Conformational analysis of piezoelectric vinylidene cyanide–vinyl acetate copolymer via two-dimensional J-resolved ^{1}H nuclear magnetic resonance spectroscopy

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The conformations of the piezoelectric copolymer of vinylidene cyanide and vinyl acetate in solution have been investigated by using two-dimensional J-resolved ^{1}H nuclear magnetic resonance spectroscopy. It was found that this copolymer takes predominantly *trans*-rich conformation around the $H_AH_BC–CH_X$ bond in deuterated dimethylformamide as well as in deuterated dimethylsulphoxide solutions, although the preference for the *trans* conformer in the former solution is not so strong as in the latter solution.

INTRODUCTION

The copolymer of vinylidene cyanide and vinyl acetate, P(VDCN/VAc), has received much attention because it has high piezoelectricity, notwithstanding the amorphous state[1,2]. From the ^{13}C n.m.r. analysis of microstructure[3], it was found that P(VDCN/VAc) is a highly alternating copolymer with completely atactic configuration with respect to the side-chain of VAc unit. The main-chain conformation is considered to be an essential factor in determining the extent of piezoelectric activity for the amorphous polymer. If the main chain of P(VDCN/VAc) has an all-*trans* conformation, the dipoles of cyanide groups, which of course are the chemical origin of high piezoelectricity, align regularly and it would exhibit high piezoelectricity[4].

Previously, we have analysed the conformation of P(VDCN/VAc) in some polar solvents by using 500 MHz ^{1}H n.m.r. spectroscopy[4,5], since the preferred conformation of P(VDCN/VAc) in the film was expected to reflect that in the solution from which the film was cast. The main findings were that the mole fraction of the *trans* conformer (T) along the $H_AH_BC–CH_X$ bond (*Figure 1*) is overwhelmingly large (83.3 and 70.0 mol% for isotactic and syndiotactic sequences, respectively) in deuterated dimethylsulphoxide (DMSO-d$_6$), while in deuterated dimethylformamide (DMF-d$_7$) the dominant conformer is not the *trans* (37.8 and 44.4 mol%, respectively) but the *gauche* (G) one (56.6 and 48.9 mol%). These results explain qualitatively the observed casting-solvent-dependent piezoelectric strain constant d_{31}, i.e. the d_{31} value is larger for the film cast from DMSO than that from DMF.

Recently[6], we have investigated the conformational characteristics of P(VDCN/VAc) on the basis of molecular mechanics calculation, which predicted that P(VDCN/VAc) takes predominantly a *trans* conformation around the $H_AH_BC–CH_X$ bond irrespective of the chain

configuration. This prediction is in good agreement with the ^{1}H n.m.r. result obtained in DMSO-d$_6$ solution but not with that in DMF-d$_7$ solution. The n.m.r. results include possible ambiguity, since the methylene proton resonances, which have been used in the conformational analysis, indicate complicated line shapes, as shown in *Figure 2*, due to the splittings not only by the geminal and vicinal spin–spin couplings but also by the configurational heterogeneity. Spectral analysis, even with the aid of computer simulation, was also hampered by the severe overlapping of the residual proton resonances of solvents.

In the present work, the conformation of P(VDCN/VAc) in DMSO-d$_6$ and DMF-d$_7$ solutions is reinvestigated via two-dimensional J-resolved (2D-J) 500 MHz ^{1}H n.m.r. spectroscopy. In the 2D-J spectra, the splittings due to the spin–spin couplings can be easily discriminated from those due to the difference in stereochemical configuration. Further, the analysis of 2D-J spectrum is not hampered by the solvent resonance.
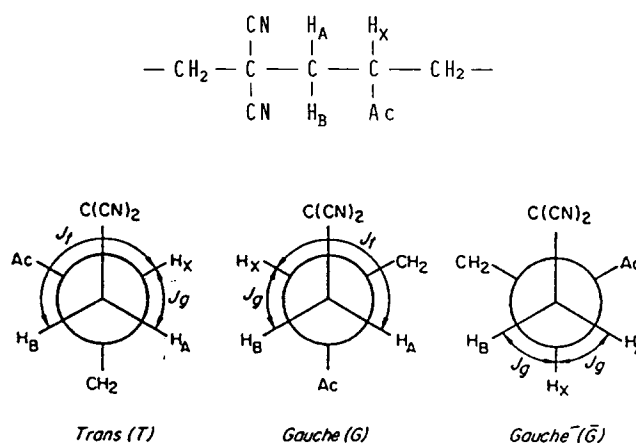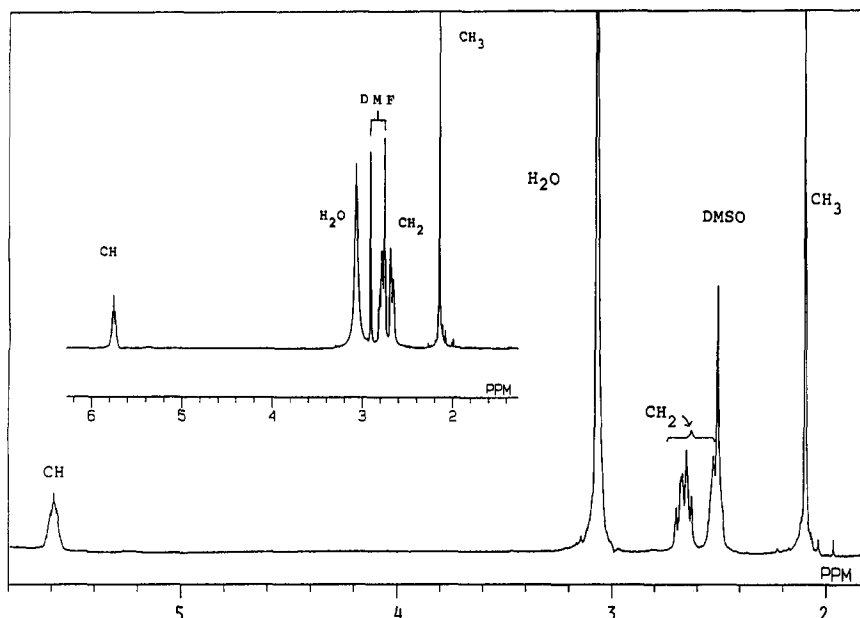

Figure 1 Newman projections illustrating the stable conformers along the $H_AH_BC–CH_X$ bond in P(VDCN/VAc)

**Figure 2** 500 MHz ¹H n.m.r. spectra of P(VDCN/VAc) observed at 86.5°C in 1% (w/v) solutions in DMSO-d₆ and DMF-d₇ (inset)

EXPERIMENTAL

The P(VDCN/VAc) sample used here was the same as that reported in the previous papers[3-5]. ¹H n.m.r. spectra were observed on a Jeol GX-500 spectrometer operated at 500 MHz and 86.5°C in solutions of DMSO-d₆ and DMF-d₇ with sample concentration of 1 w/v% in a 5 mm o.d. sample tube. The 2D-J spectra were observed using the standard pulse sequence and data processing procedures equipped on the spectrometer. The digital resolution in the 2D-J spectra was 2.44 Hz and 0.2 Hz in the axes of chemical shifts and coupling constants, respectively.

RESULTS AND DISCUSSION

Figures 3 and *4* show the contour plots of methylene proton resonance regions of the 2D-J 500 MHz ¹H n.m.r. spectra of P(VDCN/VAc) in DMSO-d₆ and DMF-d₇ solutions, respectively. The 2D-J resonances of copolymer represented by the contour plots are not hampered by the solvent resonances and the values of coupling constant can be read straight away. Each methylene resonance splits into two parts, corresponding to the presence of two magnetically non-equivalent methylene protons, H_A and H_B (*Figure 1*). The assignments of the upper- and lower-field components in each spectrum had not been well established, although in the previous papers[4,5] they have been assigned to H_A and H_B protons, respectively, as shown in *Figures 3* and *4*. The molecular mechanics calculation predicted that P(VDCN/VAc) takes overwhelmingly a *trans* conformation around the H_AH_BC–CH_X bond[5]. As will be seen later, the *trans* conformer is found to be predominant in accord with the prediction of the molecular mechanics calculation when the two components of the methylene resonance are assigned as shown in *Figures 3* and *4*.

Each resonance of A and B methylene protons in the 2D-J spectra exhibits further two clearly split peaks different in chemical shifts, indicating that the methylene resonances are resolved at the level of diad tactic
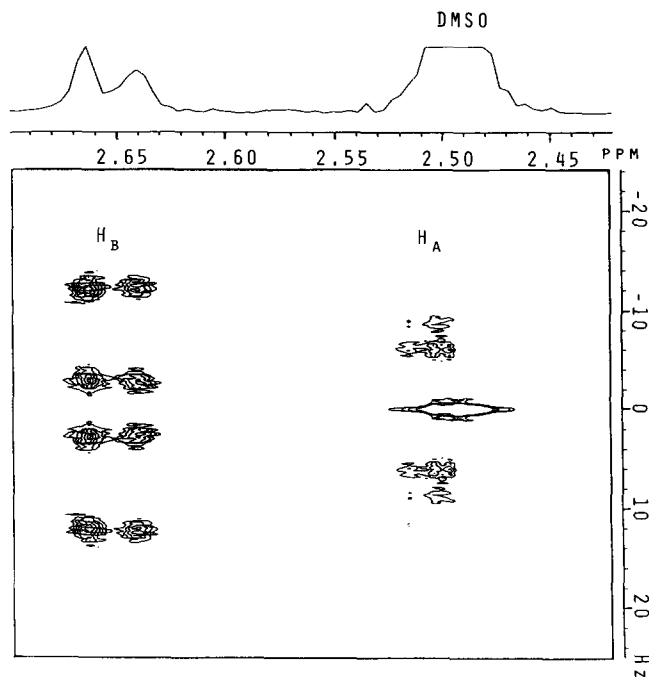
Figure 3 Contour plot of the methylene resonance region of the 2D J-resolved spectrum of P(VDCN/VAc) in DMSO-d₆ solution at 86.5°C

sequence. Although the assignments related to the tactic structure are also not yet well established, the lower- and upper-field peaks of each resonance are tentatively assigned to the ε-syndiotactic ($r_ε$) and ε-isotactic ($m_ε$) diad sequences, respectively, in a way similar to that shown in the previous papers[3,4].

The values of vicinal (J_{AX}, J_{BX}) and geminal (J_{AB}) coupling constants observed in the 2D-J spectra were verified by calculating the normal ¹H n.m.r. spectra by using the observed J values[3,4]. An example is shown in *Figure 5*. By assuming that the conformation around the H_AH_BC–CH_X bond in solution can be represented by a combination of three types of preferred conformers as shown in *Figure 1*, the mole fractions X of the conformers
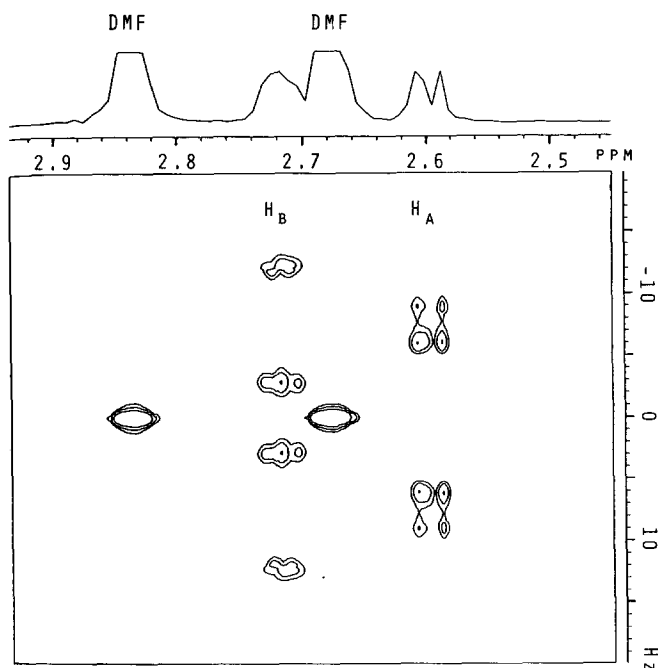
Figure 4 Contour plot of the methylene resonance region of the 2D *J*-resolved spectrum of P(VDCN/VAc) in DMF-d₇ solution at 86.5°C
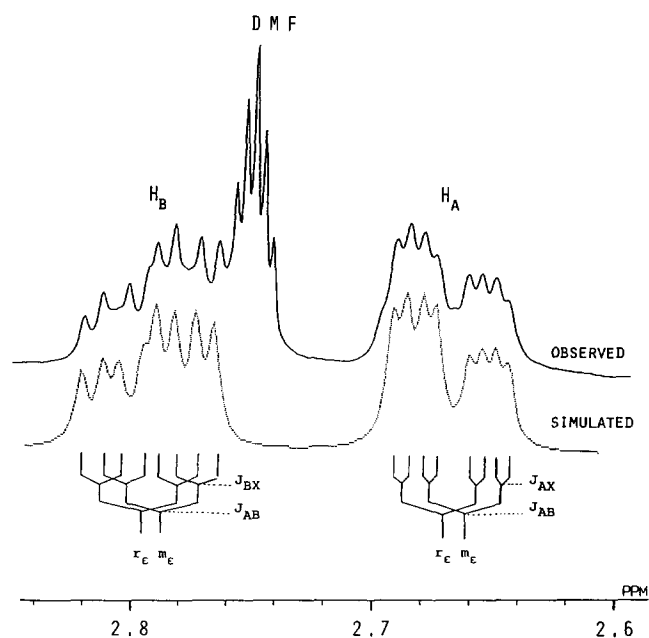

Figure 5 Methylene resonance region of 500 MHz ¹H n.m.r. spectrum of P(VDCN/VAc) in DMF-d₇ at 86.5°C, including simulated H_A and H_B methylene proton resonances

Table 1 Proton coupling constants and conformer populations along the $H_A H_B C-CH_X$ bond of P(VDCN/VAc) in DMSO-d₆ and DMF-d₇ solutions at 86.5°C

Solvents		*J* (Hz)			Fraction (%)		
		J_{AX}	J_{BX}	J_{AB}	Trans (*T*)	Gauche (*G*)	Gauche⁻ ($\bar{G}$)
DMSO-d₆	ε-iso	2.8	10.1	−14.0	90.0	8.9	1.1
	ε-syndio	2.7	8.5	−15.2	72.2	7.8	20.0
DMF-d₇	ε-iso	2.7	8.8	−15.0	75.6	7.8	16.6
	ε-syndio	2.8	8.2	−14.0	66.7	8.9	24.4

are estimated from the observed vicinal coupling constants as follows:

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

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

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

where J_{AX} and J_{BX} are vicinal coupling constants between H_A or H_B and H_X and the subscripts *t* and *g* indicate *trans* and *gauche* forms, respectively, with respect to the H–C–C–H bonds. The J_t and J_g values are assumed to be 11 and 2 Hz[7].

In *Table 1* are shown the observed coupling constants and the calculated conformer fractions. The data indicate that, in DMF-d₇ as well as in DMSO-d₆ solutions, the ε-isotactic and ε-syndiotactic sequences have the same conformer preference around the $H_A H_B C-CH_X$ bond, namely both sequences take the predominantly *trans*-rich conformation. The new data of conformer fractions in DMSO-d₆ solution are not very different from the previously reported ones.

Although the results in DMF-d₇ solution obtained from the 2D-*J* spectrum are in contrast with those from the previous 1D ¹H n.m.r. analysis[3,4], the fractions of

trans conformer with ε-isotactic and ε-syndiotactic sequences in DMSO-d₆ solution are larger than those with corresponding tactic sequences in DMF-d₇ solution. Thus, the new data still explain qualitatively the observed casting-solvent-dependent piezoelectric strain constants d_{31} as described above. Conformational analyses based on 2D-*J* n.m.r. are now in progress for other VDCN copolymers.

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