suggested by Daoud and Jannink.[4]

Assuming that the simple relations $\Gamma^* = a^*\tau^{-0.88}$ and $\Gamma^{**} = a^{**}\tau^{0.0167}$ hold for the respective crossover lines, where a^* and a^{**} are numerical constants, we display the calculated values of Γ^* and Γ^{**} by the dashed lines in Figure 7. The values of a^* and a^{**} are selected to be 2.50×10^{-3} and 0.397, fitting the measured values in the experimental range of τ, respectively. Above $\tau\Theta = 5$ °C the measured values of Γ^* deviate from the calculated line Γ^* and have almost a constant value. This fact may reveal that the temperature range is not in the vicinity of the Θ temperature. In the range $0 < \tau\Theta < 1$ °C the measured value of Γ^* deviates downward from the calculated curve and falls on the vertical line separating a dilute tricritical regime and a concentrated regime.

Conclusions

By choosing relatively low molecular weight poly(methyl acrylate) samples, we determined definitely the crossover between the dilute and semidilute regimes and the crossover between the semidilute and concentrated regimes in two-dimensional space in the vicinity of the Θ temperature from surface pressure measurements. For each regime we have tested the theoretical predictions of Daoud and Jannink and obtained good agreement between experimental data and theoretical predictions for the temperature dependency. However, the molecular weight dependency is not in agreement with the theoretical predictions. Finally, we have constructed a temperature–concentration diagram of PMA monolayer using the experimental results. However, we could not confirm the existence of the concentrated regime.

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Estimating the Limiting Values of the Macroscopic Piezoelectric Constants of Poly(vinylidene fluoride) Form I

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ABSTRACT: Limiting values of the macroscopic piezoelectric constants of poly(vinylidene fluoride) form I have been estimated: $d^{M}_{31} = 144.9$ pC/N, $d^{M}_{32} = 16.7$ pC/N, $d^{M}_{33} = -186.3$ pC/N, $e^{M}_{31} = 161.1$ mC/m^2, $e^{M}_{32} = 17.8$ mC/m^2, and $e^{M}_{33} = -202.5$ mC/m^2. The calculated values of $d^{M}_{31} = 145$ pC/N and electromechanical coupling constant $k^{M}_{31} = 63\%$ are comparable to those of piezoelectric inorganic materials such as Rochelle salt, PZT ($PbTiO_3/PbZrO_3$), and $BaTiO_3$ ceramics. An essential point in approaching the limiting values in the actual experiment is found to be how the degree of orientation of crystalline dipole along the electric field is increased during the poling process.

In a previous paper,[1] we discussed the origin of the piezoelectric effect in poly(vinylidene fluoride) (PVDF) form I from the molecular-theoretical point of view and estimated the role that the intrinsic piezoelectric effect of the crystalline region plays in the macroscopic piezoelectric effect. We proposed in that paper[1] that it is not an inherent piezoelectricity of the crystal but an electric and mechanical coupling between the polar crystal and nonpolar amorphous matrix that governs the essential features of the macroscopic piezoelectric phenomena. Such an idea of piezoelectric mechanism lead us to a good reproduction of the experimental values of the macroscopic piezoelectric constants as well as to an overall interpretation of the piezoelectric phenomena commonly observed for PVDF form I samples (e.g., the piezoelectric constant d^{M}_{31} is proportional to such factors as the content of polar form I crystal, the degree of dipole orientation along the electric field, the electrostriction constant, etc., and it also shows a large temperature dependence).[1]

The second important problem concerning the piezoelectricity of this polymer involves estimating the limiting values of the macroscopic piezoelectric constants. In the mechanical cases of ultrahigh-modulus polyethylene[2] and aromatic polyamides (Kevlar etc.),[3] the crystallite modulus or the Young's modulus of the crystalline region along the chain axis has supplied an important guiding measure as a limiting case for the production of polymer materials with much higher modulus. Similarly, an evaluation of limiting piezoelectric constants will give us a significant measure for the industrial production of effective piezoelectric polymer films. It may be also important in clarifying the situation of PVDF sample among a large number of piezoelectric materials. It should be noted here that, different from the case of Young's modulus, we need to estimate the limiting piezoelectric constants by taking into account the coupling effect of both the amorphous and crystalline phases and not simply the piezoelectric effect originating from the crystalline phase.

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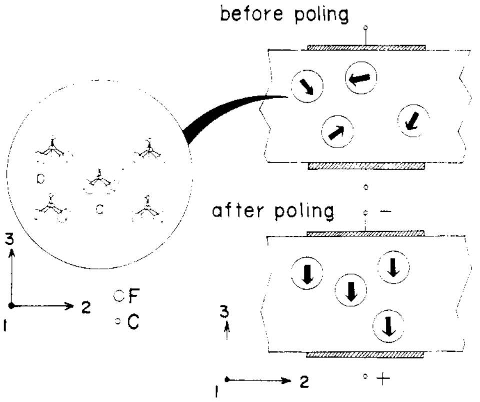

Figure 1. Composite model and poling process of poly(vinylidene fluoride) form I sample.

Modified Equations for Macroscopic Piezoelectric Constants

In the previous paper[1] we utilized a composite model where the spherical particles of polar crystal form I are embedded within the noncrystalline and nonpiezoelectric matrix as shown in Figure 1. Here the coordinate axes fixed on the film are defined as follows: the 1 axis is parallel to the draw direction, the 3 axis is normal to the film plane, and the 2 axis is perpendicular to the 1 and 3 axes. Broadhurst et al.[12] calculated the piezoelectric constant $d^{\mathrm{M}}_{\mathrm{p}}$ for the hydrostatic pressure ($d^{\mathrm{M}}_{\mathrm{p}} = \partial P_{\mathrm{s}}/\partial P$, where P_{s} is the polarization and P is the pressure) based on a model of thin lamellar crystals embedded in the amorphous phase. However, their model cannot explain the electrostriction effect, one important factor governing the macroscopic piezoelectricity of PVDF form I sample. Odajima et al. measured the crystallite sizes of PVDF form I by X-ray diffraction;[13] the crystal has almost equal sizes both along the chain direction and along the directions normal to the chain axis (80–100 Å). Thus it may be reasonable to employ here the spherical charge model for PVDF crystallites. In the previous paper,[1] starting from the definition of, e.g.

$$e^{\mathrm{M}}_{31} = \frac{1}{A}\left(\frac{\partial Q_{\mathrm{e}}}{\partial \sigma^{\mathrm{M}}_{1}}\right)_{E=0}$$

where Q_{e} is the charge on the electrode on the film surface, A is the area of the electrode, and σ^{M}_{1} is the macroscopic tensile strain, we derived the equations for the macroscopic piezoelectric stress constants e^{M}_{31} and e^{M}_{33}. In more general fashion, e^{M}_{3j} (j = 1–3) is written as

$$e^{\mathrm{M}}_{3j} = P^{\mathrm{M}}_{\mathrm{s}}\left(\frac{\epsilon^{\mathrm{c}}}{2\epsilon^{\mathrm{a}} + \epsilon^{\mathrm{c}}}\frac{\kappa^{\mathrm{a}}_{3j}}{\epsilon^{\mathrm{a}}} + m^{\mathrm{M}}_{3j} + \frac{1}{V}\frac{\partial V}{\partial \sigma^{\mathrm{M}}_{j}}\right) + \frac{3\epsilon^{\mathrm{a}}}{2\epsilon^{\mathrm{a}} + \epsilon^{\mathrm{c}}}\phi\frac{\partial P_{\mathrm{s}}}{\partial \sigma^{\mathrm{M}}_{j}} \quad (1)$$

The notations of the parameters are essentially the same as in the previous paper;[1] the superscripts a, c, and M denote the amorphous, crystalline, and macroscopic quantities, respectively. ϵ is the dielectric constant, ϕ is the volume fraction of particles, m^{M}_{3j} is the macroscopic Poisson ratio, and V is the volume of a crystalline particle. $P^{\mathrm{M}}_{\mathrm{s}}$, the macroscopic polarization along the 3 axis, and P_{s}, the spontaneous polarization of a particle, are given respectively by

$$P^{\mathrm{M}}_{\mathrm{s}} = \frac{3\epsilon^{\mathrm{a}}}{2\epsilon^{\mathrm{a}} + \epsilon^{\mathrm{c}}}\phi P_{\mathrm{s}} \quad (2)$$

$$P_{\mathrm{s}} = \chi P^{0}_{\mathrm{s}} \quad (3)$$

Here P^{0}_{s} is the intrinsic polarization of the crystal and assumed to be reduced by χ due to the incomplete dipole orientation along the 3 axis. κ_{3j} is the electrostriction constant; κ^{c}_{3j} of the crystal is neglected in an approximation because of its small value compared with that of κ^{a}_{3j}. σ^{M}_{j} is the macroscopic strain and only the tensile components of j = 1–3 are taken into account for the e^{M}_{3j} with j = 1–3 because the shearing components (j = 4–6) are blocked out of the tensile ones in the case of stretched and poled film.

In calculating the numerical values of the piezoelectric stress and strain constants, e^{M}_{3j} and d^{M}_{3j}, we need to rewrite the terms $\partial V/\partial \sigma^{\mathrm{M}}_{j}$ and $\partial P_{\mathrm{s}}/\partial \sigma^{\mathrm{M}}_{j}$ in eq 1 in more concrete fashion. In the previous paper,[1] using only the relation between σ^{M}_{j} (j = 1–3) and f^{M}_{1}, the tensile stress along the 1 axis, we estimated d^{M}_{31} and d^{M}_{33}. However, such a treatment was only an approximation since our aim at that time was to clarify the essential features of piezoelectricity by using equations as simple as possible. In order to provide a more rigorous treatment, we must consider all of the components of f^{M}_{j} and σ^{M}_{j} for such an anisotropic system as PVDF film. Then the terms $\partial V/\partial \sigma^{\mathrm{M}}_{j}$ and $\partial P_{\mathrm{s}}/\partial \sigma^{\mathrm{M}}_{j}$ will be developed as follows, with some modification from those reported previously.[1]

(a) $\partial P_{\mathrm{s}}/\partial \sigma^{\mathrm{M}}_{j}$: as in eq 28 of the previous paper,[1] $\partial P_{\mathrm{s}}/\partial \sigma^{\mathrm{M}}_{j}$ is expressed as

$$\frac{\partial P_{\mathrm{s}}}{\partial \sigma^{\mathrm{M}}_{j}} = \sum_{k=1}^{6}\frac{\partial P_{\mathrm{s}}}{\partial \sigma^{\mathrm{c}}_{k}}\frac{\partial \sigma^{\mathrm{c}}_{k}}{\partial \sigma^{\mathrm{M}}_{j}} = \sum_{k=1}^{3}\chi e^{\mathrm{c}}_{3k}\frac{\partial \sigma^{\mathrm{c}}_{k}}{\partial \sigma^{\mathrm{M}}_{j}} \quad (4)$$

where e^{c}_{3k} is the piezoelectric stress constant of the crystalline phase. If we assume a mechanical series model of crystalline and amorphous phases, we may relate σ^{c}_{k} to σ^{M}_{j} as follows.

$$\text{macroscopic stress } \boldsymbol{f}^{\mathrm{M}} = \boldsymbol{c}^{\mathrm{M}}\boldsymbol{\sigma}^{\mathrm{M}} \quad (5)$$

$$\text{crystalline stress } \boldsymbol{f}^{\mathrm{c}} = \boldsymbol{f}^{\mathrm{M}} \quad (6)$$

Then

$$\boldsymbol{\sigma}^{\mathrm{c}} = \boldsymbol{s}^{\mathrm{c}}\boldsymbol{f}^{\mathrm{c}} = \boldsymbol{s}^{\mathrm{c}}\boldsymbol{f}^{\mathrm{M}} = \boldsymbol{s}^{\mathrm{c}}\boldsymbol{c}^{\mathrm{M}}\boldsymbol{\sigma}^{\mathrm{M}} \quad (7)$$

where $\boldsymbol{c}$ and $\boldsymbol{s}$ are elastic and compliance tensors, respectively. Using eq 7 and the relation of Poisson's ratio

$$m^{\mathrm{M}}_{pj} = -s^{\mathrm{M}}_{pj}/s^{\mathrm{M}}_{jj} = -\sigma^{\mathrm{M}}_{p}/\sigma^{\mathrm{M}}_{j} \quad (8)$$

we express σ^{c}_{k} as follows:

$$\sigma^{\mathrm{c}}_{k} = \sum_{i}\sum_{p}s^{\mathrm{c}}_{ki}c^{\mathrm{M}}_{ip}\sigma^{\mathrm{M}}_{p} = \sum_{i}\sum_{p}s^{\mathrm{c}}_{ki}c^{\mathrm{M}}_{ip}(-m^{\mathrm{M}}_{pj}\sigma^{\mathrm{M}}_{j}) = \sum_{i}s^{\mathrm{c}}_{ki}c^{\mathcal{M}}_{ij}\sigma^{\mathrm{M}}_{j} \quad (9)$$

where

$$c^{\mathcal{M}}_{ij} = -\sum_{p}c^{\mathrm{M}}_{ip}m^{\mathrm{M}}_{pj} \quad (10)$$

Therefore eq 4 is written as

$$\frac{\partial P_{\mathrm{s}}}{\partial \sigma^{\mathrm{M}}_{j}} = \chi\sum_{k}e^{\mathrm{c}}_{3k}\frac{\partial \sigma^{\mathrm{c}}_{k}}{\partial \sigma^{\mathrm{M}}_{j}} = \chi\sum_{k}e^{\mathrm{c}}_{3k}(\sum_{i}s^{\mathrm{c}}_{ki}c^{\mathcal{M}}_{ij}) = \chi\sum_{i}(\sum_{k}e^{\mathrm{c}}_{3k}s^{\mathrm{c}}_{ki})c^{\mathcal{M}}_{ij} = \chi\sum_{i}d^{\mathrm{c}}_{3i}c^{\mathcal{M}}_{ij} \quad (11)$$

Here d^{c}_{3i} is the piezoelectric strain constant of the crystalline phase.

(b) $(\partial V/\partial \sigma^{\mathrm{M}}_{j})/V$: Using eq 9 and the relation $\Delta V/V \approx \sigma^{\mathrm{c}}_{1} + \sigma^{\mathrm{c}}_{2} + \sigma^{\mathrm{c}}_{3}$, we obtain

$$\frac{1}{V}\frac{\partial V}{\partial \sigma^{\mathrm{M}}_{j}} = \frac{1}{V}\sum_{k}\frac{\partial V}{\partial \sigma^{\mathrm{c}}_{k}}\frac{\partial \sigma^{\mathrm{c}}_{k}}{\partial \sigma^{\mathrm{M}}_{j}} = \sum_{k}\left(\frac{1}{V}\frac{\partial V}{\partial \sigma^{\mathrm{c}}_{k}}\right)\frac{\partial \sigma^{\mathrm{c}}_{k}}{\partial \sigma^{\mathrm{M}}_{j}} = \sum_{k}\frac{\partial \sigma^{\mathrm{c}}_{k}}{\partial \sigma^{\mathrm{M}}_{j}} = \sum_{k}(\sum_{i}s^{\mathrm{c}}_{ki}c^{\mathcal{M}}_{ij}) = \sum_{i}(\sum_{k}s^{\mathrm{c}}_{ki})c^{\mathcal{M}}_{ij} = \sum_{i}\beta^{\mathrm{c}}_{i}c^{\mathcal{M}}_{ij} \quad (12)$$

Table I
Numerical Parameters Used in the Calculation of d^{M} and e^{M} [a]

Room Temperature

$m^{\mathrm{M}}_{31} = 0.7,^{b}$ $m^{\mathrm{M}}_{21} = 0.2,^{b}$ $m^{\mathrm{M}}_{23} = 0.2$ (assumed)
$Y^{\mathrm{M}}_{1} = 2.2$ GPa,[b] $Y^{\mathrm{M}}_{2} = 1.6$ GPa,[b] $Y^{\mathrm{M}}_{3} = 1.6$ GPa
$P^{0}_{\mathrm{s}} = 0.25$ C/m²,[a] $\chi = 0.2,^{c}$ $\epsilon^{a} = 34,^{c}$ $\epsilon^{c} = 3.4^{c}$
$\kappa^{\mathrm{a}}_{31}/\epsilon^{\mathrm{a}} = 2.0,^{c}$ $\kappa^{\mathrm{a}}_{32}/\epsilon^{\mathrm{a}} = -0.2,^{c}$ $\kappa^{\mathrm{a}}_{33}/\epsilon^{\mathrm{a}} = 0.4^{c}$

$$s^{\mathrm{M}} = \begin{bmatrix} 0.46 & -0.09 & -0.32 \\ -0.09 & 0.63 & -0.13 \\ -0.32 & -0.13 & 0.63 \end{bmatrix} \mathrm{GPa}^{-1\,d}, \quad c^{\mathrm{M}} = \begin{bmatrix} 3.97 & 1.02 & 2.22 \\ 1.02 & 1.93 & 0.91 \\ 2.22 & 0.91 & 2.92 \end{bmatrix} \mathrm{GPa}$$

Below T_{g}

$m^{\mathrm{M}}_{31} = 0.43,^{e}$ $m^{\mathrm{M}}_{21} = 0.3,^{e}$ $m^{\mathrm{M}}_{32} = 0.1$ (assumed)
$Y^{\mathrm{M}}_{1} = 10$ GPa,[c] $Y^{\mathrm{M}}_{2} = Y^{\mathrm{M}}_{3} = 7$ GPa[c]
$\epsilon^{\mathrm{a}} = \epsilon^{\mathrm{c}} = 3.4,^{c}$ $\kappa^{\mathrm{a}}_{3j}/\epsilon^{\mathrm{a}} = 0.0$ ($j = 1$–3)

$$s^{\mathrm{M}} = \begin{bmatrix} 0.10 & -0.03 & -0.04 \\ -0.03 & 0.14 & -0.02 \\ -0.04 & -0.02 & 0.14 \end{bmatrix} \mathrm{GPa}^{-1\,d}, \quad c^{\mathrm{M}} = \begin{bmatrix} 12.70 & 3.08 & 4.13 \\ 3.08 & 7.81 & 1.71 \\ 4.13 & 1.71 & 8.40 \end{bmatrix} \mathrm{GPa}$$

[a] The values of d^{c}_{3j}, e^{c}_{3j}, s^{c}_{ij}, and c^{c}_{ij} are from ref 1. As pointed out by Broadhurst et al.[12] the intrinsic polarization P^{0}_{s} is raised from 0.14 to 0.25 C/m² if one includes the enhancement of the vacuum moment by the reaction field of the solid surroundings. Thus, correspondingly, the piezoelectric constants d^{c} and e^{c} of the crystal should be raised by the ratio 0.25/0.14, neglecting the change in dielectric constant ϵ^{c} induced by an infinitesimal structural change by strain. [b] From the data of Tasaka and Miyata.[6] [c] From ref 1. [d] Calculated from the relation $s^{\mathrm{M}}_{ii} = 1/Y^{\mathrm{M}}_{i}$ and $s^{\mathrm{M}}_{ij} = -m^{\mathrm{M}}_{ij}s^{\mathrm{M}}_{jj}$. [e] Assumed from the data of Richardson and Ward for low-density polyethylene samples.[7]

Table II
Calculated d^{M} and e^{M} for PVDF Form I Film under Normal Conditions

parameter	obsd	calcd	% contribution to factors a–d			
			κ	m	ΔV	d^{c}, e^{c}
		Room Temperature				
d^{M}_{31}, pC/N	~20	25.3	5.4	87.9	−6.6	13.4
d^{M}_{32}, pC/N	~2	7.0	−8.8	96.2	8.7	3.8
d^{M}_{33}, pC/N	~−30	−35.4	1.7	88.6	−7.9	17.6
e^{M}_{31}, mC/m²	~40	28.7	11.9	87.8	0.8	−0.5
e^{M}_{32}, mC/m²	~3	7.2	−4.8	100.1	27.9	−23.2
e^{M}_{33}, mC/m²	~−48	−40.7	−1.7	88.5	−12.3	25.5
		Below T_{g}				
d^{M}_{31}, pC/N	~1	2.8	0.0	74.8	−27.7	52.9
d^{M}_{32}, pC/N	~1	0.8	0.0	51.2	81.4	−32.6
d^{M}_{33}, pC/N	~−8	−6.5	0.0	63.9	−33.3	69.4
e^{M}_{31}, mC/m²	~10	11.0	0.0	97.9	6.2	−4.1
e^{M}_{32}, mC/m²	~6	3.6	0.0	70.0	170.0	−140.0
e^{M}_{33}, mC/m²	~−40	−41.6	0.0	60.6	−36.8	76.2

where $\beta^{\mathrm{c}}_{i} = \sum_{k=1}^{3} s^{\mathrm{c}}_{ki}$ is a linear compressibility along the i axis of the crystal.

From eq 1, 11, and 12 we obtain the final result

$$e^{\mathrm{M}}_{3j} = P^{\mathrm{M}}_{\mathrm{s}}\left(\frac{\epsilon^{\mathrm{c}}}{2\epsilon^{\mathrm{a}} + \epsilon^{\mathrm{c}}} \frac{\kappa^{\mathrm{a}}_{3j}}{\epsilon^{\mathrm{a}}} + m^{\mathrm{M}}_{3j} + \sum_{i} \beta^{\mathrm{c}}_{i} c^{\mathrm{M}}_{ij} \right) + \frac{3\epsilon^{\mathrm{a}}}{2\epsilon^{\mathrm{a}} + \epsilon^{\mathrm{c}}} \phi \chi \sum_{i} d^{\mathrm{c}}_{3i} c^{\mathrm{M}}_{ij} \qquad (13)$$

The macroscopic piezoelectric strain constant d^{M}_{3j} can be expressed as

$$d^{\mathrm{M}}_{3j} = \sum_{i} e^{\mathrm{M}}_{3i} s^{\mathrm{M}}_{ij} \qquad (14)$$

As seen in eq 13 and 14 and as already pointed out in the previous paper, the piezoelectric constants e^{M}_{3j} and d^{M}_{3j} consist of two main parts: the first term represents the contribution of mechanical and electric coupling of the amorphous and crystalline phases to the macroscopic piezoelectric effect and the second term is from the intrinsic piezoelectric effect of the crystalline phase. The first term can be furthermore divided into three kinds of factors: (a) the electrostriction effect or the contribution of dielectric change caused by deformation of the film, (b) Poisson's ratio or the contribution of the change in sample thickness, and (c) the piezoelectric effect due to the volume change of the crystalline particle. In all, four kinds of factors [(a), (b), (c), and (d), the intrinsic piezoelectric effect of the crystal] are included in the macroscopic piezoelectric effect.

Calculation of Macroscopic Piezoelectric Constants for Normally Prepared PVDF Form I Film

Using eq 13 and 14, we will now try to estimate the values of d^{M}_{3j} and e^{M}_{3j} for PVDF form I film prepared under normal conditions. Some parameters are replaced by typical experimental values (Table I). d^{c}_{3j} and s^{c}_{ij} are theoretical values.[1] The calculated d^{M}_{3j} and e^{M}_{3j} at room temperature and below the glass transition temperature ($T_{\mathrm{g}} \approx -40$ °C) are compared with the observed values in Table II. The observed data vary from sample to sample, and so the experimental values in Table II provide only a measure for comparison with the theoretical ones. They are as a whole reproduced well by the present calculation for both d^{M}_{3j} and e^{M}_{3j}. In the right four columns in Table II are listed the percentages of contribution of the above-mentioned factors a–d. The largest and decisive contribution is from factor b (Poisson's ratio) for all d and

e constants, consistent with the discussion by Sussner,[4] Wada and Hayakawa,[5] and Tasaka and Miyata.[6] Below the glass transition point the contribution from the crystalline piezoelectric effect (factor d) becomes significant.[1]

Estimation of the Limiting Values of d^M and e^M

We now estimate the limiting maximal values of the piezoelectric constants. As described in the previous section, Poisson's ratio plays an overwhelmingly large and so essentially significant role in the macroscopic piezoelectric effect. Therefore it will be a good and acceptable approximation to estimate the limiting values by controlling the parameters directly relating to Poisson's ratio or the second term of eq 1 ($P^M{}_s m^M{}_{3j}$), i.e., $m^M{}_{3j}$, ϕ, χ, and Young's moduli $Y^M{}_i$.

(i) According to measurements by Tasaka and Miyata,[6] Poisson's ratio $m^M{}_{31}$ increases from 0.4 to 0.7 with a rise of rolling ratio from 100 to 400% of the original length of film and approaches a value of about 0.75–0.8 for a much higher rolling ratio. Poisson's ratio $m^M{}_{21}$ approaches the value of 0.1. These are comparable to the Poisson ratios of low-density polyethylene samples measured by Richardson and Ward.[7] Thus we assume here $m^M{}_{31} = 0.8$ and $m^M{}_{21} = m^M{}_{32} = 0.1$ as the limiting Poisson ratios of PVDF form I film.

(ii) The piezoelectric constant $d^M{}_{31}$, for example, is approximately proportional to the term $\phi(1 - \phi)$ as seen in eq 36 of the previous paper,[1] which is maximized at $\phi = 0.5$. [The maximal point at $\phi = 0.5$ can be reasonably understood from the physical point of view. In the range $\phi = 0$–1, $\phi = 1$ means that the sample is equivalent to the single crystal and then $d^M{}_{31}$ ($=d^c{}_{31}$) becomes negligibly small. $\phi = 0$ corresponds to the nonpolar sample and $d^M{}_{31} = 0$. That is to say, $d^M{}_{31}$ may become largest at the midpoint of $\phi = 0$–1.]

(iii) The degree of dipole orientation is, of course, largest at $\chi = 1$, corresponding to a completely parallel arrangement of CF_2 dipoles along the 3 axis (Figure 1).

(iv) In the process of numerical calculation of d^M and e^M for the various possible values of Young's moduli $Y^M{}_j$, we have found that $e^M{}_{3j}$ is almost independent of $Y^M{}_j$, while $d^M{}_{3j}$ is inversely proportional to $Y^M{}_j$. Thus the higher $d^M{}_{3j}$ is expected for the lower Young's modulus. The sample with the lower modulus is prepared by drawing at not so high a draw ratio. Such a sample, however, does not contain a large amount of polar form I crystals but rather contains an appreciable amount of nonpolar crystal form II, resulting in the reduction of the piezoelectric effect. In contrast, a high draw ratio produces almost pure form I film but the modulus is also increased.[8] In the present estimation, then, we adopt the values of Young's moduli for the sample rolled to about 400%, which is a point giving almost pure form I crystals and comparatively low moduli; $Y^M{}_1 = 2.2$ GPa and $Y^M{}_2 = Y^M{}_3 = 1.6$ GPa. It should be noted again that the Young's moduli have practically no influence on $e^M{}_{3j}$. Using the parameters thus selected, we calculated the limiting values of $d^M{}_{3j}$ and $e^M{}_{3j}$ as shown in Table III. The calculated values of $d^M{}_{31} = 145$ pC/N and the electromechanical coupling constant $k^M{}_{31} = 63\%$ are comparable to those of such piezoelectric inorganic materials as Rochelle salt, PZT, and $BaTiO_3$ ceramics:

	d, pC/N	k, %
PVDF form I	145	63
Rochelle salt	275	66
PZT	110	31
$BaTiO_3$	78	21

Table III
Calculated Limiting Values of d^M and e^M for PVDF Form I Sample

parameter	calcd value	% contribution to factors a–d κ	m	ΔV	d^c, e^c
$d^M{}_{31}$, pC/N	144.9	4.4	86.7	−6.1	14.8
$d^M{}_{32}$, pC/N	16.7	−12.7	96.8	27.5	−11.6
$d^M{}_{33}$, pC/N	−186.3	2.0	88.9	−8.0	16.9
$e^M{}_{31}$, mC/m^2	161.1	10.6	89.3	0.6	−0.4
$e^M{}_{32}$, mC/m^2	17.8	−10.1	101.0	55.6	−46.5
$e^M{}_{33}$, mC/m^2	−202.5	−1.8	88.8	−12.4	25.4

Fukada et al.[9] and Miyata et al.[10] developed the processing methods of simultaneous drawing and poling of the films and obtained a stable value of $d^M{}_{31} \approx 40$ pC/N, which may be the highest among the experimental values reported so far. It is about 28% of our predicted limiting value.

In the selection process of numerical values of parameters, we notice that parameters such as Poisson's ratio etc. may not be much improved over the present experimental values even if better methods of sample preparation are used. However, the degree of orientation of crystalline dipole χ may still be increased by about a factor of 5 over the value of 0.2 experimentally obtained at present. That is to say, we still have the possibility of increasing the piezoelectric constants by controlling the parallel array of CF_2 dipoles along the poling electric field. The methods developed by Fukada et al.[9] and Miyata et al.[10] may possibly be along this line.

The present calculation for the limiting values of d^M and e^M constants may be rather rough and should be assumed to be only preliminary because there remain several problems to be solved.

(i) Piezoelectricity of crystal: recently, the ferroelectricity of crystal form I has been clarified[11] and thus the spontaneous strain etc. originating from such a characteristic property must be positively taken into consideration in developing the equations of piezoelectricity. The electrostrictive effect of the crystal, neglected here, must also be included.

(ii) We treated here the several parameters as independent of each other. However, as pointed out above, the Young's modulus and the piezoelectric constant are in opposite tendency to each other. Therefore if we aim to produce a sample film having both a high modulus and high piezoelectric effect, as Ward et al.[8] have been trying, it may be necessary to carry out the so-called optimization of the modulus and piezoelectric constants: we start from a composite model of amorphous and crystalline phases with a concrete and known morphology, express the modulus and piezoelectric constants as a function of the degree of orientation of the lamellae, for example, and then find out the optimal condition for these constants. The details will be reported in the future.

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References and Notes

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Dielectric and NMR Relaxation of Poly(methyl vinyl ketone) in Dilute Solution

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ABSTRACT: Complex permittivities of poly(methyl vinyl ketone) in dioxane solution were measured at 20 °C over a wide frequency range extending from 1 MHz to several gigahertz by time-domain reflectometry. Two relaxation peaks were found, one at a frequency of 50 MHz and the other at 1 GHz. The lower frequency dispersion is assigned to a local conformational transition in the chain backbone, and the higher frequency dispersion to internal rotation of the side acetyl group. The backbone motions were also observed by ^{13}C spin–lattice relaxation.

I. Introduction

Solid amorphous polymers usually exhibit two (and occasionally more than two) regions of dielectric dispersion.[1-3] The slower (α) process becomes immeasurably slow in the glassy state, is thus related to motions of the polymer chain backbone, and accordingly follows WLF-type temperature dependence. In contrast, the more rapid (β) process is, at ordinary frequencies, usually observed below the glass temperature and follows Arrhenius temperature dependence. When the temperature is raised or the system diluted, the characteristic average relaxation times of the two processes approach each other, and frequently the two loss peaks merge into a single dispersion region, often dubbed $\alpha\beta$. If the polymer chains bear flexible polar side groups, it is natural and surely correct to relate[4] the β process to motions involving such side groups. However, the β dispersion has also been seen[1] in systems for which all dipoles are rigidly fixed to the main chain. Further, the relative strength of the two dispersions is not simply a function of the molecular geometry: for example,[1] for poly(methyl acrylate) $\Delta\epsilon_\alpha > \Delta\epsilon_\beta$, but under some conditions the reverse is true for poly(methyl methacrylate).

In dilute solution,[3] barring only those rare species carrying longitudinal dipoles within each repeat unit,[5-7] only a single absorption peak has been found (as far as we are aware) in all polymers, whether or not they have flexible polar side groups; it thus seems likely that in the latter case the backbone and sidechain motions are strongly enough coupled so that a merged $\alpha\beta$ type of process is being observed. The loss peak in solution usually falls in the frequency range from 1 MHz to 1 GHz, which in the past has posed relatively formidable experimental difficulties, and thus the existing data are both sparse and of limited precision. With the advent of recent improvements[8-10] of the time-domain reflectometry method, it seemed worthwhile to search anew for some evidence of a side-group dispersion, since absorptions with $\epsilon_{\max}''$ of the order of 0.01 can now be easily and accurately measured in just the previously difficult frequency range. In the present investigation, we elected to study a dilute dioxane solution of poly(methyl vinyl ketone), which according to semiempirical conformational energy calculations[11] should offer unusually low impedance to side-group motions. We indeed observe two partially overlapping dielectric loss peaks, one of which can confidently be ascribed to motions of the side acetyl groups. The main-chain motions have also been probed by ^{13}C spin relaxation measurements.

II. Experimental Section

The sample of PMVK was the same one used earlier[12] to determine the equilibrium dipole moment: presumably of atactic head-to-tail structure, it had a viscosity-average molecular weight of about 1×10^6. Dioxane was dehydrated and distilled before use. Dioxane-d_8 (99%, Aldrich) for the NMR measurements was used as received.

The TDR apparatus and the methods of making the measurements are described in detail in previous papers.[8-10] Here we applied the difference method, which is very useful for measurement of the small difference between a dilute polymer solution of permittivity ϵ_x^* and the reference solvent of permittivity ϵ_s^*. The relation between these quantities at a circular frequency ω is

$$\epsilon_x^* = \epsilon_s^* \frac{(v_0 - r_s) + (r_s - r_x)}{(v_0 - r_s) - i\omega(\gamma d_c/cf_2)(r_s - r_x)} \frac{f_x}{f_s} \quad (1)$$

where v_0, r_s, and r_x are the Laplace transform of the incident pulse, that of the reflected pulse from the known solvent, and that of the reflected pulse from the unknown solution, respectively; d_c is the length of cylindrical central conductor of the sample cell, γd_c the effective length of the conductor, and c the speed of propagation in vacuo (0.300 mm/ps). The function f is given by

$$f = z \cot z \quad (2)$$

where $z = (\omega d_c/c)\epsilon^{*1/2}$ and accounts for propagation and multiple reflection in the sample. The difference between the reflected pulse from the solvent and that from the solution was evaluated before transformation to give $r_s - r_x$ for precision measurements.

Equation 1 places a definite restriction on the choice of the cell length,[3] because f diverges at $|z| = \pi/2$ and eq 1 is hence useful only for $|z| < 1$. Therefore we chose d_c = 20 mm for the measurement from 1 MHz to 1 GHz and d_c = 5.0 mm for 0.1 GHz to several gigahertz.

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