Solvent-dependent conformations and piezoelectricity of the copolymer of vinylidene cyanide and vinyl acetate

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Conformations in deuterated dimethyl sulphoxide (DMSO-d_6), dimethyl acetamide (DMA-d_9) and dimethyl formamide (DMF-d_7) solutions for the copolymer of vinylidene cyanide and vinyl acetate, P(VDCN/VAc), have been investigated by using 500 MHz ^{1}H nuclear magnetic resonance spectroscopy. Making use of the vicinal coupling constants, which were obtained from spectral simulation, the conformer populations as well as the conformational energies were calculated with respect to the ε-tacticity. The mole fraction of *trans* conformer around the H_AH_BC–CH_X bond increases with the polarity of the solvent used. The anisotropy of the dipole moment with various conformations for P(VDCN/VAc) was also considered. The calculated dipole moment in the direction of the $C(CN)_2$ bond dipole was 6 debye for the all-*trans* conformation along the main chain composed of eight carbons, which amounts to twice that of the other conformations. The effect of casting solvent species on physical properties in a solid film was investigated by measuring the piezoelectric strain constant and the enthalpy relaxation. It was concluded that molecules with an all-*trans* rich conformation obtained from DMSO solution would be arranged with compact packing, resulting in a large enthalpy relaxation.

(Keywords: poly(vinylidene cyanide-*co*-vinyl acetate); conformation; ^{1}H nuclear magnetic resonance; dipole moment; piezoelectricity; enthalpy relaxation; solvent)

INTRODUCTION

The copolymer of vinylidene cyanide and vinyl acetate, P(VDCN/VAc), has received considerable attention because it exhibits high piezoelectricity even in the amorphous film state[1,2]. X-ray analysis, which has provided direct information concerning crystal structure, is unavailable for amorphous samples. In the previous paper[3], ^{13}C n.m.r. spectroscopy was successfully applied to elucidate the microstructure of P(VDCN/VAc) with monomer-unit composition VDCN:VAc = 1:1, where it was found that P(VDCN/VAc) is a highly alternating copolymer with reactivity ratios of r_{VDCN} and r_{VAc} being nearly zero. Because the alternating sequence of the chain microstructure, a VAc monomer unit separated by two VDCN units is considered to facilitate rotation of the main chain, which ultimately causes dipole orientation of the cyanide groups to show significant piezoelectricity. Moreover, the tacticity with respect to the VAc side chain, which we called the ε-isotacticity[3], determined from the cyanide carbon as well as from the methine carbon resonances is about 0.5. This means that P(VDCN/VAc) is almost completely atactic. The amorphous phase of this copolymer may be attributed to this atactic configuration, which prevents crystallization and formation of a highly ordered structure.

Besides microstructure, conformation is an essential factor in determining the piezoelectricity of P(VDCN/VAc). If the main chains have an all-*trans* conformation, piezoelectric polymers would exhibit a large anisotropy of the dipole moment and show high piezoelectricity. In particular, the dipole orientation of an amorphous polymer is achieved by the conformation of individual chains. Poly(vinylidene fluoride), PVDF, which has been extensively investigated owing to its piezo- and pyroelectricity[4-6], shows several crystal modifications, i.e. the $TGT\bar{G}$ conformation (α-phase), the all-*trans* conformation (β-phase) and the $T_3GT_3\bar{G}$ conformation (γ-phase), which is intermediate between that of the α- and β-phases[7,8]. Here, T and G represent *trans* and *gauche* conformations, respectively. Because of the all-*trans* conformation with a planar zigzag structure as well as a large spontaneous polarization, β-PVDF shows much higher piezoelectricity than other crystal modifications. It is also well known that the crystal modifications of PVDF depend on the casting solvent species. Crystals in the α-phase have been obtained from a xylene solution mixed with a little acetone or highly concentrated solution of cyclohexanone[9]. On the other hand, crystallization from dimethyl formamide (DMF) and dimethylacetamide (DMA) produces γ-phase crystals[10]. According to ^{1}H n.m.r. studies, Ando and coworkers[11] reported that the conformation of PVDF in solution is closely related to the polarity of the solvent used in crystallization, where the fraction of TT conformation increased with the dielectric constant of a

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monochlorobenzene (MCB)–dimethyl sulphoxide (DMSO) solution system.

Previously, we have reported an analysis of the configuration and conformation for P(VDCN/VAc) in DMF-d$_7$ solution by using 500 MHz ^{1}H n.m.r. spectroscopy[12]. In the ^{1}H n.m.r. spectra of P(VDCN/VAc), not only spin–spin splittings but also splittings due to ε-tacticity are simultaneously observed. However, in the 500 MHz ^{1}H n.m.r. spectra recorded in DMF-d$_7$ solution they were readily assigned separately by the technique of ^{1}H homo-decoupling. The data for conformer populations calculated from vicinal coupling constants show that the conformation of P(VDCN/VAc) in DMF-d$_7$ solution is predominantly *TG* around the CH_2–CH–CH_2 unit, whereas the all-*trans* conformer is less populated (about 25%).

In the present work we report the effects of solvents on the conformation of P(VDCN/VAc) studied by 500 MHz ^{1}H n.m.r. spectroscopy. In carrying out the spin analysis, we make use of computer simulation with the LAOCON III program. For solid films of P(VDCN/VAc), moreover, the corresponding effects of casting solvent on the piezoelectric properties are investigated and explained in terms of solvent-dependent conformation.

EXPERIMENTAL

P(VDCN/VAc) was synthesized by radical polymerization in benzene at 45°C with equimolar initial feed of VDCN and VAc monomers. The detailed procedure has been described elsewhere[3]. The powder samples of P(VDCN/VAc) were a generous gift from Mitsubishi Petrochemical Co. Ltd.

^{1}H n.m.r. spectra of P(VDCN/VAc) were obtained at 500 MHz by using a JEOL GX-500 high-resolution spectrometer. The spectra were observed at 85°C as 1 wt% solutions in DMSO-d$_6$ (Merck) and DMA-d$_9$ (Merck) in 5 mm outside-diameter n.m.r. glass tubes. Chemical shifts were referenced to internal tetramethylsilane and indicated as parts per million (ppm). The n.m.r. operating conditions, which were the same as those previously used in DMF-d$_7$ solution[12], were as follows: pulse angle, 90°; pulse repetition time, 15 s; spectral width, 5000 Hz; data points for Fourier transform, 32 000; accumulation, 30 scans.

The film samples of P(VDCN/VAc) were cast at 85°C from solution and followed by a subsequent heating at 140°C in vacuum in order to eliminate any remaining solvent. These samples were confirmed to contain no residual solvent by i.r. spectroscopy. Measurements of piezoelectric constant d_{31} and dielectric constant ε were performed at a frequency of 10 Hz at 20°C, according to the methods developed by Furukawa *et al.*[13]. The coordinate axes 1 and 3 of piezoelectric constants refer to the stretching direction and the direction perpendicular to the film surface, respectively. The instrument employed to measure enthalpy relaxation was a TG-DSC Rigaku differential scanning calorimeter.

RESULTS AND DISCUSSION

Conformations in solution

In a comparison of the 500 MHz ^{1}H n.m.r. spectra of P(VDCN/VAc) in DMF-d$_7$, DMA-d$_9$ and DMSO-d$_6$ solutions, noticeably different spectral patterns are observed in the methylene proton resonances. Apparently, this means that the splitting pattern due to spin–spin coupling depends on the solvents species, since the solvent does not affect the steric configuration. P(VDCN/VAc) is a highly alternating copolymer consisting only of the head-to-tail arrangement[3]. Hence, the methylene protons H_A and H_B are spin-coupled to the methine proton H_X, forming the ABX spin system, as illustrated in *Figure 1*. In the case of the ^{1}H n.m.r. spectrum in DMF-d$_7$, which was previously reported[12], spectral assignment is readily made using only ^{1}H homo-decoupling because the splitting due to vicinal couplings are well resolved from those due to ε-tacticity. For the ^{1}H n.m.r. spectrum in DMSO-d$_6$ solution, the resonance of the methylene H_A proton is completely overlapped by solvent peaks, so that the vicinal coupling constant J_{AX} is estimated by comparison between two methine proton resonances with and without irradiation of H_A, while the vicinal coupling constant J_{BX} and the geminal coupling constant J_{AB} are obtained from the methylene H_B proton resonance. According to the estimated values of J_{AB}, J_{AX} and J_{BX}, the resonances of methylene protons H_A and H_B are computer-simulated by using the LAOCON III program, where the linewidths are taken as 5 Hz for all peaks. Taking into account the ^{13}C n.m.r. result that the ε-isotacticity is 0.5, the calculated spectral patterns due to ε-isotactic (m_ε) and ε-syndiotactic (r_ε) diads are superimposed with equal intensity in the computer-simulated methylene spectra. Here, the chemical shifts $\delta(r_\varepsilon) = 1334.5$ Hz and $\delta(m_\varepsilon) = 1323.5$ Hz are used. The simulated methylene H_B proton resonance in DMSO-d$_6$ solution is in good agreement with the observed one, as shown in *Figure 2*. A similar method for the spin simulation can be applied to the ^{1}H n.m.r. spectrum in DMA-d$_9$ solution. In computer simulation of the methylene proton resonance in DMA-d$_9$, the chemical shifts $\delta(r_\varepsilon)$ and $\delta(m_\varepsilon)$ for the H_A proton are introduced as 1344.6 and 1337.7 Hz, and for the H_B proton as 1391.2

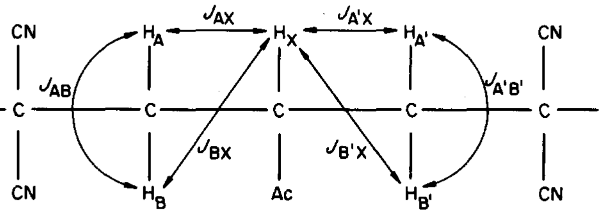

Figure 1 A schematic illustration of the proton–proton spin coupling in the ABX system for P(VDCN/VAc)

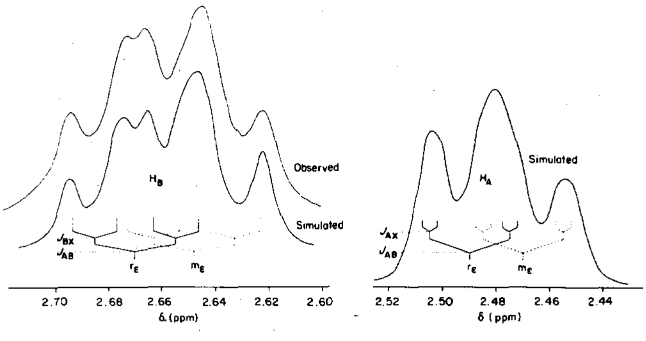

Figure 2 500 MHz ^{1}H n.m.r. spectra of methylene groups of P(VDCN/VAc), observed in DMSO-d$_6$ at 85°C, including the spectra of protons H_A and H_B calculated by the computer simulation

and 1379.0 Hz, respectively. The linewidth is taken as 7.5 Hz. For the case of the methylene proton resonances in DMA-d_9 solution, the vicinal coupling constants J_{AX} and J_{BX} can be obtained from the simulated methylene peaks, as seen in *Figure 3*. The coupling constants J_{AX}, J_{BX} and J_{AB} in DMSO-d_6 and in DMA-d_9 solution, which are obtained from spectral simulation, are summarized in *Table 1*. Here, the results in DMF-d_7 are also included for comparison. Apparently we know that the values of J_{AX} and J_{BX} are different dependent on the solvent. The J_{BX} value is largest in DMSO-d_6, intermediate in DMA-d_9 and smallest in DMF-d_7. The J_{AX} values are almost the same in both DMF-d_7 and DMSO-d_6 solutions, but are smaller than that in DMA-d_9 solution. The vicinal coupling constants have usually been used to analyse the conformation along the main chains of vinyl polymers[14]. With the observed vicinal coupling constants, we consider the conformer distributions under the assumption that the conformation around the H_A–H_BC–CH_X bond in solution comprises three types of preferred conformers denoted *trans* (T), *gauche* (G) and *gauche*$^-$ ($\bar{G}$), as represented in *Figure 4*. Because of rapid interconversion between the above three conformers in solution (the characteristic time of bond rotation at 85°C is much shorter than the reciprocal of the spectral line spacing), the observed J_{AX} and J_{BX} are time-averaged over the three preferred conformers. Referring to the conformer diagrams in *Figure 4*, these can be expressed in terms of J_t and J_g as follows:

$$J_{AX}(\text{obs.}) = X_T J_g + X_G J_t + X_{\bar{G}} J_g \qquad (1)$$

$$J_{BX}(\text{obs.}) = X_T J_t + X_G J_g + X_{\bar{G}} J_g \qquad (2)$$

$$1 = X_T + X_G + X_{\bar{G}} \qquad (3)$$

where the X's represent the mole fractions of the corresponding conformers. As seen in *Figure 4*, J_t and J_g are vicinal coupling constants between H_A and H_X (or H_B and H_X) where the subscripts *t* and *g* indicate *trans* ($\psi = 180°$) and *gauche* ($\psi = 60°$) forms, respectively, with respect to the H–C–C–H bonds. In calculation, J_t and J_g are assumed to be constant, irrespective of the species of not only the conformers but also the solvent used. The values of J_t and J_g are introduced as 11 and 2 Hz, respectively, which are popularly used in a conformational analysis of the vinyl polymer system[14]. Rearranging equations (1)–(3), the conformer populations can be given by the following relationships:

$$X_T = (J_{BX} - J_g)/(J_t - J_g) \qquad (4)$$

$$X_G = (J_{AX} - J_g)/(J_t - J_g) \qquad (5)$$

$$X_{\bar{G}} = (J_t + J_g) - (J_{AX} + J_{BX})/(J_t - J_g) \qquad (6)$$

In *Table 2*, the calculated conformer populations in the three solutions are summarized with respect to both ε-isotactic and ε-syndiotactic sequences. The data of the conformer populations around the H_AH_BC–CH_X bond have the same tendency between ε-isotactic and ε-syndiotactic sequences. The mole fraction of the *trans* conformer is largest in DMSO-d_6, intermediate in DMA-d_9 and smallest in DMF-d_7. In DMSO-d_6 solution the strong preference for the *trans* conformer is noticed, whereas both the *trans* and *gauche* conformers are dominantly populated in DMF-d_7. In DMA-d_9 solution, the intermediate situation is observed. The above

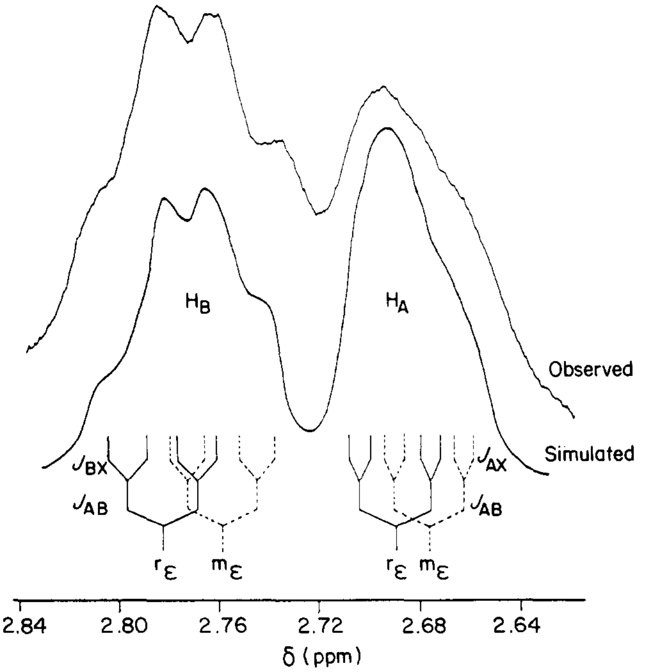

Figure 3 500 MHz ^1H n.m.r. spectra of methylene groups of P(VDCN/VAc), observed in DMA-d_9 at 85°C, including the spectra of protons H_A and H_B calculated by the computer simulation

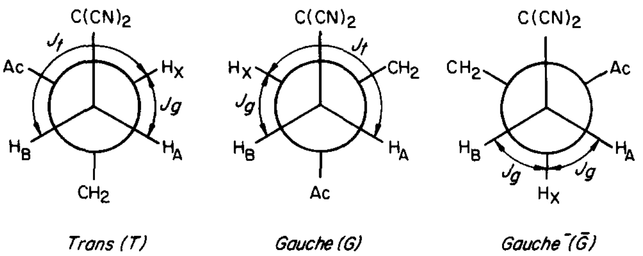

Figure 4 Newman projections along the H_AH_BC–CH_X bond, illustrating the stable conformers in P(VDCN/VAc)

Table 1 Proton–proton coupling constants along the H_AH_BC–CH_X bond of P(VDCN/VAc) in DMF-d_7, DMA-d_9 and DMSO-d_6 solutions measured at 85°C

	ε-Isotactic			ε-Syndiotactic		
J (Hz)	DMF-d_7	DMA-d_9	DMSO-d_6	DMF-d_7	DMA-d_9	DMSO-d_6
J_{AX}[a]	2.5	3.8	2.7	2.6	3.8	2.7
J_{BX}	5.4	7.0	9.5	6.0	7.8	8.3
J_{AB}	−14.2	−14.0	−15.0	−14.2	−14.0	−15.0

[a] The spin system is ABX, as seen in *Figure 1*

Table 2 Conformer populations along the $\mathrm{H_AH_BC{-}CH_X}$ bond in DMF-d_7, DMA-d_9 and DMSO-d_6 solutions at 85°C for P(VDCN/VAc)

Conformer[a]	Mole fraction (%)					
	DMF-d_7		DMA-d_9		DMSO-d_6	
	ε-Iso.	ε-Syn.	ε-Iso.	ε-Syn.	ε-Iso.	ε-Syn.
Trans (*T*)	37.8	44.4	55.6	64.4	83.3	70.0
Gauche (*G*)	5.6	6.7	20.0	20.0	7.8	7.8
Gauche⁻ ($\bar{G}$)	56.6	48.9	24.4	15.6	8.9	22.2

[a] Definition of conformers is referred to *Figure 4*

difference in conformer populations has been seen also in PVDF, although the ^{1}H n.m.r. spectra were measured in the mixed solvent system of MCB and DMSO.[11] The conformer populations were calculated as a function of the volume fraction X_R of MCB. As a result, it was found that the population of the all-*trans* (*TT*) conformation decreases and the population of the *TG* conformation increases with increasing X_R. Thus, the conformation of PVDF is considerably influenced by the polarity of the solvent. In a more polar solvent, polar polymers tend to form a more extended structure due to the dipolar interaction between the solvent and the molecules.

Using the data of conformer population, we can calculate the conformational energy for each conformer state. Assuming that the conformer populations X are determined according to the Boltzmann distribution, then the mole fraction X_i for conformer i can be given as follows:

$$X_i = X_0 \exp(-E_i/NkT) = X_0 \exp(-E_i/RT) \qquad (7)$$

where E_i is the conformational energy for conformer i, N is the Avogadro number, k is the Boltzmann constant, T is the temperature in kelvin, R is the gas constant and X_0 is a constant independent of the conformer species. At a given temperature T, the population ratio of conformers i and j can be expressed as

$$X_i/X_j = \exp[-(E_i - E_j)/RT] \equiv \exp(-\Delta E_{ij}/RT) \qquad (8)$$

Here ΔE_{ij} represents the difference of conformational energy between conformers i and j. Considering the ^{1}H n.m.r. results concerning the conformer population around the $\mathrm{H_AH_BC{-}CH_X}$ bond, the calculated values of ΔE_{ij} can readily be obtained from the following relationship:

$$\Delta E_{ij} = -RT \ln(X_i/X_j) \qquad (9)$$

Putting T in equation (9) equal to 358 K, which is the temperature of the ^{1}H n.m.r. measurement, ΔE_{ij} can be calculated for the different ε-tacticities in DMF-d_7, DMA-d_9 and DMSO-d_6 solutions, as shown in *Figure 5*. In the calculation, all the ΔE_{ij} values are estimated by taking the conformer state as a reference (i.e. conformer j in equation (9) is taken as the *trans* conformer). The G conformer state is more unstable compared with other conformer states in all the solutions. The $\bar{G}$ conformer has low conformational energy in DMF-d_7 but has relatively high conformational energies in DMSO-d_6 as well as in DMA-d_9 solutions.

As discussed earlier, all the proton peaks observed in the ^{1}H n.m.r. spectra of P(VDCN/VAc) are due to alternating sequences of VDCN and VAc units with only the head-to-tail arrangement. Hence, we should note that the chain conformation from the spin analysis is associated not only with the $\mathrm{H_AH_BC{-}CH_X}$ bond but also with the $\mathrm{H_XC{-}CH_{A'}H_{B'}}$ bond, as illustrated in *Figure 1*. Because of the symmetrical molecular structure in the $\mathrm{H_AH_BC{-}CH_X{-}CH_{A'}H_{B'}}$ unit, the mole fractions X' of the three conformers around the $\mathrm{H_XC{-}CH_{A'}H_{B'}}$ bond are also calculated in the same way as for the $\mathrm{H_AH_B{-}CH_X}$ bond. In comparison to X for the mole fractions of the conformers around the $\mathrm{H_AH_BC{-}CH_X}$ bond, the calculated mole fractions X' can be written as $X'_T = X_T$, $X'_G = X_{\bar{G}}$ and $X'_{\bar{G}} = X_G$. Furthermore, we can elucidate the conformations around the $\mathrm{H_AH_BC{-}CH_X{-}CH_{A'}H_{B'}}$ unit. Here, we should note that the number of possible conformers is restricted because of steric hindrance between the acetate and cyanide groups. As a result, the only stable conformers are TT, $TG + \bar{G}T$ and $T\bar{G} + GT$ (TG and $\bar{G}T$ conformers or $T\bar{G}$ and GT conformers are indistinguishable in n.m.r. signals) from the nine conformers. Under the assumption of Bernoullian trials, the conformer populations around the $\mathrm{H_AH_BC{-}CH_X{-}CH_{A'}H_{B'}}$ unit are calculated, which are summarized in *Table 3*. The $TG + \bar{G}T$ and TT are the most preferable conformers in DMF-d_7 and DMSO-d_6 solutions, respectively, while in DMA-d_9 all the possible conformers prevail almost equally. The population data suggest that, on increasing the dielectric constant of the solvent, the main chains of polymers have an extended structure with a dominant fraction of all-*trans* conformation, whereas, on decreasing the dielectric constant of the solvent, the main chains have a helical structure with a conformation mixed with TG (or $\bar{G}T$) and TT conformers. Here, the conformation around the $\mathrm{CH_2{-}C(CN)_2{-}CH_2}$ unit, which cannot be understood by spin analysis, is assumed as TT because of the symmetrical molecular structure. Maybe, if P(VDCN/VAc) is soluble in a less-polar solvent than DMF or DMA, the corresponding structure would be a random coil with a dominant fraction of TG (or $\bar{G}T$) conformation. Especially, the considerable fraction of all-*trans* conformer in DMSO-d_6 solution suggests some significance with respect to the piezoelectric property. In the case of PVDF, high piezoelectricity originates from the all-*trans* conformation of the main chains as well as from the existence of spontaneous polarization in the crystalline structure. Taking into account that P(VDCN/VAc) is amorphous, the conformation of the

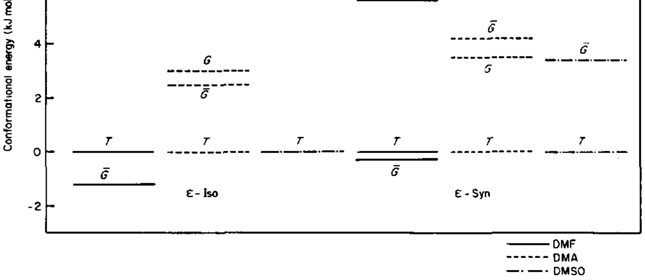

Figure 5 Conformational energies around the $\mathrm{H_AH_BC{-}CH_X}$ bond for the different ε-tacticities in DMF-d_7, DMA-d_9 and DMSO-d_6 solutions at 85°C for P(VDCN/VAc)

Table 3 Conformer populations along the $H_AH_BC–CH_X–CH_{A'}H_{B'}$ unit of P(VDCN/VAc) in DMF-d_7, DMA-d_9 and DMSO-d_6 solutions measured at 85°C

	Mole fraction (%)						
	DMF-d_7		DMA-d_9		DMSO-d_6		
Conformer[a]	ε-Iso.	ε-Syn.	ε-Iso.	ε-Syn.	ε-Iso.	ε-Syn.	Equation[b]
TT	23.3	28.5	38.5	47.5	71.2	53.8	X_T^2/N^c
$TG+\bar{G}T$	69.8	62.9	33.8	23.0	15.2	34.2	$2X_TX_{\bar{G}}/N$
$T\bar{G}+GT$	6.9	8.6	27.7	29.5	13.3	12.0	$2X_TX_G/N$

[a] Conformers of GG (or $\bar{G}\bar{G}$), $G\bar{G}$ and $\bar{G}G$ are excluded because of considerable steric hindrance between acetate and cyanide groups
[b] X values are the mole fraction of the corresponding conformers along the $H_AH_BC–CH_X$ bond
[c] N represents the normalization factor during the Bernoullian trial

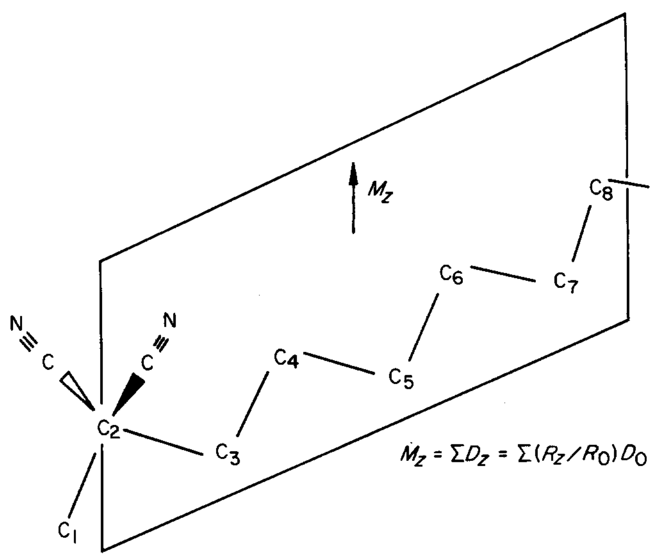

Figure 6 A schematic illustration of the dipole moment in the direction of the $C(CN)_2$ bond dipole for the VDCN–VAc–VDCN–VAc sequence, where D_z is the dipole moment component in the z direction, R_z/R_0 is the direction cosine in the z direction and D_0 is the bond dipole (in debye units)

main chains becomes the major factor in determining piezoelectricity. Because of this amorphous feature the weight-averaged conformation in a P(VDCN/VAc) film cast from solution may correspond to the time-averaged conformation in the solution, if the temperature of casting is far lower than the glass transition temperature (T_g) of P(VDCN/VAc). Consequently, higher piezoelectricity is expected for a film cast from DMSO solution compared with that from DMF and DMA solutions.

In order to elucidate the anisotropy of the dipole moment for the molecular structure of P(VDCN/VAc), we calculate the dipole moment in the direction of the $C(CN)_2$ bond dipole moment for the VDCN–VAc–VDCN–VAc unit, as indicated in *Figure 6*. Because of the poling process the z direction corresponds to the axis parallel to the direction of the film thickness. The calculated data for various conformations along the main chain composed of eight carbons are summarized in *Table 4*. The molecular structure of the all-*trans* conformation has a dipole moment of 6 debye, which amounts to twice that of other conformations. In the calculation, it is also found that the total dipole moment in this direction is considerably reduced by the existence of the carbonyl bond dipole moment in the direction opposite to that of the $C(CN)_2$ bond. (If the carbonyl group is attached to the side chain in such a way that the corresponding dipole moment is in the same direction as the $C(CN)_2$ bond dipole moment, large steric hindrance exists between the methyl group in the side chain and the cyanide group.) If the $C(CN)_2$ dipoles are oriented in the film thickness direction during the polling process, the conformation dependence on the anisotropy of the dipole moment would have an effect on the piezoelectricity.

Table 4 Conformation dependence of the dipole moment in the direction of the $C(CN)_2$ bond dipole for VDCN–VAc–VDCN–VAc unit

	Dipole moment[b] (debye)					
Conformation[a]	CH	CCN	–CO–	CO	$–CH_3$	Total
$TTTTTTTT$	1.39	8.09	1.71	−4.80	−0.34	6.04
$TTTGTTT\bar{G}$	0.46	4.04	0.85	−2.14	0.09	3.30
$TTT\bar{G}TTTG$	0.92	4.04	0.85	−2.44	−0.42	2.95
$GTTT\bar{G}TTT$	0.92	4.04	0.85	−2.44	−0.43	2.96
$\bar{G}TTTGTTT$	0.46	4.04	0.85	−2.14	0.09	3.31

[a] Conformations along the bonds of $C_1–C_2$, $C_2–C_3$, $C_5–C_6$ and $C_6–C_7$ in *Figure 6* are assumed as the *trans* conformation due to the symmetrical property
[b] Dipole moments are calculated from the values of the bond dipole moments

Physical properties of cast films

P(VDCN/VAc) shows strong piezoelectricity, which is based on a large remanent polarization by poling[2]. This is evidenced by a large dielectric relaxation strength resulting from free segmental rotation of several monomers as well as cooperativity in paracrystalline or amorphous phase. Furukawa and coworkers have reported the results of dielectric relaxation and shown that several *trans* sequences with a cooperative movement caused by poling play an important role in the piezoelectricity of P(VDCN/VAc)[15].

The effect of casting solvent on physical properties in a solid film of P(VDCN/VAc) was investigated by measuring the piezoelectric strain constant and the d.s.c. thermograms. Because of the amorphous structure no change was observed in X-ray diffraction and i.r. absorbance.

Table 5 shows the results of the piezoelectric strain constant for poled films cast from DMF, DMA and DMSO solvents. The sample cast from DMSO shows higher piezoelectricity than those from DMF and DMA. Taking into account the ^1H n.m.r. results, an all-*trans*

Table 5 Piezoelectric strain constant d_{31} and dielectric constant ε of P(VDCN/VAc) cast films, measured at 10 Hz and at 20°C

	d_{31} (pC N^{-1})		
Casting solvent	Under 20 MV cm^{-1}	Under 40 MV cm$^{-1\,a}$	ε
DMF	4.0	6.0	4.7
DMA	3.8	6.2	4.8
DMSO	5.4	8.0	4.8

[a] Poled at 170°C

rich conformation is expected in the sample cast from DMSO.

P(VDCN/VAc) has shown a remarkable enthalpy relaxation by annealing below T_g (ref. 16). This phenomenon may be due to the regularity in molecular packing and in chain conformation. In *Figure 7* is shown the d.s.c. thermograms of samples annealed at 167°C for 6 h. The large enthalpy relaxation is seen for the sample cast from DMSO, whereas for the samples from DMA and DMF broad d.s.c. thermograms are seen in the region of T_g. Such a broad curve may be attributed to the distribution of molecular packing, namely, in one region molecules are arranged in a compact packing while in other regions they are in a loose packing. If the molecules are arranged in an extended structure, in general, the corresponding packing becomes compact. Therefore, the molecules with all-*trans* rich conformation would be arranged with a compact packing, resulting in a large enthalpy relaxation.

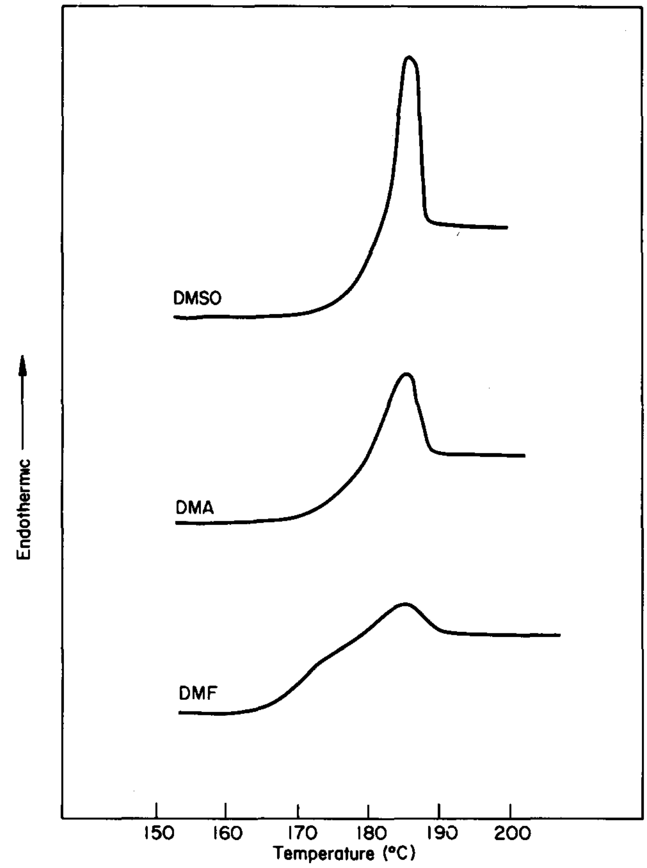

Figure 7 D.s.c. thermograms of P(VDCN/VAc) samples which were cast from DMSO, DMA and DMF solutions (samples annealed at 167°C for 6 h)

CONCLUSIONS

From the data of conformer populations in different solvents we can conclude that the mole fraction of the *trans* conformer along the H_AH_BC–CH_X bond is largest in DMSO-d_6, intermediate in DMA-d_9 and smallest in DMF-d_7. The main chains of P(VDCN/VAc) have an extended structure with increasing polarity of solvents used.

The molecular structure of the all-*trans* conformation along the main chain composed of eight carbons is found to have a dipole moment in the z-direction of 6 debye, which amounts to twice that of other conformations.

For the cast films, it is also found that the molecules with all-*trans* rich conformation, which are obtained from DMSO solution, would be arranged with a compact packing, resulting in a large enthalpy relaxation.

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