures and melting points, but the magnitudes of the effects are different for the different "transitions." These effects can be understood in terms of pressure-induced hindrance of the molecular motions and/or reorientations. A unique application of these polymers as time-resolved dynamic stress gauges based on PVDF studies under very high pressure shock compression is discussed.

1. Introduction

The discovery of strong piezoelectricity in the polar linear polymer polyvinylidene fluoride, $[-CH_2-CF_2-]_n$ (or PVDF) and the subsequent findings of pyroelectricity and ferroelectricity in it opened an important and exciting chapter in the study and applications of these phenomena. PVDF has long been recognized for its chemical inertness, durability and desirable mechanical and insulating properties; however, it was the discovery of such phenomena in a material that can be produced in a flexible thin film form that made PVDF by far the most studied electrically-active polymer.

PVDF is a partially crystalline polymer which exhibits a variety of molecular conformations and crystal structures depending on the method of preparation [1]. The most common and most studied of these are the α phase which has a trans/gauche conformation and the β phase in which the conformation is the all-trans planar zigzag with the dipole moments perpendicular to the chain axis. It is the β phase which is the ferroelectric and most useful phase. Among ferroelectrics, β – PVDF has the unusual property that the forces responsible for the ordering of the dipoles in the ferroelectric phase are sufficiently strong that the polymer melts before it undergoes a ferroelectric-to-paraelectric phase transition. It has been found, however, that copolymers of VDF and trifluoroethylene (TrFE) with about 50-80 mol% VDF favor the β phase, and these copolymers exhibit ferroelectric transitions below the melting point (T_m) [1].

PVDF and its copolymers are useful in a variety of transducer and detector applications. One of the most unique of these applications is the use of these polymers as the active piezoelectric elements in self-powered, time-resolved, dynamic stress gauges for the

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study of shock-wave compression phenomena. Made of very thin (~ 25 μm thick) films, such gauges are nonintrusive and are ideal for many shock-wave applications [2]. A remarkable feature of the results is that the electrical output signal of properly-prepared gauges is a continuous function of shock pressure up to hundreds of kilobars. In addition to extending the direct pressure range of piezoelectric shock gauges by over an order of magnitude, this finding is truly remarkable since, at these high dynamic pressures, gauge temperatures can be expected to be well over 1000 K. These temperatures are, of course, well above the normal melting temperatures (~ 440 K) of PVDF and its copolymers. The shock results raise important questions about the mechanism responsible for the shock-induced electrical output from these polymers. Our static pressure studies were, in part, motivated by such questions.

We have investigated the combined effects of hydrostatic pressure, temperature and frequency on the dielectric properties, molecular relaxations and phase transitions (including melting) of PVDF and a copolymer with 70% VDF, P($VDF_{0.7}$ - $TrFE_{0.3}$). We have also investigated the piezoelectric response of PVDF under dynamic compression. The results have provided insights into the physics of the molecular motions and energy barriers which determine the above properties; additionally, they are important to the understanding of the use of these polymers as dynamic stress gauges. Space limitations do not allow us to discuss the results in detail here, and therefore we restrict this paper to a summary of the principal findings. Details and physical interpretation can be found elsewhere [1,3,4].

2. General Features in the Dielectric and Thermal Response

The β-relaxation process, ferroelectric-to-paraelectric (FE-PE) transition and melting of PVDF and P($VDF_{0.7}$ - $TrFE_{0.3}$) are easily discernible features in the dielectric and/or thermal responses of these polymers. Figure 1 shows the temperature (T) dependences of the real (ε') and imaginary (ε'') parts of the dielectric constant of the copolymer measured at 100 kHz and atmospheric pressure. Several of the features are similar to those of PVDF [1]. Between 240 K and 230 K, ε' exhibits a shoulder and ε'' a sharp peak. These features, which are strongly frequency dependent (as will be discussed below), are qualitatively similar to those observed in many polar polymers and are the signatures of the β-relaxation process (not to be confused with the β crystallographic phase). This process is associated with micro-Brownian dipolar motion in the amorphous regions of the copolymer. The rapid increases in both ε' and ε'' with increasing T starting at ~ 350 K are due to the approach of the FE→PE transition. We take the temperature at the peak in ε' at 390 K to be T_c. (This feature is missing in PVDF.) The value of T_c is independent of the measuring frequency for a given sample, but varies from sample to sample depending especially on the degree of poling [4]. On increasing T further, there is an additional $\varepsilon''(T)$ peak and a corresponding change in the $\varepsilon'(T)$ slope at ~ 415 K. These features are analogous to (but better defined) than those observed for PVDF [1] and most likely correspond to the α-relaxation process which involves molecular motion in crystalline regions of the polymer. At still higher temperatures there is a sharp minimum in both $\varepsilon'(T)$ and $\varepsilon''(T)$ at 424 K. This feature, which exhibits a weak frequency dependence [1], corresponds to the dynamic melting

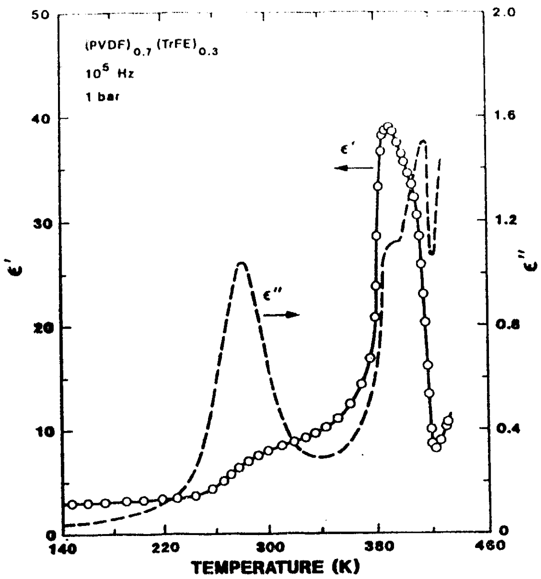

Fig. 1: Temperature dependence of the dielectric constants of the copolymer.

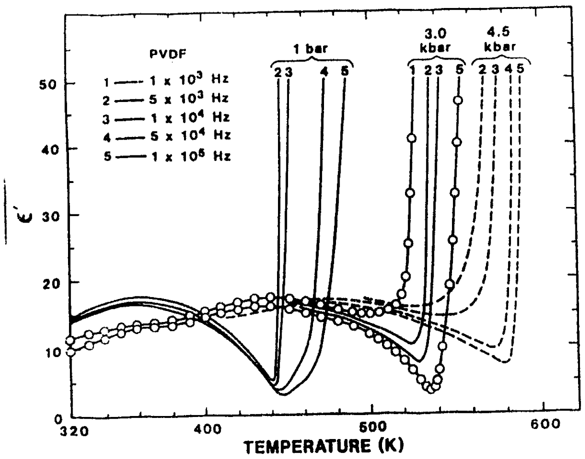

Fig. 2: Temperature dependence of the real part of the dielectric constant near the melting transition.

temperature (T_m) of the copolymer. Both T_c and T_m are clearly defined by well-resolved endothermic peaks in the differential-thermal-analysis spectra of these polymers.

3. The Melting Transition

Unlike crystalline solids, the melting points of these polymers depend on both the heating rate and the probe frequency. This reflects their partly amorphous (i.e., glassy) nature. The frequency dependence for PVDF is shown in Fig. 2, which also shows the variation of this dependence with pressure. Plotted is ε' versus T at different frequencies and pressures with emphasis on the behavior near melting. At any one pressure, the $\varepsilon'(T)$ minimum becomes deeper and shifts to higher temperature with increasing frequency. These are glass-like characteristics which emphasize the fact that the melting process in these polymers is a relaxational dynamic, not a static, phenomenon.

Figure 3 shows the pressure dependence of the melting point of the copolymer at 100 kHz. The initial slope is 53±2 K/kbar and the corresponding slope for PVDF is 29.5±1.5 K/kbar. Thus, whereas PVDF and the copolymer have nearly the same values for T_m (446 K vs. 420 K at 100 kHz), the pressure derivatives are markedly different. In particular the logarithmic derivatives $d\ln T_m/dP$ are 6.6 and 12.6 %/kbar, respectively. Clearly, the presence of TrFE molecules in PVDF strongly hinders the movement of polymer chains and segments which are necessary to disrupt the crystalline order on melting at high pressure, a fact that is undoubtedly related to the large size of the F atom.

4. The Ferroelectric Transition

The FE-PE transition temperatures of P(VDF-TrFE) copolymers increase with pressure [1]. Results for our 0.7/0.3 copolymer are shown in Fig. 3. At 1 bar $T_c = 389$ K, is independent of frequency, and its initial pressure derivative is $dT_c/dP = 30 \pm 2$ K/kbar, a value that is 23 K/kbar smaller than that of dT_m/dP. This results has an interesting implication with respect to PVDF. As already noted, β-PVDF is unusual in that it melts before it undergoes a FE-PE transition. The large difference between $T_c(P)$ and $T_m(P)$ for the copolymer noted above clearly indicates that the difference (T_m - T_c) increases rapidly with pressure (Fig. 3). It is reasonable to expect a qualitatively similar behavior for PVDF and its hypothetical T_c. Atmospheric pressure results on copolymers suggest that the hypothetical of T_c PVDF is 20 K higher than T_m. If the difference in the pressure derivatives of T_m and T_c of PVDF were even a fraction of that of the copolymer, then we would expect the $T_m(P)$ and $T_c(P)$ curves to cross at a modest pressure leading to T_c below T_m; i.e., we expect to observe a pressure-induced FE-PE transition in PVDF. Our highest pressure dielectric data are suggestive of the presence of such a transition, but more work is needed to confirm it.

5. The β-Relaxation Process

The β-relaxation process strongly influences the electrical and mechanical responses of these polymers. The dielectric signature of this relaxation for the present polymers is the classic one observed for other polar polymers (Fig. 1) and can be described by the methods used to treat relaxational phenomena in polymers, liquids and glasses [3,4]. With increasing frequency, the $\varepsilon'(T)$ and $\varepsilon''(T)$ curves shift to higher temperatures, and the magnitude of $\varepsilon''(T)$ peak increases. These are well known dipolar glass-like features characteristic of the freezing of dipolar motion in the absence of long-range correlations. With increasing pressure there is a large displacement of the $\varepsilon''(T)$ and $\varepsilon'(T)$ responses to higher temperatures. This effect is seen explicitly in Fig. 3 where we have plotted the shift with pressure of the $\varepsilon''(T)$ peak, T_{max} (≡ T_β), at 100 kHz.

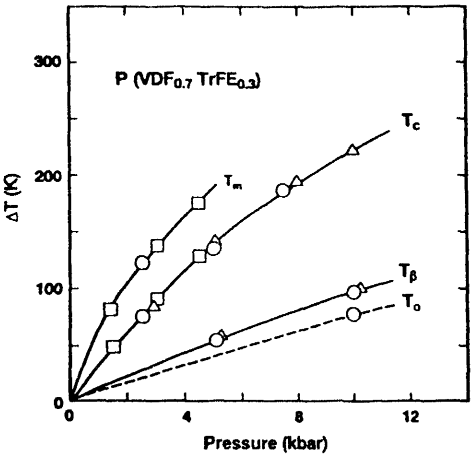

Fig. 3: Shifts of the various transition temperatures of the copolymer with pressure.

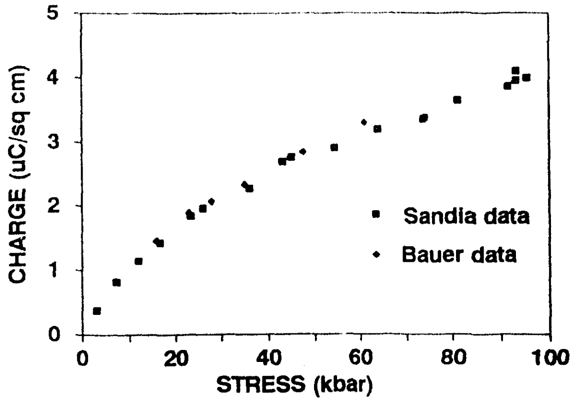

Fig. 4: Shock-induced polarization of PVDF.

The $T_{\max}(P)$ dependence is somewhat nonlinear, the average slope between 0 and 5 kbar being $dT_{\max}/dP = 10.0\pm0.5$ K/kbar. This result is qualitatively and quantitatively very similar to that for PVDF [3] demonstrating that the β-relaxation process is essentially independent of composition. The increase of $T_{\max}$ with pressure can be qualitatively understood in terms of closer packing of polymer chains and chain segments which hinders the motion and reorientation of dipolar groups in the amorphous phase. Thus, a higher temperature (and thereby a higher T_β) is required to induce this motion.

The $\varepsilon''(T,\omega)$ responses define relaxation frequencies, f, and characteristic relaxation times, $\tau = 1/\omega$, where ω is the angular frequency ($= 2\pi f$). We have analyzed and interpreted our results in terms of the Vogel-Fulcher equation [3,4]

$$\tau^{-1} \equiv \omega = \omega_0 \exp[- E/k\,(T_{\max} - T_0)],$$

where ω_0 is an attempt frequency related to the cut-off frequency of the distribution of relaxators, E is an activation energy and T_0 is a reference temperature where all relaxation times diverge (and where the distribution of τ's becomes infinitely broad). T_0 can thus be viewed as the "static" dipolar freezing temperature for the relaxation process.

Our analysis [3,4] has produced the first evaluation of the pressure dependences of T_0, E and ω_0 for any polymer. All three parameters increase with pressure (e.g., see $T_0(P)$ in Fig. 3). The results can be qualitatively understood in that pressure, by reducing the sample volume and available free volume, causes closer packing of PVDF chains and chain segments and hinders the motion of the dipolar groups responsible for the β relaxation. This hindrance is reflected by a higher energy barrier E and thereby by the need to go to higher temperature (and hence higher $T_{\max}$ and T_0) to overcome this higher barrier.

6. Piezoelectric Response Under Shock Compression

In the shock-compression work, high velocity, precisely controlled impacts of z-cut single crystals of quartz and sapphire upon PVDF backed with those same materials are used to determine peak pressures to an accuracy of about 0.5%. The impacting and target materials are stressed within their elastic limits. The electrical signals produced by the shock compression are recorded with high frequency digitizers and the resulting piezoelectric polarizations are determined to accuracy of a few percent. A summary of the data is shown in Fig. 4. The observed piezoelectric polarizations are found to be independent of loading path and show smooth variation with increasing pressure. Although the pressure dependence is nonlinear, the volume dependence of the observed polarizations is found to be approximately linear. Perhaps more critical from the point of view of the application of PVDF in shock gauges, no electrical anomalies or evidence of shock-induced phase changes are found in the dielectric properties; the behavior appears to be fully accounted for by piezoelectric polarization. These properties make PVDF a truly remarkable material with the ability to serve as a nanosecond, time-resolved pressure gauge whose pressure range is an order of magnitude higher than other piezoelectric gauges. Important to the success of this application was the development of a special poling technique which made available PVDF films with piezoelectric and dielectric properties reproducible to a few percent [5].

7. Concluding Remarks

As noted above and shown in Fig. 3 all "transition" temperatures increase with pressure. The initial slopes dT_x/dP (in K/kbar) are +53 ±4, +30 ±2, 11±1.5, and +8 for T_m, T_c, T_β and T_o, respectively. The corresponding logarithmic pressure derivatives $d\ln T_x/dP$ (in %/kbar) are 12.5, 7.8, 4.4 and 4.0, respectively. The magnitudes of these slopes increase in the order of the transition temperatures, i.e., $T_m(P) > T_c(P) > T_\beta(P) > T_o(P)$. This sequence can be rationalized as follows. We expect the process involving the motion and/or reorientation of the larger chain segments (i.e., melting) to be more strongly influenced by pressure than that involving the torsional/rotational motion of the crystalline dipoles attached to main chains (i.e., all trans to trans/gauche conformation changes at T_c), which in turn should be more strongly influenced than the process involving the motions/reorientations of small segments in the amorphous phase (i.e., the β relaxation). The logarithmic pressure derivatives for T_β, and T_o, which is the limiting (or "static") dipolar freezing temperature for the β relaxation, are comparable as expected because both temperatures describe the same process.

As seen in Fig. 3, the $T_x(P)$ responses are highly nonlinear. We have earlier shown [1] that this nonlinearity is largely a manifestation of the expected large decrease in the compressibility with increasing pressure. When plotted vs. change in volume the changes in T_x are essentially linear. The same is true of the shock-induced polarization in Fig. 4.

The strong increase in T_m with pressure and the relaxational responses provide a rational explanation for why it is possible to use these polymers as piezoelectric shock gauges to relatively high shock pressures and accompanying high temperatures [1].

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