Two-dimensional ^1H n.m.r. studies of conformations of piezoelectric vinylidene–cyanide copolymers

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The conformations of the piezoelectric copolymers of vinylidene cyanide with vinyl benzoate, vinyl pivalate and styrene in solution have been investigated using two-dimensional *J*-resolved ^1H n.m.r. spectroscopy. It was found that these copolymers take a predominantly *trans*-rich conformation around the $H_AH_BC{-}CH_X$ bond in deuterated dimethylformamide and in deuterated dimethylsulphoxide solutions, although the piezoelectric d_{31} constant of the styrene copolymer is one order lower than those of the other two copolymers.

(**Keywords:** poly(vinylidene cyanide-*co*-vinyl benzoate); poly(vinylidene cyanide-*co*-vinyl pivalate); poly(vinylidene cyanide-*co*-styrene); piezoelectricity; conformation; ^1H n.m.r.)

INTRODUCTION

Some of the copolymers of vinylidene cyanide (VDCN), such as VDCN copolymers with vinyl acetate, P(VDCN/VAc)[1,2], vinyl benzoate, P(VDCN/VBe)[2] and vinyl pivalate, P(VDCN/PiV)[3], are known to exhibit fairly high piezoelectric activity in the amorphous state. The side-chain cyanide groups, which have large dipole moments, would mainly contribute to the high piezoelectricity of these copolymers. The piezoelectric activity of other amorphous VDCN copolymers, such as VDCN–methyl methacrylate, P(VDCN/MMA)[2], and VDCN–styrene copolymers, P(VDCN/St)[4], is quite low, although they also have side-chain cyanide groups. It was found from n.m.r. analysis that the microstructures of these VDCN copolymers did not differ greatly from each other except for the chemical structure of the comonomer units, namely, they were copolymers with highly alternating and configurationally random sequences[4–7]. Thus, molecular factors other than the microstructure must be considered to explain why only some VDCN copolymers have high piezoelectric activity.

Chain conformation is supposed to be one of the important factors in determining the piezoelectric activity of VDCN copolymers, as copolymers with an all-*trans* main-chain conformation would have the largest resultant dipole moment[8]. According to recent conformational analysis on the basis of a molecular mechanics calculation[9], P(VDCN/VAc) takes predominantly the *trans* conformation around the $C(CN)_2{-}CH_2$ and $CH_2{-}CH(OCOCH_3)$ bonds (*Figure 1*). The preference for the *trans* conformation around the latter bond was experimentally confirmed in solution by ^1H n.m.r. spin analysis through the aid of the two-dimensional *J*-resolved (2D-*J*) technique[10]. The molecular mechanics calculation also predicted that P(VDCN/MMA) preferentially takes the *trans* conformation around the $C(CN)_2{-}CH_2$ and $CH_2{-}C(COOCH_3)(CH_3)$ bonds, but the fraction of *trans* conformation around the latter bond is not larger than that around the corresponding bond in the P(VDCN/VAc). Unfortunately, P(VDCN/MMA) has no proton spin system, which gives experimental information concerning the main-chain conformation. Further investigation is required to elucidate the molecular origins which govern the degree of piezoelectric activity of VDCN copolymers.

In this paper, the conformational characteristics of highly piezoelectric P(VDCN/VBe) and P(VDCN/PiV), and weakly piezoelectric P(VDCN/St) in solution are investigated via 2D-*J* 500 MHz ^1H n.m.r. spectroscopy.

EXPERIMENTAL

The preparation and microstructures of the VDCN copolymers used have been reported elsewhere[4–7]. The details of the 2D-*J* n.m.r. measurements have also been described in a previous paper[10].

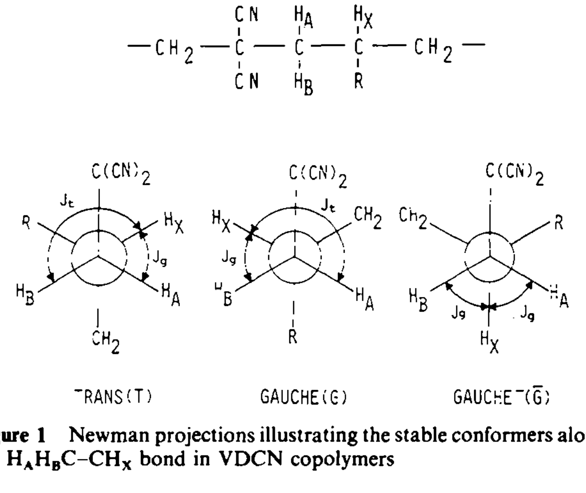

Figure 1 Newman projections illustrating the stable conformers along the $H_AH_BC{-}CH_X$ bond in VDCN copolymers

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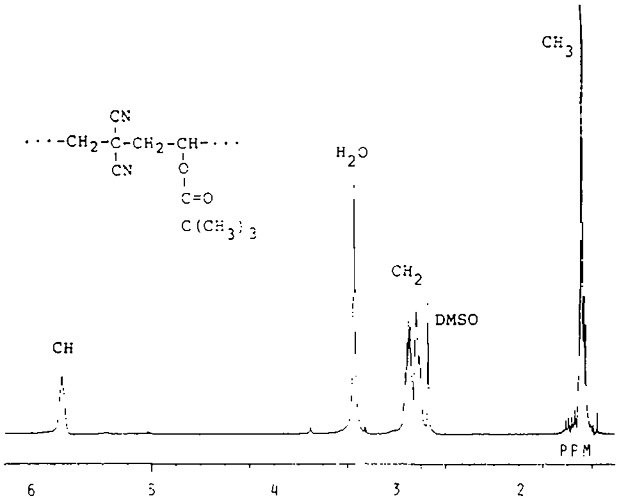

Figure 2 The 500 MHz ^1H n.m.r. spectrum of P(VDCN/PiV) observed at 86°C in 1% (w/v) solution in DMSO-d_6

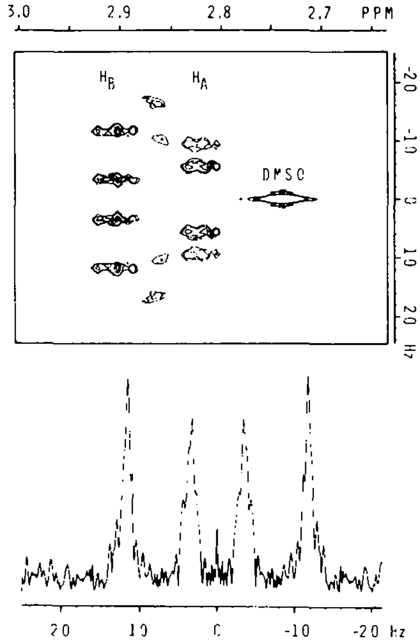

Figure 3 Contour plot of the methylene proton resonance region of the 2D-J spectrum and the cross-section shift parallel to the J axis on the chemical shift axis at 2.92 ppm of P(VDCN/PiV) in DMSO-d_6 solution

RESULTS

Figure 2 shows the 500 MHz ^1H n.m.r. spectrum of P(VDCN/PiV) observed in deuterated dimethylsulphoxide (DMSO-d_6) solution. The corresponding contour plot of the methylene proton resonance region of the 2D-J spectrum is shown in *Figure 3*. Due to the two magnetically non-equivalent methylene protons, H_A and H_B (*Figure 1*), the methylene resonance splits into two components, which are assigned in the same way as before for P(VDCN/VAc)[8,11], i.e. the upper- and lower-field components are assigned to H_A and H_B, respectively.

Owing to the tactic sequence distributions, both components of the methylene proton resonance in the 2D-J spectrum exhibit further splittings, which have different chemical shifts but have almost the same values for the spin coupling constant within the component resonances H_A and H_B. Similar splittings were also observed in the P(VDCN/VAc) spectra and were tentatively assigned to the syndiotactic and isotactic diad sequences, although the assignments are not yet well established. The values of the vicinal (J_{AX}, J_{BX}) and geminal (J_{AB}) coupling constants may be precisely determined by taking the cross-section parallel to the J axis of the 2D-J spectrum at a distinct location on the chemical shift axis. For example, *Figure 3* shows the cross-section parallel to the J axis on the chemical shift axis at 2.92 ppm, indicating splittings due to the H_A–H_B and H_B–H_X spin couplings of the lowest-field peak of the H_B resonance. A weak resonance at ~2.86 ppm in the 2D-J spectrum, which could not be detected in the one-dimensional (1D) spectrum, is unidentified. A corresponding resonance could not be found in the 2D-J and 1D spectra of P(VDCN/PiV) in deuterated dimethylformamide (DMF-d_7) (*Figure 4*).

Figures 4–8 show the 1D normal and the 2D-J ^1H n.m.r. spectra of P(VDCN/PiV) in DMF-d_7, P(VDCN/VBe) in DMSO-d_6 and in DMF-d_7, and P(VDCN/St) in DMSO-d_6 and in DMF-d_7. In the 1D spectrum of P(VDCN/PiV) in DMF-d_7, the resonance of methylene protons of P(VDCN/PiV) largely overlaps with that of residual protons of the solvent, but the spin-coupling information can be confidently obtained from the 2D-J spectrum, as shown in *Figure 4*. The H_B component of the methylene resonance of P(VDCN/St) in the 2D-J spectra in both solvents (*Figures 7* and *8*) exhibits more than two split peaks, indicating that this is resolved due to the tactic structures longer than the diad sequence. These split peaks have almost the same spin coupling characters.

The spin coupling constants observed in the 2D-J spectra are shown in *Table 1*, where the values averaged over the coupling constants of component peaks are listed for the tactically split resonances.

By assuming that the conformation around the methylene–methine bond in solution is the time-average of the three preferred conformers, denoted *trans*(T), *gauche*(G), and another *gauche*($\bar{G}$), the observed vicinal coupling constants J_{AX} and J_{BX} are expressed as (*Figure 1*):

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

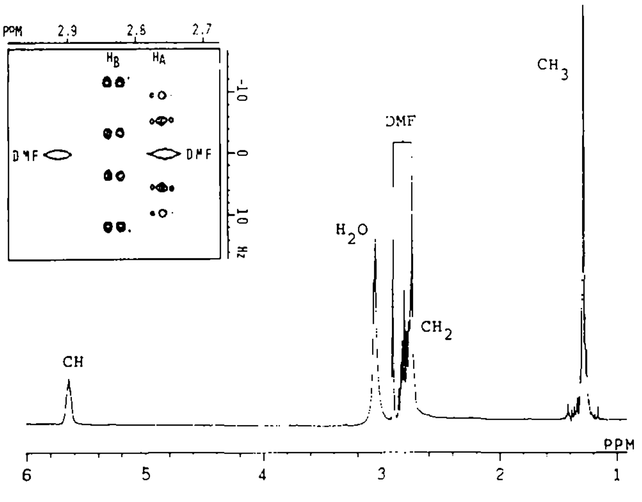

Figure 4 The 500 MHz ^1H n.m.r. spectrum of P(VDCN/PiV) observed at 86°C in 1% (w/v) solution in DMF-d_7 and corresponding contour plot of the methylene proton resonance region of the 2D-J spectrum (inset)

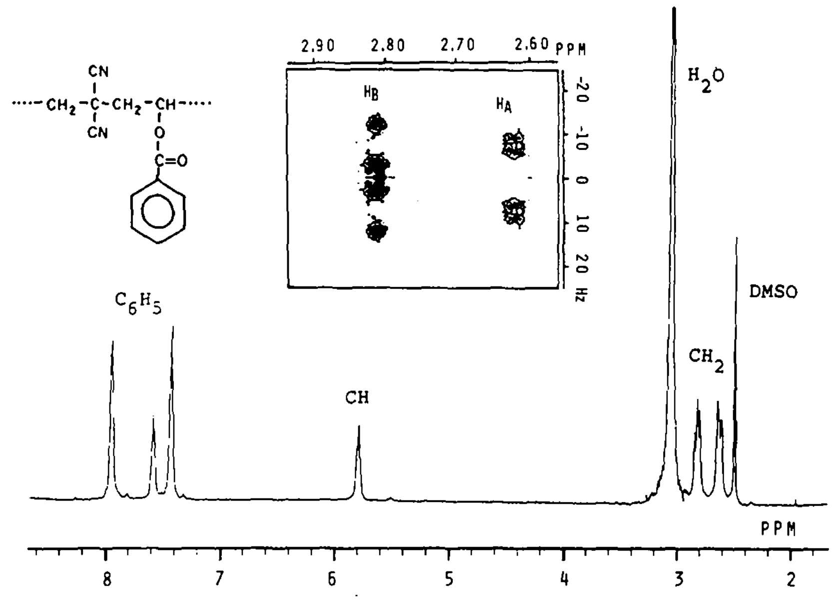

Figure 5 The 500 MHz ^1H n.m.r. spectrum of P(VDCN/VBe) observed at 86°C in 1% (w/v) solution in DMSO-d_6 and corresponding contour plot of the methylene proton resonance region of the 2D-*J* spectrum (inset)

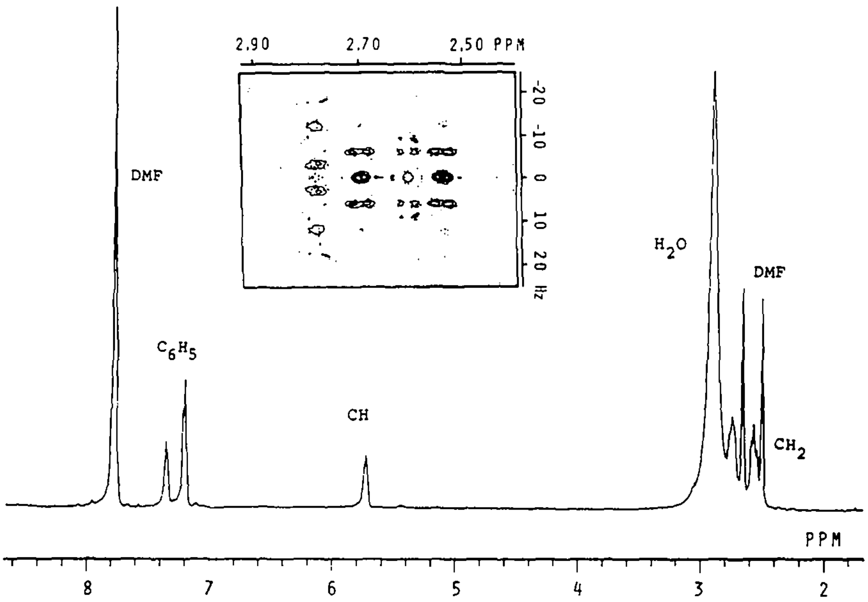

Figure 6 The 500 MHz ^1H n.m.r. spectrum of P(VDCN/VBe) observed at 86°C in 1% (w/v) solution in DMF-d_7 and corresponding contour plot of the methylene proton resonance region of the 2D-*J* spectrum (inset)

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

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

where the subscripts t and g indicate *trans* and *gauche* forms, respectively, with respect to the $H_AH_BC-CH_X$ bonds. The J_t and J_g values are assumed to be 11 and 2 Hz, which are the values generally used in conformational analysis of vinyl polymers[12].

Rearranging equations (1)–(3), the conformer fractions can be estimated as follows:

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

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

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

In the case of P(VDCN/St), the values of the fraction $X_{\bar{G}}$ in both DMSO-d_6 and DMF-d_7 solutions become negative, according to equation (6), because the sum $J_{AX} + J_{BX}$ is larger than the sum $J_t + J_g$ (= 13 Hz). Here, for P(VDCN/St) the fraction of conformer $\bar{G}$ is tentatively assumed to be zero, and the fractions X_T and X_G are normalized so that the sum of X_T and X_G is equal to 100%. *Table 2* gives the calculated conformer fractions.

DISCUSSION

According to the simple calculation for the P(VDCN/VAc) segments shown elsewhere[8], the dipole moment of the all-*trans* chain amounts to twice that of the other

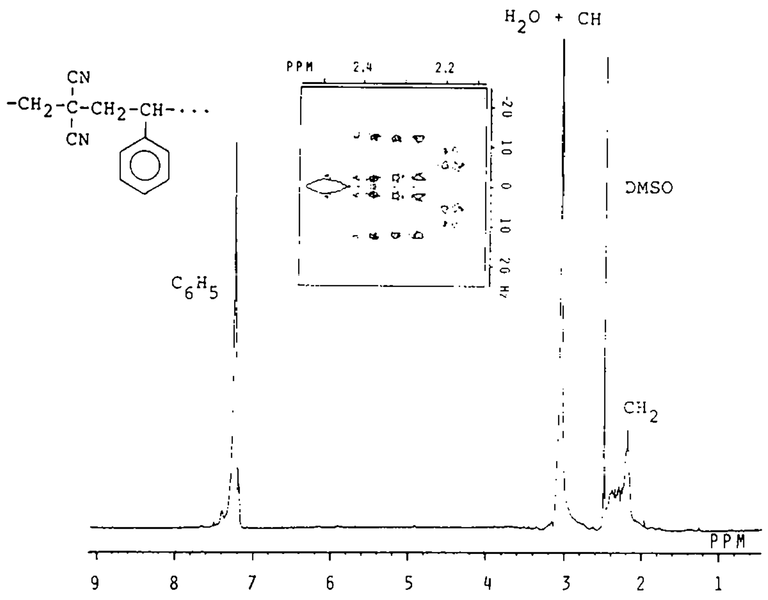

Figure 7 The 500 MHz ^1H n.m.r. spectrum of P(VDCN/St) observed at 86°C in 1% (w/v) solution in DMSO-d_6 and corresponding contour plot of the methylene proton resonance region of the 2D-*J* spectrum (inset)

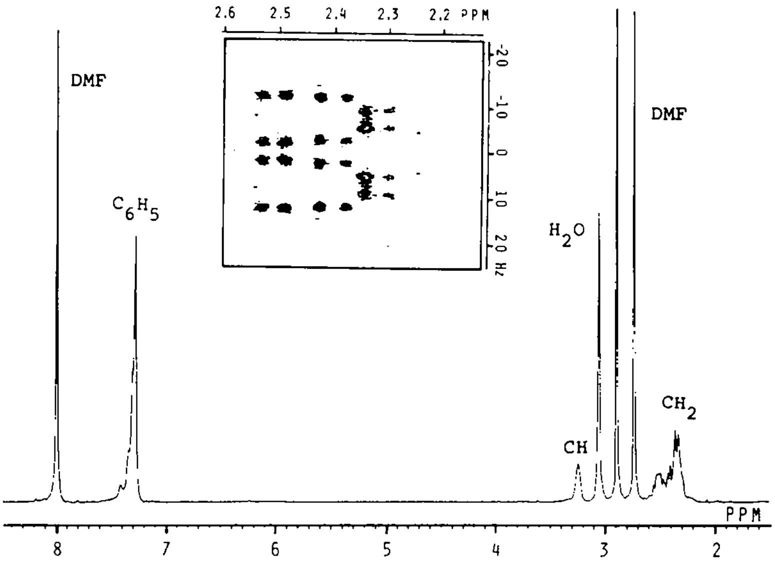

Figure 8 The 500 MHz ^1H n.m.r. spectrum of P(VDCN/St) observed at 86°C in 1% (w/v) solution in DMF-d_7 and corresponding contour plot of the methylene proton resonance region of the 2D-*J* spectrum (inset)

Table 1 Proton coupling constants for the H_AH_BC–CH_X spin system of VDCN copolymers

		J (Hz)		
Copolymers	Solvents	J_{AX}	J_{BX}	J_{AB}
P(VDCN/PiV)	DMSO-d_6	4.0	8.3	−15.1
	DMF-d_7	4.1	8.2	−15.0
P(VDCN/VBe)	DMSO-d_6	2.7	8.8	−14.5
	DMF-d_7	2.7	8.5	−14.7
T				
P(VDCN/St)	DMSO-d_6	3.9	10.2	−15.1
	DMF-d_7	3.7	10.0	−15.1

Table 2 Conformer populations along the H_AH_BC–CH_X bond of VDCN copolymers

		Fraction (%)		
Copolymers	Solvents	*Trans* (*T*)	*Gauche* (*G*)	*Gauche* ($\bar{G}$)
P(VDCN/PiV)	DMSO-d_6	70.0	22.2	7.8
	DMF-d_7	68.9	23.3	7.8
P(VDCN/VBe)	DMSO-d_6	75.6	7.8	16.6
	DMF-d_7	72.2	7.8	20.0
P(VDCN/St)	DMSO-d_6	81.2	18.8	0.0
	DMF-d_7	82.5	17.5	0.0

conformations containing *gauche* bonds. Thus, the main-chain conformation should play an important role in inducing high piezoelectric activity. The results shown in *Table 2* indicate that not only the highly piezoelectric P(VDCN/PiV) and P(VDCN/VBe) but also the weakly piezoelectric P(VDCN/St) copolymers take predominantly the *trans*-rich conformation around the $H_AH_BC-CH_X$ bond in both solvents. The trends are in general accord with those previously found for highly piezoelectric P(VDCN/ VAc) by the 2D-*J* n.m.r. method[10] and by the molecular mechanics calculation[9] and for weakly piezoelectric P(VDCN/MMA) by the molecular mechanics calculation[9]. Hence, it may be difficult to relate directly the preference of the *trans* conformation in solution to the piezoelectric activity in the solid state, although the solvent-dependent conformation in solution is reflected more or less in the piezoelectricity of solid film cast from solution[8].

In order to attain high piezoelectricity, the $C(CN)_2$ dipoles of VDCN copolymers should be aligned in the film thickness direction. It is possible to force the dipole to align in the film thickness direction by applying high direct current (d.c.) electric field, namely, by poling treatment. In the case of VDCN copolymers, high piezoelectric activity is achieved only after drawing followed by simultaneous poling and annealing treatments at higher temperatures but just below the glass transition temperature (T_g)[1]. The T_g of VDCN copolymers is generally high. For example, the T_gs of P(VDCN/VAc) and P(VDCN/VBe) are ~170 and ~180°C, respectively[2]. The aligned dipoles attained by the poling/annealing treatments of the films under the d.c. field at a temperature near T_g are expected to remain almost unchanged after quenching to room temperature, if the d.c. electric field is continuously applied during quenching. If this is true, the magnitude of the resultant piezoelectric activity should depend on the extent of the d.c. field forced dipole alignment during the poling/annealing treatments. Here, chain flexibility or mobility is suggested to be important in determining dipole alignment, and hence the magnitude of piezoelectricity. The chain flexibilities of P(VDCN/St) and P(VDCN/MMA) should be low compared with the highly piezoelectric VDCN copolymers, as the former have a bulkier side-chain directly bonded to the backbone. The results of n.m.r. conformational analysis for P(VDCN/St) presented here seem to support this supposition. Namely, the suppression of one of three conformers, i.e. $\bar{G}$ around the $H_AH_BC-CH_X$ bond indicates the limited flexibility of this bond, although the discussion on chain flexibility based on the conformer fractions is not rigorous due to the assumption made for their determinations. Experimental and theoretical studies of chain flexibility of some VDCN copolymers are now in progress.

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