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Dielectric and pyroelectric properties of poly[2,3-bis(trifluoromethyl)norbornadiene]

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The fluoropolymer poly[2,3-bis(trifluoromethyl)norbornadiene] (poly(BTFMND)) has been synthesized via ring-opening metathesis polymerization, using initiators based on W, Mo or Ru compounds or via variations of the Schrock-type initiator $Mo(CHR)(N–2,6\text{-}C_6H_3\text{–i-}Pr_2)(OR')_2$ ($R = CMe_3$, CMe_2Ph; $R' = CMe_3$, $CMe(CF_3)_2$), giving poly(BTFMND) with controllable proportions of *trans*-vinylene units. Analysis of the ^{13}C nuclear magnetic resonance fine structure establishes that the high-*trans* (>98%) polymer is 92% tactic and the high-*cis* (>98%) polymer is 75% tactic, but these methods cannot determine whether the material is predominantly isotactic or syndiotactic. Dielectric and thermally stimulated current measurements have been performed and give relaxed permittivities ε_R strongly dependent on *trans* content, ranging from above 40 for the 98% *trans* material through 15 for the 54% *trans* polymer to 6 for 98% *cis* polymer. The significantly higher permittivity above T_g for the high-*trans* material than for the 54% *trans* polymer and the significantly reduced value for the 98% *cis* polymer suggest that both the high-*cis* and high-*trans* materials have syndiotactic structures. The total polarization for free films of 98% *trans* poly(BTFMND) saturates at about 20 mC m^{-2}, with a pyroelectric coefficient approaching 6 μC m^{-2} K^{-1} above poling fields of 200 MV m^{-1}. These usefully high values combined with low dielectric loss in its glassy state at ambient temperatures indicate an excellent material for potential use as a pyroelectric transducer, with a figure of merit comparable with or better than that of poly(vinylidene fluoride).

(Keywords: fluoropolymer; dielectric properties; pyroelectric properties)

INTRODUCTION

Ring-opening metathesis polymerization (r.o.m.p.) of fluorinated monomers[1,2] was first reported in 1979, and the precision and control of such syntheses have steadily advanced through the introduction of well defined initiators. The polymerization of 2,3-bis(trifluoromethyl) norbornadiene to produce poly[2,3-bis(trifluoromethyl)-norbornadiene] (poly(BTFMND)) is the most extensively studied of these systems. Various microstructures, from virtually 100% *trans* to 100% *cis*, have been synthesized in well controlled living and highly stereoregular polymerizations via a range of initiators. However, the standard analytical probe, ^{13}C n.m.r. spectroscopy, has not enabled the tacticities of these materials to be unambiguously established.

The potentially high polarity of fluorinated polymers led us to explore the pyroelectric properties of these materials for possible application as active components in various types of electrical device, particularly heat sensors, electromagnetic radiation detectors and thermal imaging systems.

Much of the work on the piezoelectric and pyroelectric behaviour of polymers has focused on poly(vinylidene fluoride) (PVDF), which works as a composite in which the crystalline phase provides the locked-in polarization and the soft deformable amorphous phase responds to the applied stress[3,4]. Our longer-term aim is to mimic this mechanism by synthesizing two-phase systems comprising a high-T_g highly polar phase dispersed in a low-T_g high-permittivity amorphous phase, which will allow changes of phase composition and morphology to optimize the piezoelectric and pyroelectric response. In the course of our studies on a potential highly polar phase for such a two-phase system, poly(BTFMND), we have discovered high permittivities above T_g for the *trans* materials contrasted with much lower values for the *cis* polymers, and these results have enabled the tacticity of the *trans* polymer to be defined.

EXPERIMENTAL

Chemical synthesis

The ring-opening metathesis polymerization (r.o.m.p.) of BTFMND[1,2,5] was initially explored with classical initiator systems based on W, Mo and Ru compounds. These produced polymers with varying proportions of *cis*- and *trans*-vinylenes (specified here by the percentage *trans* content as determined by ^{13}C n.m.r.) ranging from 54 to 86% *trans*-vinylene content. Subsequently r.o.m.p. of BTFMND has been investigated using the Schrock initiator $Mo({=}CH\text{–t-Bu})({=}N\text{–}2,6\text{-}C_6H_3\text{–i-}Pr_2)(O\text{–t-Bu})_2$

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*To whom correspondence should be addressed (refs. 6–8). This initiator (*Scheme 1*) allowed much greater precision and control of the polymerization, and yields a polymer with >98% *trans*-vinylenes with a highly tactic microstructure.

More recently it has been found that replacing two methyl groups in each alkoxy ligand of the initiator by trifluoromethyl groups (*Scheme 1*) produces poly(BTFMND) with >98% *cis*-vinylene content[9,10]. Moreover, by initiating the polymerization of BTFMND with an equilibrating mixture of the three initiators shown in *Scheme 2*, excellent control of the *cis*/*trans*-vinylene content, from 2% to 98% *trans*, is obtained[9].

Microstructure determination

For ring-opened polymers derived from 2,3-disubstituted norbornadienes, there are only four assembly modes, leading to the four diad repeat units shown in *Scheme 3*.

Previous papers[5,6] have reported ^{13}C n.m.r. spectra for poly(BTFMND) and it has been particularly useful to compare the spectrum for the polymer with 54% *trans*-vinylene content with that for the 98% *trans* material. The polymer with 54% *trans* shows multiple resonances whereas the spectrum for the 98% *trans* material contains only sharp resonances with contributions from *cis* poly(BTFMND) units barely observable. The origin of the multiplet resonances has been clarified[10] by concentrating on the methylene carbon multiplicities arising from possible triad structures. It is expected that the central methylene unit in these triads will experience a shift effect from the neighbouring vinylene units, giving rise to signals due to *cc*, *ct* (=*tc*) and *tt* environments. In an all-*cis* or an all-*trans* polymer, only one environment and one signal will be seen unless the methylene experiences a *meso*/*racemic* (*m*/*r*) shift effect as a consequence of the stereochemistries of the nearest ring placements, in which case there can be up to three distinct triad environments (*mm*, *mr*=*rm* and *rr*). By comparing n.m.r. spectra of poly(BTFMND) of different tacticities and integrating the peaks for the methylene carbon resolved at 125 MHz for the >98% *trans* content material, it is calculated that this polymer is 92% tactic. However, it is not possible to assign the specific tacticity from these data. By a similar analysis it is found that the >98% *cis*-vinylene content material is 75% tactic, again with no assignment of the tacticity made on the basis of these n.m.r. data[10].

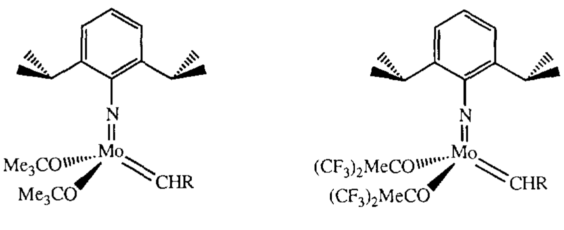
Preparation of samples for measuring physical properties

Samples for the electrical measurements were prepared by solvent casting from 8 to 15 wt% solutions of poly(BTFMND) in h.p.l.c.-grade acetone or butanone. Thin films were prepared by casting onto glass slides and allowed to dry at room temperature. The samples were then baked in a vacuum oven at 80°C to remove the solvents and annealed at 10°C above the T_g for a further hour. Free film samples were removed from the glass slides using a flat blade and 1 cm square aluminium electrodes were evaporated onto each side. Constrained samples were cast onto pre-aluminized glass cover slips and annealed in a similar manner prior to evaporating a second aluminium electrode onto the upper surface.

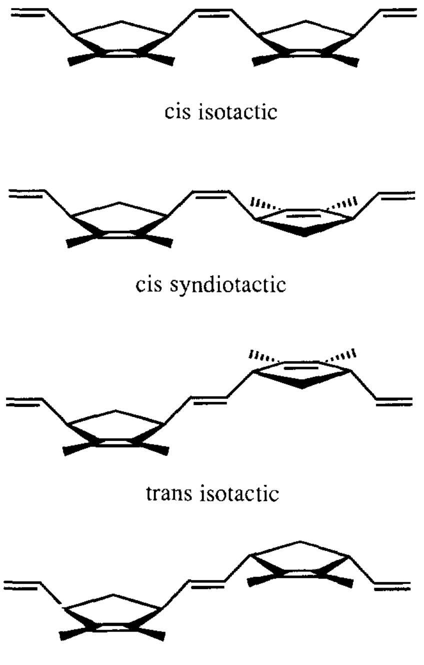
Experimental methods

Differential scanning calorimetry. D.s.c. measurements were made on a Perkin–Elmer DSC 7 over the temperature range 0 to 250°C, generally at a heating rate of 10°C min^{-1}.

Linear thermal expansion coefficient. Thin strips of poly(BTFMND) film were held vertically and clamped



Scheme 1 Schrock initiators for r.o.m.p.

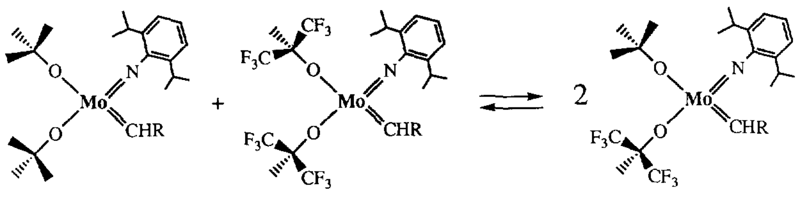

cis isotactic

cis syndiotactic

trans isotactic

trans syndiotactic

Scheme 3



Scheme 2

at the free end to a linear variable displacement transducer. The temperature was controlled by passing heated dry nitrogen gas into the sample chamber, and the thermal expansion coefficient was determined from the change in sample length as the temperature was abruptly changed between two temperatures about 2.5°C above and below 20°C. Measurements were made at various loads and extrapolated to zero load to compensate for the weight of the lower clamp and transducer[11].

Dielectric measurements. Dielectric measurements were carried out in the temperature range 20 to 150°C and over a frequency range 0.1 to 100 kHz using a Schlumberger 1260 gain-phase analyser alone for the higher frequencies and in conjunction with a Kistler charge amplifier for lower frequencies (0.1 to 100 Hz). Accurate measurements of capacitance and $\tan\delta$ have been made at 1 kHz on samples at 20°C and at various other temperatures as a check using a General Radio 1620AP capacitance bridge.

Poling and thermally stimulated current measurements. Films were normally poled by applying a static field across the evaporated electrodes at or within 3°C of the T_g of the sample, held for 2 min and then steadily cooled at 10°C min^{-1} to 20°C. Increasing the poling times did not reveal any changes in the t.s.c. or pyroelectric values obtained.

To attain very high fields, samples were corona poled by applying a high voltage of up to 8 kV between a sharp needle and a metal plate on which the sample was placed. The samples were poled at T_g as described above and allowed to cool in the field before evaporating the electrodes.

To measure the polarization, the thermally stimulated current (t.s.c.) released was recorded as samples were heated steadily (generally at 10°C min^{-1}) to 10°C above their poling temperatures. A typical t.s.c. depole for poly(BTFMND) (*Figure 1a*) shows a single sharply defined peak at T_g from which an accurate measurement of T_g is obtained that is typically about 5°C below d.s.c. estimates.

Integrating the t.s.c. with respect to time gives the total charge released ΔQ and thence the polarization $\Delta P = \Delta Q/A$, where A is the area of the sample between the electrodes. From this, the relaxed electric susceptibility χ_p due to the permanent dipoles is calculated:

$$\chi_p = \varepsilon_R - \varepsilon_U = \Delta P/\varepsilon_0 E \tag{1}$$

where E is the poling field, ε_R is the relaxed (low-frequency or 'static') permittivity due to the free movement of the permanent dipoles above T_g, and ε_U is the unrelaxed or high-frequency permittivity (typically ε_U is the square of the refractive index). Typically ε_R determined via t.s.c. is slightly higher in value than that measured by dielectric spectroscopy at 0.1 Hz. This is not unreasonable since t.s.c. is effectively a low-frequency measurement (≈ 1 mHz)[12].

Pyroelectric measurements. Pyroelectric measurements were obtained by varying the temperature of the poled sample using a triangular waveform with a peak-to-peak amplitude of 3°C with a period of 100 s and a mean temperature of 20°C, using a dry nitrogen gas flow and a fast-response heater[13]. The charge or current generated was measured using a Keithley electrometer and the pyroelectric coefficient ($\gamma = \mathrm{d}P/\mathrm{d}T$) was obtained from the ratio of the first Fourier coefficient of the current or charge signals and the signal from a fine-wire thermocouple mounted in the gas flow immediately above the sample.

Characterization

Differential scanning calorimetry. D.s.c. for 98% *trans* poly(BTFMND) shows slow crystallization at about 180°C. Studies of the unoriented material show a maximum heat of crystallization of about 14 J g^{-1}, which, by comparison with a value of about 140 J g^{-1} for poly(ethylene terephthalate)[14]—which is itself less than 35% crystalline—indicates that even in a highly annealed state the crystallinity of the 98% *trans* poly(BTFMND) is low.

Dependence of T_g *on* trans *content.* Glass transition temperatures T_g determined by d.s.c. and t.s.c. are shown

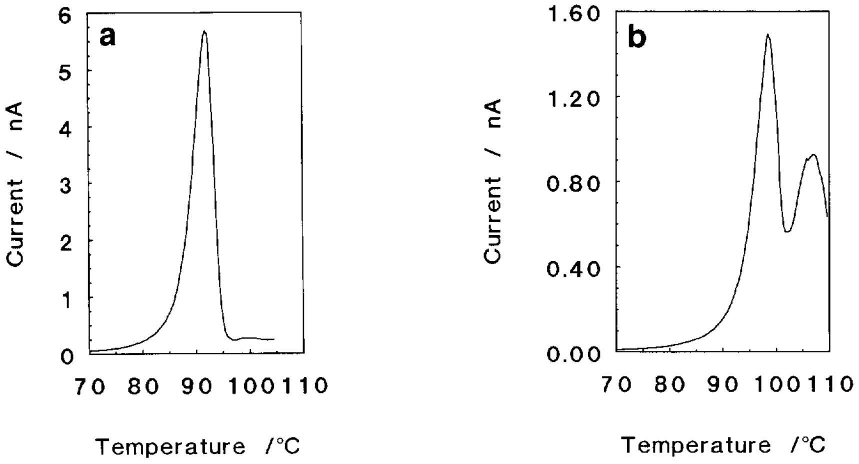


Figure 1 Typical t.s.c. dipole depolarization recordings of current released at 1 cm^2 electrodes during a ramp at 10°C min^{-1}. (a) A clean sample of 98% *trans* poly(BTFMND) poled at 100 V. (b) A sample of 86% *trans* poly(BTFMND) poled at 50 V, showing a space-charge peak on the high-temperature side of the dipolar peak at T_g

Table 1 Variation of T_g with *trans* content

Initiator	*Trans* content (%)	T_g (°C) D.s.c.	T_g (°C) T.s.c.
$Mo(=CH\text{-}t\text{-}Bu)(=N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OCMe_3)_2$	99.6	94	93
$Mo(=CH\text{-}t\text{-}Bu)(=N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OCMe_3)_2$	98	97	93
$MoCl_5/Me_4Sn$	86	104	100
$RuCl_3/Me_4Sn$	70	117	–
WCl_6/Me_4Sn	54	125	119
$Mo(=CH\text{-}t\text{-}Bu)(=N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OCMe(CF_3)_2)_2$	2	141	144

in *Table 1*, and show a monotonic decrease with *trans*-vinylene content, ranging from above 144°C for the 2% *trans*-tactic material to 94°C for the >99.6% *trans* material.

RESULTS

Theory

In an isotropic polar material, the polarization and static permittivity arise from contributions from the permanent dipoles and the normal deformable polarization. Calculations of permittivity need to consider both the dipolar contribution to the polarizability and the local field acting on the molecule in terms of the external applied field. Various theories have progressively refined the calculation from Debye[15] through Onsager[16] and Kirkwood[17] to Fröhlich[18].

From the Debye theory[15] for uncorrelated and isolated permanent dipoles in a local electric field E_L, the polarization is Langevin in form and given by:

$$P = P_{\max}[\coth(\mu_p E_L/kT) - kT/\mu_p E_L] \qquad (2)$$

At the limit of low fields:

$$\frac{P}{E_L} = \frac{n\mu_p^2}{3kT} = \frac{P_{\max}\mu_p}{3kT}$$

where $P_{\max} = n\mu_p$, $n = \rho N_A/M_W$ is the number of dipoles per unit volume and the permanent dipole moment μ_p is related to the vacuum moment μ via $\mu_p = (\varepsilon_U + 2)\mu/3$.

The Debye theory only applies to uncorrelated dipoles in rarefied media; for dense media, Onsager's[16] local-field approach is required. To incorporate the effect of local ordering, Fröhlich[18] extended Kirkwood's[17] statistical-mechanical approach for rigid dipoles to a system of polarizable dipolar molecules and obtained:

$$\frac{(\varepsilon_R - \varepsilon_U)(2\varepsilon_R + \varepsilon_U)}{\varepsilon_R(\varepsilon_U + 2)^2} = \frac{ng\mu^2}{9\varepsilon_0 kT} \qquad (3)$$

where μ is the electric dipole moment of the molecule *in vacuo*. The Kirkwood g-factor is a correlation factor introduced to take account of local ordering and is an ensemble average defined by:

$$g = 1 + \sum_{j \neq 1} \langle \cos\gamma_{1j} \rangle$$

where $\langle \cos\gamma_{1j} \rangle$ is the average of the cosine of the angle γ_{1j} made between dipole j and typical dipole 1. If each dipole acts independently of its neighbours (Onsager model), then $g = 1$. Similarly an analysis of randomly correlated dipoles considered on the basis of a random-walk problem also gives $g = 1$. Thus experimental determination of the parameters of equation (3) can enable a measure of the local ordering between adjacent dipoles to be ascertained. This approach may be extended to polymer systems[19] by identifying the repeat unit of dipole moment μ as the basic unit in the Fröhlich theory and g as a segmental correlation factor to be determined from the permittivity measurements via equation (3).

For amorphous polymers, the principal contributions to the pyroelectric coefficient, $\gamma = dP/dT$, are from changes in the sample dimensions and dipole libration angles with temperature. Although the dipoles have a fixed mean direction, there is always thermal motion (libration) with a mean-squared amplitude proportional to temperature in the simple harmonic approximation. Thus increasing the temperature of the dipole reduces the average projection of its moment.

Now the frozen-in polarization at zero applied field is given by[20]:

$$P = Q/A = (N/V)\mu_p\langle \cos\theta \rangle \qquad (4)$$

where N/V is the number of dipoles per unit volume, and $\mu_p\langle \cos\theta \rangle$ is the average component of the permanent dipole moment (μ_p) in the direction of P. It should be noted that experimentalists do not report dP/dT since the change in area is difficult to contend with, and it has become accepted practice to report $(dQ/dT)/A$ as the pyroelectric coefficient[3]. For electrodes that deform with the sample (e.g. with evaporated electrodes), the total number of dipoles between the electrodes remains constant. Thus, differentiating with respect to temperature, we obtain the 'experimental' pyroelectric coefficient:

$$\gamma = (dQ/dT)/A$$

$$= -(P/b)\partial b/\partial T + (P/\langle \cos\theta \rangle)\partial\langle \cos\theta \rangle/\partial T \qquad (5)$$

where b is the sample thickness. The first term is $-P\alpha_3$ where α_3 is the coefficient of thermal linear expansion along the poling field. Both these contributions are proportional to P, so that if P is a Langevin function of field so also is γ, and γ/P is a constant independent of field. The term γ/P is useful experimentally since it is independent of sample thickness.

Dielectric measurements

Dielectric measurements have been made on samples of poly(BTFMND) of various *trans* contents; a typical set of ε' and $\tan\delta$ plots with frequency and temperature are shown in *Figures 2a* and *2b*.

Table 2 Permittivities compared

Trans content (%)	T_g (t.s.c.) (°C)	ε_U	ε_R	Max tan δ
98	93	2.6	42.0	0.90
86	100	2.6	30.4	0.76
54	119	2.6	13.8	0.45
2	144	2.6	4.9	0.10

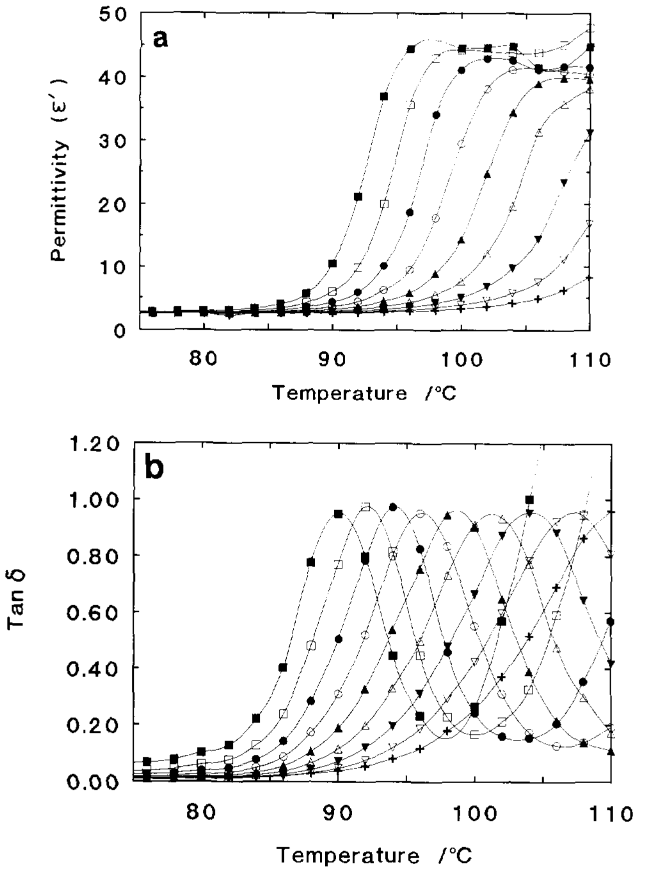


Figure 2 Dielectric measurements on 98% *trans* poly(BTFMND). (a) Relative permittivity ε' and (b) tanδ *versus* temperature, at various frequencies: 0.1 (■), 0.3 (□), 1.0 (●), 3.2 (○), 10.0 (▲), 31.6 (△), 100 (▼), 316 (▽) and 1000 Hz (+)

The limiting values of the relaxed and unrelaxed permittivities, ε_R and ε_U, are compared in *Table 2*. Because the absolute values of ε_U and ε_R are dependent on determinations of sample thicknesses, which range from 10 to 50 μm with an accuracy of about 5–10%, the values for ε_U are found to range from 2.45 to 2.75 across all materials. As there was no systematic difference discernible in the measured values of ε_U between samples of differing *trans* contents, the differences were assumed to arise from errors in thickness measurements, and thus the sample thicknesses have been adjusted to yield the mean value for all samples for ε_U of 2.6. Tanδ values, which are independent of sample thickness, and are measured at ambient temperatures simultaneously with the ε_U determinations, consistently give values less than 0.001 at 1 kHz irrespective of *trans* content and indicate high-quality films.

The values for the relaxed permittivity ε_R are found to depend strongly on *trans* content, ranging from above 40 for the 98% *trans* material through 14 for the 54% *trans* to about 5 for the 98% *cis* material.

Accurate determinations of the values of ε_R are hindered by the presence of small amounts of impurity in the samples, which are in effect trapped charges in the dielectric medium. Above T_g these charges are released within the sample and produce an ionic conductivity signal in the ε' and ε'' plots, which increases with temperature and can be very pronounced at low frequencies (e.g. 0.1 and 0.3 Hz). While in some cases it is possible to model and fit the ionic conductivity contribution in order to eliminate it[21], for 98% *trans* poly(BTFMND) the precise reproducible data required cannot be obtained as the ε_R change through T_g is very large and above T_g samples tend to soften and distort slightly. Consequently, in these cases, the values for ε_R at 0.1 Hz have been extrapolated from the plateau values obtained at the higher frequencies.

Similarly Cole–Cole plots[22] of ε'' *versus* ε' do show a characteristic depressed semicircle from which ε_R' values are obtained, but the slight errors introduced by the ionic conductivity do not allow for a more sophisticated interpretation of these plots.

Thermally stimulated current and pyroelectric properties

T.s.c. and polarization. Samples of poly(BTFMND) of various *trans* contents have been poled and their polarizations determined from t.s.c. recordings. For poly(BTFMND) a single sharply defined peak is observed at T_g. The polarizations obtained from t.s.c. depoles are shown in *Figure 3* as a function of poling fields up to 70 MV m^{-1} for the 98% and 86% *trans* materials. The distinct curvatures in the plots at the higher poling fields indicate that the polarizations begin to saturate. For low fields, P is a linear function of E (equation (1)), and *Table 3* shows the initial low-field susceptibility $\chi_p = P/\varepsilon_0 E$ averaged for all samples of various *trans* contents, from which the static dielectric increments $\chi_p = \varepsilon_R - \varepsilon_U$ are determined (column 3). As expected these values are slightly higher than those obtained from the dielectric measurements (*Table 2*). The Langevin fitting parameters also shown in *Table 3* are discussed below.

As for the dielectric measurements, small amounts of trapped charge are revealed in the t.s.c. recordings as a space-charge peak on the high-temperature side of the

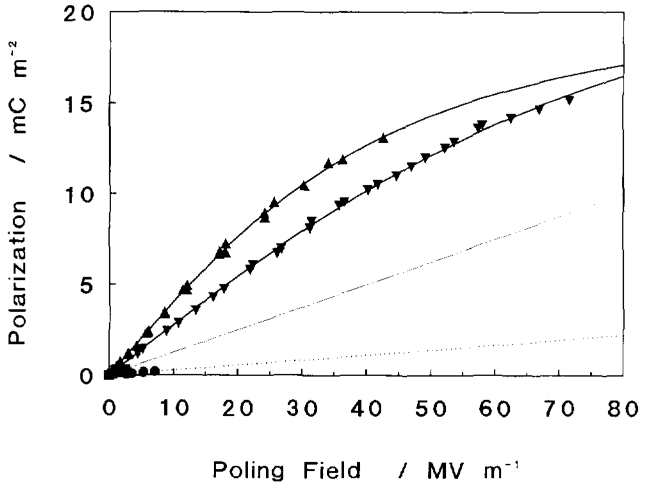


Figure 3 Polarization *versus* applied field for 98% (▲) and 86% (▼) *trans* poly(BTFMND). The initial slopes for 54% (■,– – –) and 2% (●, · · · · ·) are also shown

dipolar peak at T_g (*Figure 1b*). This can introduce errors both in P due to the difficulty in resolving the dipolar from the space-charge peak and in the true applied field due to space-charge effects and ionically conducted leakage currents within the sample. This problem is more pronounced for measurements at the high fields where thinner samples are required. While determinations of polarizations are affected by the space charge, pyroelectric properties for a given polarization are not[23].

Pyroelectric coefficients. Pyroelectric coefficients for poly(BTFMND) were measured prior to subsequent t.s.c. depoles. Typical values of the pyroelectric coefficients for poly(BTFMND) with various *trans* contents are shown in *Figure 4* as a function of poling field. Samples were studied both as free films and as constrained films on thin substrates. *Table 4* shows values for γ/E for free and constrained samples at low poling fields. Although polarization values are unaffected by constraint, for an equivalent poling field, pyroelectric coefficients for films constrained by a substrate (γ_C) are expected to be different from those for free films (γ_F), and for poly(BTFMND) the value of 50% higher for constrained samples compared to free films is not unexpected.

Table 3 Polarization parameters

Trans content (%)	T_g (t.s.c.) (K)	$\chi_P = \varepsilon_R - \varepsilon_U$	Langevin parameters E_0 (MV m^{-1})	Langevin parameters P_{max} (mC m^{-2})
98	368	45.5	17.7	21.9
86	373	30.1	32.4	27.0
54	393	14.0		
2	417	3.1		

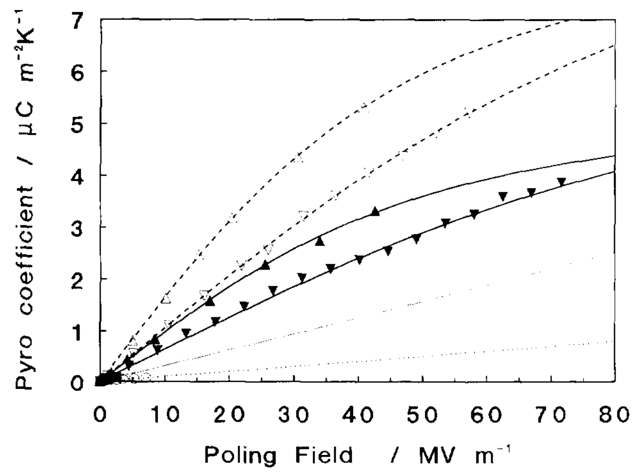


Figure 4 Pyroelectric coefficient *versus* applied field for free (f) and constrained (c) films of poly(BTFMND): 98% *trans* f (▲), 98% *trans* c (△), 86% *trans* f (▼), 86% *trans* c (▽). The initial slopes for 54% *trans* f (■, —···—) and 2% *trans* c (○, ·····) are also shown

Normally the difference between γ_C and γ_F is due to the change of stress required to maintain the same lateral strain as the substrate:

$$\gamma_C = \gamma_F - 2d_{31}\Delta\alpha Y/(1-\nu) \qquad (6)$$

where d_{31} is the piezoelectric coefficient for stress applied in direction 1 to a film poled in direction 3, Y is the tensile modulus, ν is Poisson's ratio and $\Delta\alpha$ is the difference in the thermal expansion coefficients between the polymer sample and substrate. Inserting a high-field saturation value of $\gamma_F = 6\ \mu\text{C m}^{-2}\text{ K}^{-1}$ into equation (6) and using $Y = 1.2$ GPa (from d.m.t.a. measurements), $\Delta\alpha = 110 \times 10^{-6}\text{ K}^{-1}$ and $\nu = 1/3$, we obtain an estimate of d_{31} for 98% *trans* poly(BTFMND) of 7 pC N^{-1}.

As noted above, for an amorphous polymer the pyroelectric coefficient is usually proportional to the polarization for all field strengths. Thus the plot of the pyroelectric coefficient as a function of field (*Figure 4*) follows a similar form to that for the polarization (*Figure 3*). At low fields γ is proportional to P and E, and column 3 of *Table 4* shows the average values of the initial low-field γ/E for free films and those constrained by substrates for various *trans* contents; the corresponding γ/P values are shown in column 4. For free films, γ/P is found to be $260 \times 10^{-6}\text{ K}^{-1}$, which is about twice the value of the coefficient of thermal linear expansion, α_3, of $120\ (\pm 10) \times 10^{-6}\text{ K}^{-1}$ measured for two free films of 98% *trans* poly(BTFMND). Thus it appears that, in addition to thermal expansion, there is a major contribution to the pyroelectric coefficient from the change in the dipole libration angle, a feature common in many electroactive polymers, for example PVDF[24]. At high poling fields γ/P values are not significantly different from the low-field values of 260 and $390 \times 10^{-6}\text{ K}^{-1}$ for free and constrained films, respectively.

Table 4 Pyroelectric parameters

Trans content (%)	Film type[a]	Initial γ/E (fF m^{-1} K^{-1})	γ/P (10^{-6} K^{-1})	Langevin parameters E_0 (MV m^{-1})	Langevin parameters P_{max} (μC m^{-2} K^{-1})
98	f	105	262	18.8	6.24
98	c	159	394	18.9	9.43
86	f	67.3	253	37.9	7.40
86	c	104	390	35.8	11.28
54	f	32.9	265		
2	c	10.6	390		

[a] f = free film; c = constrained film on substrate

Corona poled samples. Attempts have been made to subject samples to the maximum achievable poling field to determine the saturation values for the polarization and pyroelectric coefficient. Because of the poling procedure, it is only possible to obtain an approximate value for the applied field. These samples can only be corona poled once as the high field must be applied before electroplating the top electrode and electrodes cannot be removed without destroying the sample. Four samples of 98% *trans* poly(BTFMND) have been corona poled at estimated poling fields ranging from 200 to 450 MV m^{-1}. Values for the polarization average at 19.3 mC m^{-2} with a pyroelectric coefficient of 7.2 μC m^{-2} K^{-1} and a variation of about 10%. Since there is no clear correlation of γ or P with E at these high fields, we can assume that these values are close to the attainable maximum.

Langevin fits to polarization and pyroelectric data. While for the Debye and Onsager semi-statistical treatments the dipoles are uncorrelated and distributed according to Langevin's law, there is no *a priori* reason to assume that the Langevin function:

$$y = y_{\max}[\coth(E/E_0) - E_0/E] \tag{7}$$

where y indicates P or γ, is also applicable to correlated dipoles in dense media. However, it does appear that the data shown in *Figure 3* follow a similar functional form. Fitting the Langevin function to the polarization data for poly(BTFMND), the parameters E_0 and $P_{\max}$ shown in *Table 3* are obtained.

Similarly Langevin fits to the pyroelectric data (*Table 4*) indicate that pyroelectric coefficients for free films of 98% *trans* poly(BTFMND) saturate at about 6 μC m^{-2} K^{-1}, with 90% attained at poling fields of 150 MV m^{-1}.

For both the polarization and pyroelectric data, the variations in the fitting parameters obtained for different samples of the same material are about 10%, much greater than the variation in the raw data. Similarly there are large discrepancies in the E_0 parameter between the polarization and the pyroelectric fittings for the same material. The data for the high-field fittings have been collated from several samples and the large variation in the E_0, $P_{\max}$ and $\gamma_{\max}$ values is due to the uncertainty in discriminating the extent of the dipolar depolarization from a space-charge background, inaccuracies in determining the applied fields and small corruptions of thin samples at high poling fields leading to internal discharges.

For the 98% *trans* samples, the polarization maximum of 21.9 mC m^{-2} obtained from the Langevin fit compares well with the corona poled saturation value of 19.3 mC m^{-2}. The apparent higher values of $P_{\max}$ and $\gamma_{\max}$ obtained for the 86% *trans* than for the 98% *trans* material needs further investigation.

Now the maximum theoretical polarization is $P_{\max} = n\mu_p = \rho N_A \mu(\varepsilon_U + 2)/3M_W$. Anticipating the discussion below that the dipole moment of BTFMND is about 3.7 D, and using a density for 98% *trans* poly(BTFMND) of 1490 kg m^{-3} determined with a liquid density gradient column, we obtain a maximum theoretical polarization of about 74 mC m^{-2}. The observed maximum polarization for poly(BTFMND) is less than half this value.

For a real polymer such as poly(BTFMND) the observed saturation plateau at high poling fields will be considerably reduced from the maximum theoretical polarization due to various effects: (i) For a polymer, dipoles are constrained to rotate about chain axes, preventing them from fully aligning with the field and reducing $\langle\cos\theta\rangle_{\max}$ from unity to $\pi/4$. (ii) The ability of a dipole to align in an applied electric field will depend to some extent on the bonds linking adjacent dipoles and on the position and orientation of these neighbours. Now a polymer chain naturally kinks, coils and meanders, and thus, in an applied polarization field, some sections of dipoles will remain forced away from the applied field while other swathes of dipoles will be constrained from fully aligning with the field. To date it does not appear that this high-field alignment problem has been treated theoretically and thus no numerical estimate of the extent of the reduction on the saturation plateau due to this effect can be made here. (iii) For polymers with less than 100% stereoregularity, a further reduction in the observed saturation plateau may occur if stereochemical 'errors' suddenly switch or distort the direction of aligned sequences of dipoles.

Summary of electrical properties

The data from the dielectric, pyroelectric and t.s.c. depole measurements are consistent with a high relaxed susceptibility of above 40 for 98% *trans* poly(BTFMND) and with low values of about 3 for the 2% *trans* material. The γ/P values are 260×10^{-6} K^{-1} and 390×10^{-6} K^{-1} for free films and those constrained by substrates, respectively. To a first approximation both P and γ appear to follow the Langevin form as a function of the applied field.

DISCUSSION AND ANALYSIS

Structure modelling: estimates of dipole moment

An estimate for the dipole moment of BTFMND can be made using the measured dipole moment for (trifluoromethyl)benzene ($C_7H_5F_3$) of 2.86 D and resolving components assuming an angle between the two CF_3 dipole moments of 72°C, giving a value of 4.6 D. A better estimate for BTFMND of 3.9 D is obtained using the measured dipole moment for 3,3,3-trifluoro-1-propene ($C_3H_3F_3$) of 2.45 D. Here the fluorines are in a similar relation to the carbon–carbon double bond as for BTFMND.

Theoretical estimates of the dipole moment of BTFMND may be obtained by comparing experimental and computer-calculated values for associated small molecules such as the fluoromethanes. Restricted Hartree–Fock calculations have been performed using the semi-empirical molecular-orbital package MOPAC version 5.00[25] with the MNDO (modified neglect of diatomic overlap), AM1 (Austin model 1) or PM3 (parametric method 3) Hamiltonians, and using the *ab initio* GAUSSIAN 92 with 6-31G* basis set[26]. MOPAC with PM3 or AM1 in general gives better dipole moments than with MNDO, with average errors of about 0.35 D[25], but very close agreement with the experimental values is obtained using GAUSSIAN as shown in *Table 5*.

Using the estimates for $C_7H_5F_3$ and $C_3H_3F_3$ as the more reasonable comparisons with BTFMND, the overestimates obtained from the MOPAC packages indicate a probable dipole moment for BTFMND of about 4 D. However, GAUSSIAN 92 with 6-31G* performs substantially better than MOPAC and gives very close agreement with experimental values for $C_7H_5F_3$ and $C_3H_3F_3$, and thus we conclude that the dipole moment for BTFMND is close to the value of 3.7 D.

Table 5 Estimates of the dipole moment (D) for BTFMND[a]

	MOPAC			GAUSSIAN 92	
	+MNDO	+AM1	+PM3	6-31G*	Expt
CH_3F	1.76	1.62	1.44	1.99	1.85
CH_2F_2	2.21	2.04	1.82	2.05	1.97
CHF_3	2.23	2.08	1.89	1.70	1.65
$C_7H_5F_3$	3.83	3.30	3.11	2.87	2.86
$C_2H_3F_3$		2.70	2.91	2.49	2.45
BTFMND	4.68	4.33	4.26	3.73	

[a] 1 Debye (D) $= 3.336 \times 10^{-30}$ C m

Table 6 Dipole moments from dielectric measurements

Trans content (%)	T_g (t.s.c.) (°C)	ε_U	ε_R	μ (D) for $g=1$	g for $\mu = 3.7$ D
98	93	2.6	48.1	6.41	3.01
86	100	2.6	32.7	5.30	2.06
54	119	2.6	16.6	3.77	1.04
2	144	2.6	5.7	1.95	0.28

Dipole–dipole correlation and the structure of trans *poly(BTFMND)*

Using the experimentally determined values for ε_U and ε_R at T_g in the Fröhlich equation (equation (3)), assuming uncorrelated dipoles (i.e. with $g=1$), we obtain values for μ that vary considerably with *trans* content. From the previous discussion, the value of 2.0 D for 2% *trans* is too low, while the value of 6.4 D for 98% *trans* is unacceptably high, but the value of 3.8 D for the 54% *trans* is very close to the value of 3.7 D calculated above. Now some correlation between adjacent dipoles is expected as the BTFMND rings are connected via a non-rotating carbon–carbon double bond. For a 50% *trans*/*cis* 'atactic' material it is reasonable to assume that the dipoles are randomly correlated with $g=1$. By fixing μ at 3.7 D, a value close to that found for the 54% *trans* material, which is effectively 'atactic' with randomly correlated dipoles, estimates of g are made that range from 0.28 for 2% *trans* to 3.01 for 98% *trans* (*Table 6*).

The high g-factor determined for the 98% *trans* material implies strong local correlation between adjacent dipoles involving several nearest neighbours combining to produce a large effective dipole moment. This can only be achieved if the dipoles on adjacent rings are aligned in the same direction, and structurally this can only be obtained for a regular linear conformation with the *trans*-syndiotactic configurations. Now such a large value of g ($g>3$) implies that on average every dipole is strongly correlated to its immediate neighbour throughout the ensemble. To account for chain kinks and meanders and departures from stereoregularity, idealized *trans*-tactic poly(BTFMND) must involve sequences of at least five aligned dipoles. This requires a consistent and regular linear structure over several repeat units, which can only be met by the *trans*-syndiotactic configuration. Thus we conclude that the structure of 98% *trans* poly(BTFMND) is *trans*-syndiotactic.

The value of the g-factor is controlled in part by the average length of unbroken sequences of adjacent dipoles aligned in the same direction. Several different syntheses have produced materials with *trans* contents (as determined by n.m.r.) varying from 98 to >99.6%, which if 100% tactic should have produced measurable changes in permittivity. No observable difference was found either in the d.s.c. T_g or in any of the dielectric, t.s.c. or pyroelectric measurements. As detailed above, the 98% *trans* material has a stereoregularity of only 92%, and since this will break up the correlated dipole sequences we believe that for the high *trans* material it is the stereoregularity that is the dominant factor in determining the values of the static permittivity and g-factor. If the stereoregularity and the *trans* content are refined towards 100%, then values for ε_R and g could increase still further. The value of g clearly depends on factors such as *trans–cis* isomerism, stereoregularity, molecular geometry, and intra- and intermolecular forces. Various theoretical methods, e.g. rotational isomeric state (RIS) modelling[27], can attempt to derive g, and such studies are presently being undertaken.

The arguments above have enabled us to determine the structure of highly *trans* poly(BTFMND) as *trans*-syndiotactic. If we apply the same argument in reverse to the *cis* poly(BTFMND), the very low values for ε_R and g ($g \approx 0.28$) strongly suggest that the dipoles have an alternating antiparallel arrangement and that consequently the structure of 100% *cis* poly(BTFMND) is *cis*-syndiotactic. We concede, however, that the low values for ε_R and g could also arise from an isotactic material that adopts a conformation, helical for example, which would also allow cancellation of dipole moments.

We have also examined a sample of poly(BTFMND) that is >99% *cis* and 99% tactic[28]. ^{13}C n.m.r. shows this material to possess the same tacticity type as that which dominates in the 98% *cis* sample prepared from $Mo(=CH\text{–t-Bu})(=N\text{–}2,6\text{-}C_6H_3\text{–i-Pr}_2)(OCMe(CF_3)_2)_2$. However, it has not yet been possible to prepare samples of this material in a form that would allow accurate dielectric measurements owing to the formation of opalescent surfaces during casting. Nonetheless, preliminary measurements confirm that this highly stereoregular polymer displays a very low permittivity comparable with the values found for the 98% *cis* material.

CONCLUSIONS

Highly *trans* poly(BTFMND) is *trans*-syndiotactic with a high permittivity above T_g greater than 40, which allows us to determine the saturation polarization approaching 20 mC m^{-2} with a pyroelectric coefficient approaching 6 μC m^{-2} K^{-1}. While these values are less than for PVDF (50 mC m^{-2} and 30 μC m^{-2} K^{-1} respectively), the low $\tan\delta$ (<0.001) and permittivity at ambient temperatures ($\varepsilon_U = 2.6$) enable us to compare poly(BTFMND) favourably with PVDF. One figure of merit, F_D, used to compare the pyroelectric response of detectors[29]:

$$F_D = \gamma/(\varepsilon \tan\delta)^{1/2} \tag{8}$$

suggests that in this respect poly(BTFMND) with a value of 118 μC m^{-2} K^{-1} at 20°C is better than PVDF ($F_D \approx 64$ μC m^{-2} K^{-1}; data taken at 1.69 Hz from Davies[3]).

For the *cis* poly(BTFMND), the low ε_R of 5.7 does not allow us to obtain high γ or P at moderate fields but does suggest a *cis*-syndiotactic structure. Further work is now being undertaken to confirm this structure.

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