Piezo- and pyroelectricity in polymer blends of poly(vinylidene fluoride)/poly(methyl methacrylate)

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Compatible polymer blends of poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA) can be used as suitable model systems for investigating the relationship between the physico-chemical structure of polymers and their piezo- and pyroelectric activity. The structure of PVDF/PMMA blends can be varied over a very wide range which can lead to a strong influence on the piezo- and pyroelectric activity and the corresponding coefficients d_{31} and g_3. The values of d_{31} and g_3 were found to vary over nearly five decades whereas the normalized coefficients d_{31}/P and g_3/P remain largely unaffected. This emphasizes the importance of the molecular processes causing the macroscopic polarization P during the poling procedure. For a given polarization P and a given temperature T the properties of the polymer matrix, however, are far less important for the values obtained for d_{31} and g_3. The experimental results were compared with theoretical predictions based on models which were recently developed by Tashiro *et al.*, Broadhurst *et al.* and by Mopsik *et al.*. Considering the appropriate scope of each model a good agreement between theory and experiment is observed and general contradictions have not been found.

(Keywords: piezoelectricity; pyroelectricity; morphology; orientation; models)

INTRODUCTION

The continued interest in poly(vinylidene fluoride) (PVDF) as a piezo- and pyroelectric material stems from the fact that it can be readily prepared in the form of thin flexible sheets. The transducers made from PVDF are characterized by a broad band behaviour, high voltage output, low acoustic impedance, high flexibility and toughness and ease of fabrication[1]. Many years ago it was reported[2] that partially crystalline PVDF can be made piezo- and pyroelectric either by thermal poling methods, in which a voltage is applied directly through metallic electrodes on both sides of the film, or by methods of corona poling, in which the non-metallized or one-sided metallized film is subjected to a corona discharge from a needle, at a distance of a few centimetres.

Considerable attention has been devoted over the last few years to the study of the dependence of the electrical properties of PVDF on the poling conditions and their relation in general to the structure of the polymer and also to the processing conditions. The aim of this study was to gain more thorough understanding of the origin of the piezo- and pyroelectricity and an optimization of the properties with respect to technical applications.

A characteristic feature of PVDF is that it is able to display at least five different crystal forms[3], including polar crystal modifications. PVDF normally crystallizes from the melt in a nonpolar so-called α-modification. When stretched, however, at temperatures below about 130°C the nonpolar crystals undergo a strain induced recrystallization, leading to polar crystals (β-modification).

The strong CF_2 dipoles (2.1 debye) perpendicular to the PVDF-chain are oriented in these β-crystals in such a manner that a net dipole moment of the unit cell results. This gives the single crystal a polarization of 0.132 C/m^2 if internal field corrections are not taken into account[4] and ~0.20 C/m^2 if these corrections are made[13,17,18]. The electrical properties of PVDF are strongly influenced by the nearly randomly oriented dipoles in the amorphous phase. The poling processes are believed to result mainly in a dipolar alignment, involving the orientation of the former randomly oriented dipoles within the polar crystals in the direction of the applied field. The alignment apparently does not occur by reorientation of whole crystals but by 60°-steps of the chain segments within the crystals[4,5].

Consequently, in those cases where the backbone of the chain has a component parallel to the field direction only an incomplete orientation can be achieved. This dipolar reorientation process resembles reorientational processes in a ferroelectric material[4].

The particular piezoelectric properties of inorganic ferroelectrics are usually attributed to the strain dependence of the crystal polarization. In the case of PVDF the total piezoelectrical response (d_{31}) of the macroscopic sample has, however, been found to be much larger than the intrinsic response of the polar PVDF crystals[6]. One could therefore conclude that the nonpolar amorphous regions in the material, which amount to about 50 vol%, also contribute to the electrical properties, either independently of the crystals or dependent on them via some coupling modes. A strain dependence of the total polarization P can arise, for instance, because of differences in the strain dependence between the dielectric constants of the amorphous ε_a and crystalline ε_c regions (electrostrictive contribution). This contribution will be enlarged by the difference in the

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elastic compliances of the amorphous S_a and crystalline S_c regions as in the temperature range above the glass transition temperature T_g[6]. An additional contribution stems from a change in thickness of the polar film which is characterized by the Poisson ratio m. Furthermore there are indications[7] that a third phase (the interphase between amorphous and the crystalline regions) may also play a major role in determining the overall piezo- and pyroelectrical properties of PVDF. There is also experimental evidence in the literature that real charges, which may be injected into the polymeric film during the poling process may also contribute to the piezoelectric response of a polymer. Here the distribution of the charges within the samples is important. The distribution will be dependent on the heterogeneity of the sample structure.

It has become apparent that the piezo- and pyroelectric properties of PVDF may depend, in a very complex way, on the molecular and supermolecular structure as well as on the mechanical and electrical properties of the crystalline and amorphous regions. The particular parameters which depend on the structure and the properties of the phases will be the macroscopic polarization P as well as the normalized piezo- and pyroelectric coefficients d_{31}/P, g_3/P which correspond to the electrical response at a given polarization. By studying the polarization as well as the piezo- and pyroelectrical response of PVDF films as a function of the structure and the properties of the different phases one should be able to develop an understanding of the origin of the characteristic electrical properties of PVDF and other organic materials.

The main disadvantage with PVDF is, however, that it readily crystallizes. This prevents major changes in the degree of crystallinity that is obtainable. Furthermore, the properties of the amorphous phase cannot be varied appreciably, with the exception of those properties which are dependent on the orientation of the chains in the amorphous region, resulting from a uniaxial or biaxial drawing of the films. We therefore decided to study the structural dependence of pyro- and piezoelectric properties not only for films prepared from pure PVDF but also for films prepared from blends of PVDF with a chemically different polymer. In the case of long chain molecules the compatibility of two chemically different species is the exception rather than the rule. Atactic PMMA, however, has been reported to be compatible with PVDF at least within a limited temperature range in the molten state at all concentrations[8,9]. Thus one is able to obtain a homogeneous mixture of the two components in the molten state. It is characterized by an intimate mixing of the molecules on a molecular scale. Based on this state three different structures can be induced in thin films.

Structure I (unoriented partially crystalline films)

If the melt is slowly cooled down to temperatures below the melting temperature of PVDF crystals, pure PVDF crystals will grow within an amorphous matrix, containing both PVDF and PMMA. These films contain different amounts of polar and nonpolar crystals. The electrical and mechanical properties of the amorphous regions (and possibly also of the interface regions) vary strongly as a function of the PMMA concentration in these regions. The PMMA concentration was varied between 0 and 40 wt%.

Structure II (oriented partially crystalline films)

Oriented films were obtained by stretching non-oriented films at elevated temperatures. Due to stretching originally non-polar crystals (α-modification) are transformed into polar crystals (β-modification). One thus obtains films which contain various amounts of polar crystals, depending on the concentration of the non-crystallizable atactic PMMA. Furthermore, these films are characterized by amorphous regions having different electrical and mechanical properties. Again the PMMA concentration was varied between 0 and 40 wt%.

Structure III (amorphous films)

The molten homogeneous blends were quenched down to room temperature. Glassy amorphous films were obtained in this case provided that the PMMA concentration exceeded about 40 wt%. The structure of these films is thus characterized by a homogeneous distribution of PVDF and PMMA chain segments, as has become apparent from studies on concentration fluctuations[10] and from the observation that they exhibit a single glass transition temperature which is intermediate between the glass transition temperatures of the pure components[8,9].

The investigations carried out on these three different kinds of films were concerned with eludicating:

(1) the dependence of the macroscopic polarization on the structure and composition of the films which is induced in electric fields

(2) the dependence of the piezo- and pyroelectrical properties of these films again as a function of the structure and composition at given polarizations.

EXPERIMENTAL

Thin films of thickness ~40 μm were prepared from pure PVDF (Solvay X8N) and blends of PVDF with atactic PMMA (Röhm 8N). The polymers were melt blended at 200°C and films were then prepared by melt extrusion. These films were found to be optically clear, homogeneous and isotropic. Oriented partially crystalline films were produced by uniaxial drawing at a temperature of about 85°C, the draw ratio being between 3.3 and 4. The aim of this process was to obtain as high an orientation as possible and a total conversion of the nonpolar α-crystals into polar crystals of the β-modification. Films having a 1000 Å thick aluminium electrode on one side were corona charged for about 10 min by applying an electric field of 1.5 MV/cm. The second electrode was deposited on the other side of the film 24 h after the corona charging.

The piezoelectric coefficient d_{31} was determined by applying an alternating mechanical stress at a frequency of 15 Hz (using a dynamical mechanical spectrometer) in the 1-direction (draw direction) and by monitoring the resulting current density generated by the sample in the 3-direction (normal axis of the film).

The pyroelectric coefficient was obtained by subjecting the sample to several heating and cooling cycles employing a rate of 2°C/min, while again monitoring the resulting current density generated by the sample. The total polarization of the sample due to the corona poling was determined by measuring the total thermally stimulated discharge current as the temperature was raised rapidly above the melting temperature of the PVDF crystals.

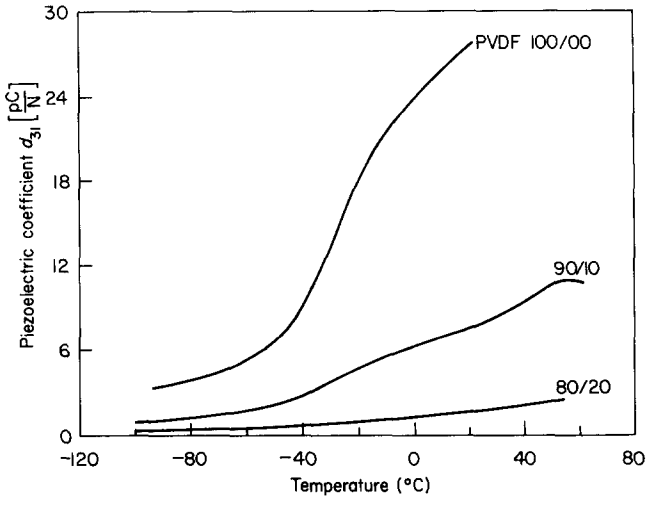

Figure 1 Temperature dependence of the piezoelectric coefficient d_{31} for uniaxially stretched PVDF and PVDF/PMMA blends containing 10 wt% and 20 wt% PMMA

RESULTS

Piezo- and pyroelectric coefficients d_{31} *and* g_3

The piezo- and pyroelectric coefficients d_{31} and g_3 were determined as a function of the temperature for oriented samples of pure PVDF as well as for oriented samples of PMMA/PVDF blends containing 10, 20 and 40 wt% PMMA. The results are displayed for PVDF and two blends in *Figures 1* and *2*. In the case of pure PVDF the two coefficients were found to increase strongly with increasing temperature above the glass transition temperature in agreement with previous reports in the literature[11]. This increase is much smaller in the blends. In addition the absolute values of the coefficients d_{31} and g_3 at all temperatures are drastically reduced as the concentration of PMMA is increased. This result is quite surprising, since i.r. and X-ray investigations have revealed that the concentration of polar crystals is only slightly reduced in these blends as compared with pure PVDF and that the total morphology also is not much influenced by the addition of PMMA[12]. *Figure 3* displays this strong dependence of d_{31} and g_3 on the composition of the blends for two different temperatures, namely 20°C and −100°C. The two coefficients d_{31} and g_3 were found to decrease by several orders of magnitude as the concentration of PMMA went from 0 to 40 wt%. By shifting the experimental curves obtained for d_{31} and g_3 along the ordinate a master curve may be constructed that characterizes the dependence of the pyro- and piezoelectrical response on the PMMA concentration for all temperatures.

It is clear from these results that d_{31} and g_3 do not only depend on the concentration of polar crystals but are strongly governed by the electrical and mechanical properties of the amorphous phase and possibly also of the interfaces between the amorphous and crystalline regions.

The values obtained for d_{31} and g_3 for the non-oriented partially crystalline films, as well as for the purely amorphous films with various amounts of PMMA, are much smaller than the corresponding values of the oriented samples. They were found to vary between 0.1 pC/N and 1 pC/N and between -0.05 nC/cm^2 K and -0.15 nC/cm^2 K for d_{31} and g_3 respectively for films with structure II whereas for the amorphous films d_{31} varied between 10^{-3} pC/N and 0.1 pC/N and g_3 between -4×10^{-3} nC/cm^2 K and -26×10^{-3} nC/cm^2 K respectively.

Relation between d_{31} *and* g_3

d_{31} and g_3 were thus found to decrease very strongly with increasing concentration of PMMA in a very similar fashion. This suggests that one should look for a possible

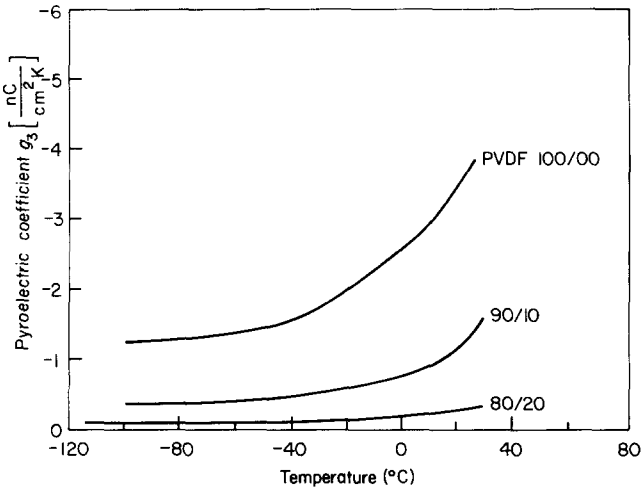

Figure 2 Temperature dependence of the pyroelectric coefficient g_3 for uniaxially stretched PVDF and PVDF/PMMA blends containing 10 wt% and 20 wt% PMMA

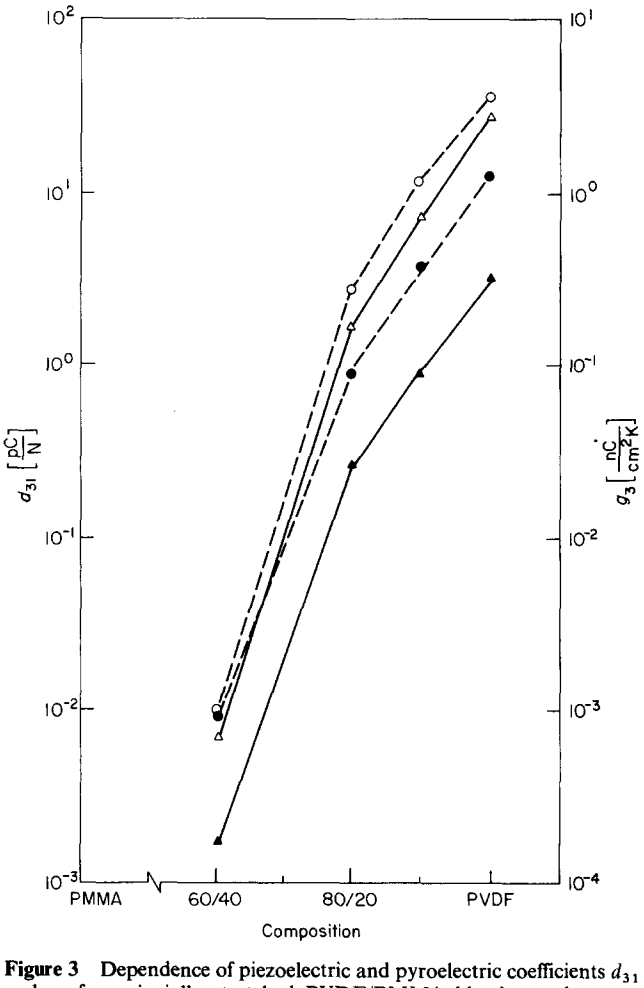

Figure 3 Dependence of piezoelectric and pyroelectric coefficients d_{31} and g_3 for uniaxially stretched PVDF/PMMA blends on the composition (solid lines: piezoelectric coefficient d_{31} at 20°C (△) and at −100°C (▲), broken lines: pyroelectric coefficient g_3 at 20°C (○) and at −100°C (●))

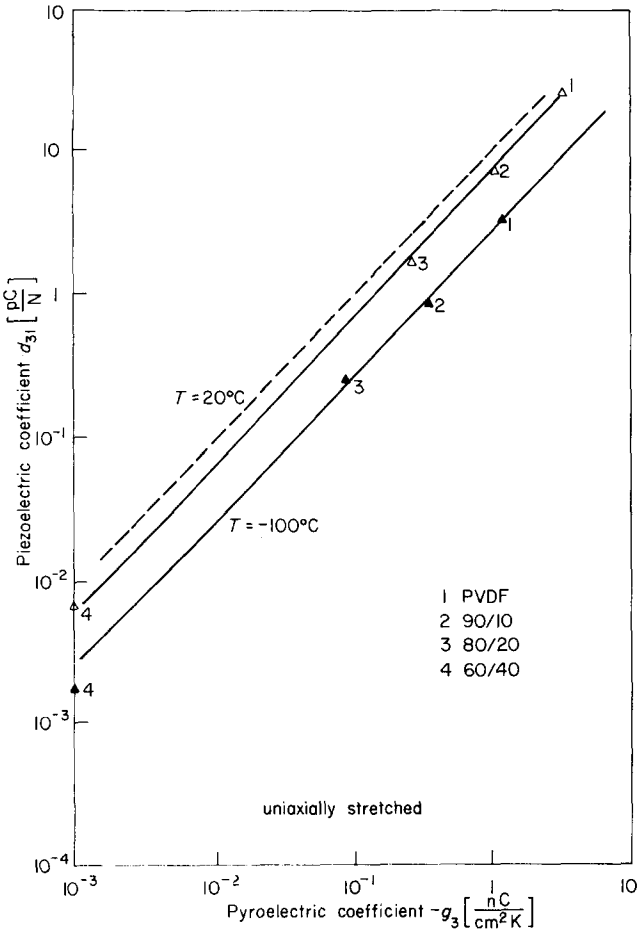

Figure 4 Relationship between piezoelectricity and pyroelectricity for stretched PVDF/PMMA blends at two different temperatures. The 45° line (broken line) is extrapolated from the ratio S/α_a of pure PVDF at 20°C

relationship between g_3 and d_{31}. *Figure 4* displays a plot of d_{31} *versus* g_3 for the oriented samples as a function of the PMMA concentration. It is quite clear that for a particular temperature a linear relation exists between the two coefficients for all concentrations of PMMA. In addition this relationship also seems to hold for different temperatures. The temperature influences only the absolute values of the coefficients d_{31} and g_3 at constant composition. The characteristic ratio of d_{31}/g_3 turns out to be about 7.9×10^{-3} cm² K/N at room temperature. The strong correlation between d_{31} and g_3 indicates an equivalence of mechanically and thermally induced deformations as far as the electrical properties are concerned[13]. Considering the compliance S and the thermal coefficient of volume expansion for comparison one calculates for pure PVDF a characteristic ratio of $S/\alpha_s = 7.6\times10^{-3}$ cm² K/N using the values $S=3.2\times10^{-6}$ cm²/N and $\alpha_s=4.2\times10^{-4}$ K^{-1}. The data for isotropic samples were used since the corresponding values for the oriented samples were not available. With decreasing temperature the compliance will decrease faster than the thermal coefficient of volume expansion and the ratio $S/\alpha s$ becomes about 4×10^{-3} cm² K/N at -100°C. When the temperature is lowered to -100°C the 45° lines in *Figure 4* were shifted parallel in a similar manner according to the ratio $d_{31}/(-g_2)=2.6\times10^{-3}$ cm² K/N.

Structure dependence of the macroscopic polarization

Based on the observation of hysteresis between the poling field and the dipole orientation, PVDF has been proposed to be ferroelectric[4]. However, no Curie temperature has been found for PVDF so far. A distribution of Curie temperatures corresponding to the actual morphological parameters such as lamellae thickness distribution or crystal perfection seems to be a more realistic approach. Thus a broad distribution of depolarization effects is always observed[12]. Furthermore, the depolarization behaviour of poled PVDF depends strongly upon its thermal and electrical history.

It has been suggested[14] that β-PVDF might be a ferroelastic rather than a ferroelectric material, the argument being that the dipole–dipole energy which causes spontaneous polarization in a ferroelectric is weak compared with the crystal energy.

Thus the variation of morphological parameters, resulting from blending PVDF with PMMA, should affect those processes involved during poling in a characteristic manner thus providing more information about these unsolved mechanisms.

The macroscopic polarization which is induced at constant poling conditions can be expected to depend on the composition of the blends as well as on their morphological structure. It should depend on the different volume fractions of polar crystals and on differences in the mechanical and electrical properties of the amorphous regions. We therefore investigated the dependence of the macroscopic polarization on the composition of the material, for oriented as well as unoriented amorphous and partially crystalline samples. The results are displayed in *Table 1*.

The polarization was found to depend strongly on the composition. In the case of the oriented samples it decays by several orders of magnitude as the concentration of PMMA is raised from 0 to 40 wt%. The partially crystalline non-oriented samples are characterized by a polarization in the range between 0.06 and 0.26 μC cm^{-2} whereas the amorphous samples exhibit an upper limit of the polarization in the range of 0.06 μC cm^{-2}. The last two samples are thus characterized by a polarization which is of the same order of magnitude as the one observed in oriented samples, containing polar PVDF crystals, provided that the PMMA concentration is in the range between 30 and 40 wt%. This again indicates that the existence of polar crystals is a necessary requirement in order to achieve a high polarization as well as large coefficients of d_{31} and g_3 but that the existence of the amorphous phase clearly plays a major role in determining the overall piezo- and pyroelectric response of the material.

The basic origin of the strong influence of the amorphous phase on the electrical performance is still an unsolved problem. In principle, the decrease of the polarization may arise from morphological as well as from mechanical and electrical effects.

Table 1 Dependence of macroscopic polarization P of uniaxially stretched PVDF/PMMA blends on their composition after poling under identical conditions (see text)

Sample		P (μC cm^{-2})
PVDF	100/0	4.620
PVDF/PMMA	90/10	1.920
PVDF/PMMA	80/20	0.483
PVDF/PMMA	60/40	0.0088

It is, for instance, conceivable that the addition of PMMA alters the structure of the amorphous phase and also possibly the interface in such a way that the rotation of chain elements carrying the dipoles in the crystalline regions is prevented or at least strongly hindered. Furthermore it seems possible that due to the particular electrical properties of PMMA (e.g. low dielectric constant) the effective poling field across the crystalline regions is reduced in comparison with that in pure PVDF. Finally in analogy to the poling process occurring in ferroelectrical materials one might assume that the motion of 'domain walls' across the crystals, which controls the reorientation of the dipoles in the crystals, is hindered due to structural defects. These arise from the presence of PMMA in the amorphous regions and at the interfaces.

Thus in order to understand the influence of the amorphous phase on the properties one has to study the structure and the molecular dynamics in the amorphous regions in more detail. Dielectric relaxation studies[12] indicated, for instance, that the amorphous regions in partially crystalline blends may not be characterized by a homogeneous intimate mixing of the two components but rather by a partial phase separation. Part of our current research[12] is concerned with elucidating the structure and dynamic properties of the amorphous phase and of the interface in PMMA/PVDF blends.

Furthermore, it has to be mentioned that the films studied in this paper have a nearly homogeneous distribution of the polarization across the film thickness as highlighted by ultrasonic step pulse measurements[15]. Without this homogeneous distribution the discussion of piezo- and pyroelectric properties would be very complicated. Also we do not go into detail as far as the crystal shape is concerned. There might be a slight difference due to some shape effects between the crystal polarization and the polarization P which is observed macroscopically.

Comparison with theoretical models

In order to gain additional information on the origin of the pyro- and piezoelectric properties of PVDF and PVDF/PMMA blends it is instructive and indeed tempting to try to interpret the data obtained so far in terms of those models which have been devised to explain the pyro- and piezoelectrical properties of pure PVDF. We will consider in particular the models that have been put forward by Broadhurst *et al.*[13] and by Tashiro *et al.*[6]. These models differ with respect to the basic assumption on the morphological structure of the material.

Piezoelectricity and the Tashiro model. Tashiro *et al.* assumed for instance that the structure of highly oriented partially crystalline PVDF, containing polar crystals, can best be represented in terms of a model consisting of a series of spherical rigid polar crystalline regions and soft, nonpolar amorphous regions in the direction 1 (i.e. in the direction in which the stress is applied). They showed that in this case the intrinsic piezoelectricity of the polar crystalline regions contributes only negligibly ($d_{31}=0.03$ pC/N at 20°C) to the macroscopic coefficient d_{31}.

According to Tashiro *et al.* d_{31} is determined mainly by differences in mechanical and electrical properties of the amorphous and crystalline regions and their concentration, on the one hand, and on the macroscopic polarization P on the other. This becomes evident from their equation for d_{31}:

$$\frac{d_{31}}{P}=\frac{3\varepsilon_a}{2\varepsilon_a+\varepsilon_c}\cdot\frac{X(1-X)}{Y_1^a}\cdot\left(\frac{\varepsilon_c}{2\varepsilon_a+\varepsilon_c}\cdot\frac{K_{31}^a}{\varepsilon_a}+m_{31}\right) \quad (1)$$

where X is the degree of crystallinity, and Y_1^a the Young's modulus of the amorphous phase in the 1-direction. The electrostriction constant K_{31} is given by $K_{31}^a=d\varepsilon_a/d\sigma_1$, σ_1 being the macroscopic stress applied in the 1-axis and ε_a the dielectric constant of the amorphous phase. The dielectric constant of the crystals is ε_c and the Poisson ratio m_{31} is given by $m_{31}=-(1/t)\,(dt/d\sigma_1)$ where t represents the film thickness. *Table 2* shows actual values used in equation (1).

At temperatures below the glass transition temperature this expression may be further simplified, since electrostrictive contributions become negligible[16] in this temperature range and since the dielectric constants of the glass and the crystal are approximately equal:

$$\frac{d_{31}}{P}=\frac{X(1-X)}{Y_1^a}m_{31} \quad (2)$$

It becomes apparent from these equations that one can separate the influence of the total polarization P and the influence of differences in properties of the amorphous and crystalline regions on the coefficient d_{31} by investigating the normalized coefficient d_{31}/P as a function of the structure as well as of the composition of the films studied. The experimentally determined dependence of d_{31}/P is presented in *Figure 5*. These values are about twice as large as the values calculated on the basis of equations (1) and (2). This is not surprising in view of the

Table 2 Experimental values used in equation (1) and equation (2) for calculating the normalized piezoelectric coefficients d_{31}/P for partially crystalline PVDF/PMMA blends (uniaxially stretched) at 20°C and at −100°C

Composition	PVDF	90/10	80/20	60/40	Reference
$T=20$°C					
m_{31}	0.7	0.6	0.5	0.4	(12, 16)
X	0.5	0.4	0.3	0.2	(12)
ε_a	22	15	10	5	(6, 12)
Y_1^a (GPa)	1.3	1.4	1.4	1.7	(12)
		$\varepsilon_c=2.5$			(12)
		$K_{31}^a/\varepsilon_a=2$			(6)
$T=-100$°C					
m_{31}	0.4	0.4	0.4	0.4	(12, 16)
X	0.5	0.4	0.3	0.3	(12)
Y_1^a (GPa)	5	5	5	5	(8, 12)
			$\varepsilon_c=\varepsilon_a=2.2$		(12)

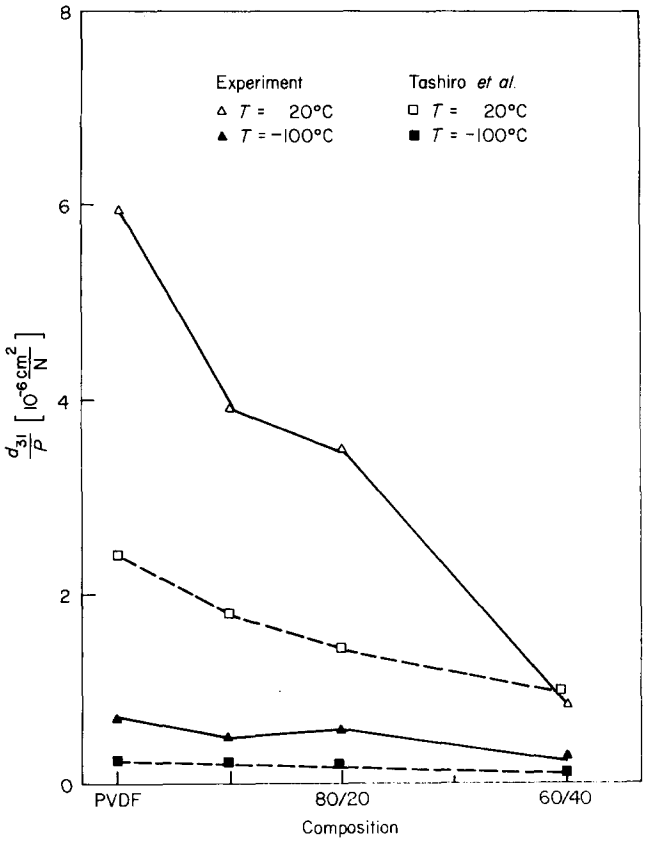

Figure 5 Dependence of normalized piezoelectric coefficient d_{31}/P on the composition at 20°C and at −100°C (solid lines: experimental values, broken lines: calculated from the model of Tashiro *et al.*)

fact that the experimental values particularly of ε_a and K^a_{31} reported in the literature[6,13,16] scatter appreciably. The important conclusion to be drawn from the results shown in *Figure 5* is that the main contribution to the strong decay of d_{31} with increasing concentration of PMMA originates from the strong drop of the polarization P. For the highly oriented samples the normalized piezoelectric coefficient d_{31}/P changes only by a factor of less than 10 as the concentration of PMMA is increased, whereas at the same time d_{31} changes by several orders of magnitude (*Table 4*). In the case of non-oriented structures, crystalline structures and for the purely amorphous structure it is observed that d_{31}/P is nominally constant as a function of the composition whereas d_{31} still changes considerably. In this case it is the macroscopic polarization which exclusively governs the piezoelectric response.

Pyroelectricity and the Broadhurst model. The model of Tashiro *et al.*, which we have successfully applied not only to oriented samples of pure PVDF but also to oriented partially crystalline samples of PVDF/PMMA blends in order to account for piezoelectric properties, has not been devised for the piezoelectric response of isotropic samples nor for the pyroelectric response of either oriented or unoriented samples. In this case the model proposed by Broadhurst *et al.*[13] is more appropriate.

Broadhurst *et al.* assumed that the structure of PVDF can be represented in terms of a model, consisting of lamellae-like crystals having a random distribution within an amorphous surrounding. Contributions to the piezo- and pyroelectrical response come from electrostrictive effects, dipole fluctuations as well as dimensional changes of the whole sample occurring as a result of either an applied stress or of being thermally induced. Based on these assumptions, Broadhurst *et al.* derived the following expression for the coefficient g_3 for the case of no charge compensation[13]:

$$\frac{g_3}{P} = -\alpha_c\left[\frac{\varepsilon_c - 1}{3} + \frac{1}{2}\phi_0^2\left(\gamma + \frac{1}{2T\alpha_c}\right) + \frac{\partial(\ln t)}{\partial(\ln v_c)}\right] \quad (3)$$

where α_c is the thermal coefficient of volume expansion of the crystals, ϕ_0 is the average amplitude of librations (frequency ω) for a dipole about the extended molecular axis and $\gamma = -\ln\omega/\ln v_c$ is the Grüneisen coefficient with v_c being the specific volume of the crystalline phase. T is the absolute temperature, t is the sample thickness and ε_c the dielectric constant of the crystals. The values used for these material parameters for calculating g_3/P from equation (3) are shown in *Table 3*.

Again g_3 is determined on the one hand by the macroscopic polarization of the sample, and on the other by properties of the amorphous and crystalline phase. The absolute value of g_3, obtained from the expression, will naturally depend on the particular choice of the parameters ϕ_0 and γ representing the crystal phase properties which are only approximately known. Nevertheless one can assume, disregarding the absolute values, that these values will not depend strongly on the composition. *Figure 6* shows a plot of g_3/P *versus* composition. It is clear that g_3/P is approximately independent of the structure and the composition of the various films which have been studied so far. The pyroelectric response is thus almost totally determined by the polarization which can be induced by poling. This holds for the isotropic as well

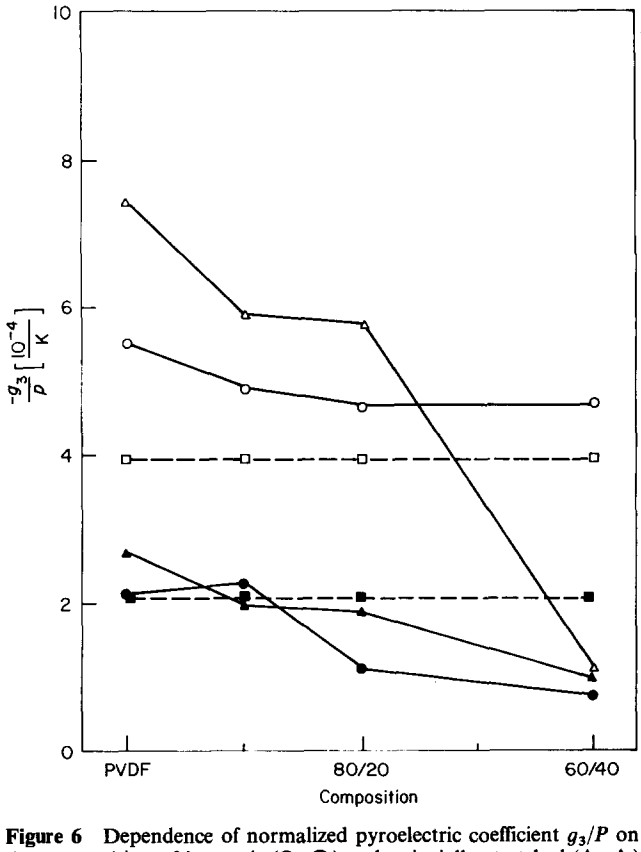

Figure 6 Dependence of normalized pyroelectric coefficient g_3/P on the composition of isotropic (○, ●) and uniaxially stretched (△, ▲) samples at 20°C (○, △) and at −100°C (●, ▲); (solid lines: experimental values, broken lines: calculated from the model of Broadhurst *et al.*)

Table 3 Experimental values used in equation (3) for calculating the normalized pyroelectric coefficients g_3/P for isotropic as well as for uniaxially stretched PVDF/PMMA blends at 20°C and at −100°C

	Reference
$T=20°C$	
$\alpha_c=1.7\times10^{-4}\ K^{-1}$	(20)
$\alpha_a=4.2\times10^{-4}\ K^{-1}$	(20)
$\gamma=5$	(18)
$\phi_0=16°$	(18)
$\varepsilon_c=2.5$	(12)
$T=-100°C$	
$\alpha_c=1.7\times10^{-4}\ K^{-1}$	(20)
$\alpha_a=\alpha_c$	
$\gamma=3.4$*	
$\phi_0=12°$**	
$\varepsilon_c=2.2$	(12)

* Calculated from $\gamma=5$ at 20°C with the assumption that γ has for PVDF a similar temperature dependence as in the case of polyethylene with $d\gamma/dT\approx80\alpha_c$ [18]

** Derived from $\phi_0=16°$ at 20°C under the condition that $\phi_0^2(-100°C)\approx0.6\phi_0^2(20°C)$ can be assumed to be valid for PVDF as it is for polyethylene[19]

as the anisotropic materials (*Table 4*). The ratio g_3/P turns out to be (1 to 7)$\times10^{-4}$ K^{-1} at 20°C in good agreement with the values calculated on the basis of equation (3) i.e. $4\times10^{-4}\ K^{-1}$. This equation holds at all temperatures below as well as above the glass transition temperature, if the appropriate values for $\partial(\ln t)/\partial(\ln v_c)$, and ϕ_0^2 were chosen.

Amorphous samples. The models of Tashiro *et al.* and Broadhurst *et al.* discussed above were based on the assumption that the materials have a two phase structure consisting of polar crystal regions and amorphous regions. In order to account for the electrical properties of a purely amorphous material, one has to consider a one phase model. For amorphous material, one can use an expression derived by Mopsik and Broadhurst[17] for the hydrostatic piezoelectric coefficient d_h:

$$\frac{d_h}{P}=-\kappa\left[\frac{\varepsilon_\infty}{3}-(\varepsilon_\infty+2)\frac{D}{v^2}\right]+\frac{J_1(\phi_0)}{J_0(\phi_0)}\frac{\partial\phi_0}{\partial p} \qquad (4)$$

where ε_∞ is the optical dielectric constant, p is the pressure, κ the volume compressibility and D a material constant which corrects the Clausius–Mosotti equation. $J_0(\phi_0)$ and $J_1(\phi_0)$ are Bessel functions of the first kind and of zero and first order. Mopsik and Broadhurst concluded that in the case of constant-temperature variable-pressure experiments the terms in D as well as the terms containing the dipole fluctuation angle ϕ_0 are small enough to be neglected. With these assumptions equation (4) can be further simplified and transformed for isotropic materials into an expression for the piezoelectric coefficient d_{31}:

$$d_{31}/P=\kappa\varepsilon_\infty/9 \qquad (5)$$

where the volume compressibility κ is expected to depend only weakly on the chemical composition of the polymers as well as on the composition of amorphous materials in the case of blends. The corresponding values for PVDF and PMMA are 2.39×10^{-10} and 2.44×10^{-10} m^2/N. We assume an average value of 2.41×10^{-10} m^2/N for the blends. Taking the optical dielectric coefficient ε_∞ as 2.2 we obtain $d_{31}/P=0.6\times10^{-10}$ m^2/N for the amorphous PVDF/PMMA blends independent of their composition. This calculated value is very close to the experimentally determined values which vary between 0.5×10^{-10} and 1.45×10^{-10} m^2/N.

CONCLUSIONS

The main conclusions which can be drawn from experimental results discussed above are:

The normalized piezo- and pyroelectrical activities d_{31}/P and g_3/P are only weakly dependent on the morphology of blends of PMMA and PVDF, that is on the degree of crystallinity, on the crystal modification as well as on the properties of the amorphous regions. Only in the case of oriented partially crystalline films did we observe that the normalized piezoelectric activity decreased with increasing concentration of PMMA and consequently with decreasing concentration of polar crystals (*Table 4*).

The magnitude of the piezoelectric and of the pyroelectric coefficients d_{31} and g_3 are to a first approximation determined by the total polarization which may be induced in the films. It was found that the total polarization depends, at constant poling conditions, very strongly not only on the concentration of polar crystals but also on the composition of the blends studied. The achievable polarization decreased by several orders of magnitude as the concentration of PMMA was increased from 0 to 40 wt%. This marked decrease in the polarization has to be attributed to a cooperative interaction of amorphous and crystalline regions with the applied electric field.

Table 4 Comparison between the experimentally determined values of the piezo- and pyroelectric coefficients d_{31} and g_3 and the normalized values d_{31}/P and g_3/P in films exhibiting three different structures ($T=20°C$)

	Structure I (nonoriented, partially crystalline)	Structure II (oriented, partially crystalline	Structure III (amorphous)
$d_{31}\left(\frac{pC}{N}\right)$	0.1 to 1	1.7 to 27	(0.3 to 35)$\times10^{-3}$
$d_{31}/P\left(10^{-6}\frac{cm^2}{N}\right)$	0.5 to 1.5	1 to 6	0.5 to 1.5
$-g_3\left(\frac{nC}{cm^2\,K}\right)$	0.05 to 0.15	0.3 to 3.4	5×10^{-3}
$-g_3/P\left(\frac{10^{-4}}{K}\right)$	5	1 to 7	5 to 15

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