Chain conformation in poly(vinylidene cyanide–vinyl acetate): solid state and solution 2D and 3D n.m.r. studies

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D.s.c. and n.m.r. in dilute solution and in the solid state are used to study chain conformation in poly(vinylidine cyanide–vinyl acetate) [P(VDNCN–VAc)], a highly alternating piezoelectric copolymer, in order to relate the molecular and macroscopic properties. The piezoelectricity as well as the temperature and breadth of the glass transition depends strongly on the casting solvent [dimethyl sulphoxide (DMSO) *versus* *N*,*N*-dimethyl formamide (DMF)] for P(VDNCN–VAc) films. Solvent effects on chain conformation are measured using through-space dipolar interactions and through-bond *J* couplings by high resolution n.m.r. in dilute solution via 2D and 3D n.m.r. The results show that P(VDNCN–VAc) exists in a predominantly *trans* conformation in both DMF and DMSO solution. No solvent effects on the ^{13}C chemical shifts are observed in films cast from DMSO or DMF, while the molecular mobility, as measured by n.m.r. relaxation, depends strongly on the casting solvent.

(Keywords: 2D n.m.r.; 3D n.m.r.; poly(vinylidine cyanide–vinyl acetate); piezoelectric)

INTRODUCTION

The molecular interactions between polymer chains are an important factor in determining the macroscopic properties of polymeric solids[1]. For this reason, spectroscopic techniques capable of probing polymer structure at the molecular level, such as n.m.r.[2,3] and optical spectroscopy[4], have been extensively used to characterize the structure and conformation of polymers both in solids and in solution. In addition to intra- and intermolecular interactions, the solvents used for casting films may also affect the behaviour of materials. Solvents can affect miscibility in blends[5], as well as the preferred conformation and the molecular mobility of polymers[3].

In this study we investigate the behaviour of poly(vinylidine cyanide–vinyl acetate) [P(VDNCN–VAc)] in solutions with different solvents, and in films cast from these solvents. P(VDNCN–VAc) (*Scheme 1*) is a highly alternating, amorphous copolymer with piezoelectric properties that are attributed to the vinylidine cyanide group with its large dipole moment[6–9]. Alternating copolymers have been investigated because homopolymeric vinylidine cyanide undergoes chain scission in the presence of oxygen at room temperature[10]. Of the vinylidine cyanide copolymers that have been synthesized and characterized (vinyl acetate, vinyl benzoate, methyl methacrylate, styrene), P(VDNCN–VAc) shows the most promising piezoelectric properties[11,12]. The n.m.r. microstructure analysis shows that P(VDNCN–VAc) is atactic[10,11], and X-ray diffraction demonstrates that the P(VDNCN–VAc) powders and films are amorphous[6,13]. However, both the thermal behaviour and the piezoelectricity depend on the sample history and casting solvent, and it has been suggested that this behaviour is related to solvent effects on the chain conformation of P(VDNCN–VAc)[7,14,15]. The polymer main chain conformation determines the relative orientations of the vinylidine cyanide groups and the resulting polymer dipole moment. The dipole moment for the all *trans* conformation is double the value calculated for any conformation with *gauche* states[8].

High resolution n.m.r. in dilute solution and cross-polarization with magic angle spinning (CP/MAS) n.m.r. in the solid state are used to study the relationship between the polymer conformation and dynamics and the behaviour of films. N.m.r. as employed here uses four probes of polymer structure and dynamics; through-space dipolar interactions, through-bond *J* couplings, ^{13}C chemical shifts and n.m.r. relaxation. Polymers such as P(VDNCN–VAc) are mobile in solution as a result of *gauche–trans* isomerizations and segmental chain motions[3,16], so the dipolar couplings, the *J* couplings and the ^{13}C chemical shifts are determined in part by the time-averaged structure that is defined by the populations of rotational isomers. In contrast, the n.m.r. relaxation depends not on the structure, but on the molecular dynamics. Solvent effects on the thermal and piezoelectric properties of P(VDNCN–VAc) are interpreted in light of these n.m.r. results.

MATERIALS AND METHODS

The protonated and deuterated solvents were obtained from Aldrich and used without purification.

The P(VDNCN–VAc) films were cast from solvent [33 wt% in dimethyl sulphoxide (DMSO) or *N*,*N*-dimethyl formamide (DMF)] at 85°C under a nitrogen atmosphere. The films were annealed for 5 days at 180°C under vacuum to remove all traces of solvent as determined by t.g.a. No residual solvent was detected in the polymer powder as received, and both the powder and the solvent-free heat-treated films degrade at 350°C.

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T.g.a. and d.s.c. data were obtained using a Perkin–Elmer TGS-7 thermogravimetric analyser and a DSC-4 calorimeter. The heating rate was 10°C min^{-1} for all thermal scans.

^{1}H n.m.r. spectra in dilute solution (1–2 wt%) were obtained at 500 MHz on a Jeol GX-500 n.m.r. spectrometer. The data were transferred to a Micro Vax-II computer for data processing with Fortran programs and with the n.m.r. data processing package FTNMR (Hare Research Inc.). Phase-sensitive nuclear Overhauser effect (NOESY) spectra[17,18] were obtained using the $(\pi/2 - t_1 - \pi/2 - \tau_m - \pi/2 - t_2)$ pulse sequence with mixing times of 0.05, 0.25 and 0.5 s. In a typical experiment, 256 complex points were acquired in the t_1 dimension and 512 complex points in the t_2 dimension; 4 Hz line broadening was used in each dimension and the spectra were zero filled to a final size of 1K × 1 K. The sweep widths in both dimensions were 3 kHz (DMSO) or 5 kHz (DMF).

3D NOE/*J*-resolved n.m.r. spectra were acquired using the $(\pi/2 - t_1 - \pi/2 - \tau_m - \pi/2 - t_2/2 - \pi - t_2/2 - t_3)$ pulse sequence[19,20] with a mixing time of 0.5 s. A total of 128, 32 and 256 complex points were acquired in the t_1, t_2 and t_3 dimensions. After processing along the t_1 and t_3 dimensions, cross-sections at a particular frequency were extracted, zero filled to 256 points, and Fourier transformed to give the *J* coupling pattern.

Solid state n.m.r. spectra were obtained on a Varian XL-200 at 50 MHz using CP/MAS[2,3]. The CP contact time was 2 ms and the spinning speeds were 3 kHz for the powder and 1.5 kHz for the films. Carbon spin-lattice relaxation times were measured with the $(\text{CP} - \pi/2 - \tau - \pi/2\text{-acquire})$ inversion–recovery pulse sequence[21], where τ is the magnetization recovery period.

RESULTS

D.s.c. and several n.m.r. methods are used to measure solvent effects on chain conformation, dynamics and intermolecular chain organization in P(VDNCN–VAc). N.m.r. is used as a tool in these studies to probe the environment of individual carbon and proton atoms along the polymer chain. The observable macroscopic properties, such as solvent effects on the piezoelectricity and the d.s.c., are related to these molecular level properties.

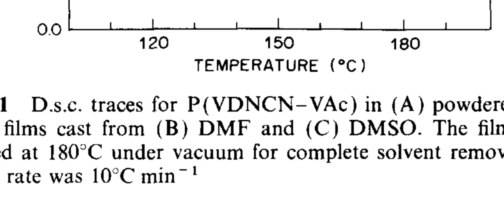


Figure 1 D.s.c. traces for P(VDNCN–VAc) in (A) powdered form and in films cast from (B) DMF and (C) DMSO. The films were annealed at 180°C under vacuum for complete solvent removal. The heating rate was 10°C min^{-1}

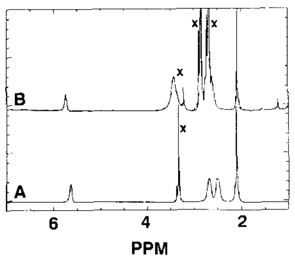
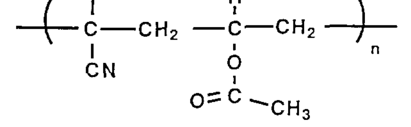


Figure 2 500 MHz ^{1}H n.m.r. spectra of P(VDNCN–VAc) (2 wt%) in deuterated (A) DMSO and (B) DMF. The residual solvent lines are marked ×



Scheme 1

Differential scanning calorimetry

The glass transition (T_g) of P(VDNCN–VAc) films depends on the casting solvent and sample history, and it has been suggested that this behaviour results from solvent effects on chain conformation[7,14,15]. *Figure 1* shows the d.s.c. traces for P(VDNCN–VAc) in powdered form and for films cast from DMSO and DMF. The powdered sample shows a T_g at 175°C with a characteristic enthalpy relaxation peak[22,23]. The films cast from DMSO and DMF show a decrease in T_g and an increase in the breadth of the transition. Initially the films were prepared as described in a previous publication[7]. However, these casting conditions are insufficient to remove all the residual solvent as judged by t.g.a. The samples in *Figure 1* were annealed at 180°C for 5 days under vacuum to remove all traces of solvent.

^{1}H n.m.r. studies

Figure 2 shows the 500 MHz ^{1}H n.m.r. spectra of P(VDNCN–VAc) (2 wt%) in DMSO_{d6} and DMF_{d7} solution. There are three resonances of interest that can be assigned to the methine (5.7 ppm), methylene (2.5–2.8 ppm) and methoxyl (2.1 ppm) protons of P(VDNCN–VAc) (*Scheme 1*). In addition, the spectra contain residual solvent resonances (DMSO, 2.49 ppm; DMF, 8.01, 2.91 and 2.74 ppm) and a signal from residual H_2O (3.2–3.4 ppm). The overlap of the solvent with the methylene protons severely limits the conformational analysis by 1D n.m.r.[7,14,15]. The methine resonances are not overlapped with any solvent or polymer peaks, but are inhomogeneously broadened by stereosequence effects on the chemical shifts[24], and the high resolution spectral features, such as the through-bond coupling to the methylene protons, cannot be resolved.

2D n.m.r. analysis

Figure 3 shows the 2D NOESY spectrum[17] of P(VDNCN–VAc) in DMF_{d7} acquired with a 0.5 s mixing time. In addition to the diagonal peaks, the well resolved cross peaks marked A and B are detected between the methine and methylene protons. As in previous ^{1}H n.m.r. studies of P(VDNCN–VAc)[7,14,15],

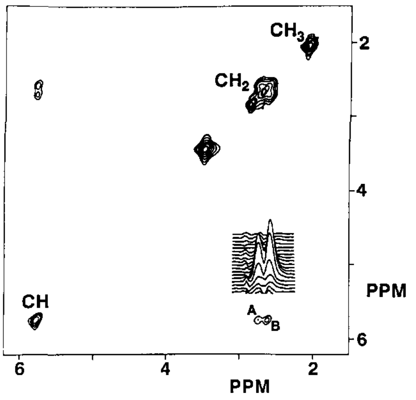
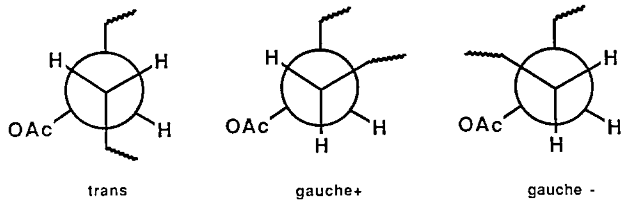


Figure 3 2D NOESY spectrum of P(VDNCN–VAc) in DMF acquired with a 0.5 s mixing time at 20°C. The inset shows a stacked plot of the methine–methylene cross peaks marked A and B



Scheme 2

the signals at 2.75 and 2.62 ppm are assigned to the geminal methylene protons. This assignment is supported by the unresolved cross peak connecting these resonances that is more clearly resolved in the NOESY spectrum in $DMSO_{d6}$ solution (not shown). The geminal cross peak has a larger intensity than the methine–methylene cross peak, as expected from the shorter internuclear distance of the geminal pair (1.8 *versus* 2.2–2.6 Å).

Polymer chain conformation can be determined by NOESY spectroscopy because the cross peak intensities depend on the inverse sixth power of the internuclear distance[17]. The cross relaxation that results in observable cross peaks is orders of magnitude slower than the *gauche–trans* isomerization and segmental motion that averages the dipolar interactions for polymers in solution, so the cross peaks depend on the time-averaged conformation[25]. The distances measured by n.m.r. are a population weighted average of the values in the *trans*, *gauche+*, and *gauche−* states[26] (*Scheme 2*). The inset in *Figure 3* shows a stacked plot of the methine–methylene cross peaks marked A and B. If all rotational isomeric states are equally probable, then the distances from the methine to both methylene protons will be equal, as will the cross peaks. The greater intensity of the high field methylene signal shows that this proton exists longer in a *gauche* orientation relative to the methine proton than does the other methylene proton. This pattern of cross peaks is consistent with a predominance of *trans* conformers, and similar observations are made from the NOESY spectrum in $DMSO_{d6}$ solution (not shown). The populations of isomeric states are quantitatively analysed in the following sections via the through-bond *J* couplings.

3D NOE/J-resolved n.m.r. spectroscopy

The magnitude of the through-bond *J* coupling between protons along the polymer main chain also depends on the time-averaged conformation[2,7,14]. The coupling constants vary with the dihedral angle between the protons in the *trans* (180°, 11 Hz) and the *gauche* (60°, 2 Hz) orientations, as expected from the Karplus relationship[2]. *Figure 1* shows that the inhomogeneous line broadening from stereosequence effects and the overlap with the residual solvent resonances precludes a simple coupling constant analysis from the 1D n.m.r. spectra. At higher temperatures (85°C), where the solvent lines are slightly shifted from the methylene protons, the spectrum may be analysed by 2D *J*-resolved n.m.r. spectroscopy[27], an experiment in which the chemical shifts appear along one axis, and the coupling constants appear along the other. To facilitate comparison of the chain conformation with that measured by solid state n.m.r. at room temperature, we measured the chain conformation using 3D NOE/*J*-resolved n.m.r. spectroscopy[19,20]. In 3D n.m.r., the *J* couplings are measured from the modulations of the NOE cross peaks. This experiment has the advantage that the couplings can be measured from the resolved cross peaks marked A and B in *Figure 3*, rather than from the methylene signals along the diagonal that are overlapped with each other and the solvent. The data from the 3D n.m.r. experiment are most effectively examined as cross-sections through the 3D data matrix, which show the coupling pattern for a particular cross peak. The most easily interpreted cross peaks are those from the methylene protons that show only geminal and nearest neighbour vicinal couplings.

Figure 4 shows the *J* coupling patterns for the methylene protons marked A and B in $DMSO_{d6}$ and DMF_{d7} solution obtained by 3D NOE/*J*-resolved spectroscopy. The methylene protons are relatively easy to analyse as they are coupled to the methine protons in one direction along the chain, and isolated from further *J* coupling by the vinylidine cyanide groups along the other direction (*Scheme 1*). Since the geminal methylene protons are resolved from each other, two types of couplings will be observed. The geminal couplings are constant at 14 Hz, while the vicinal couplings depend on the relative populations of the *trans* and *gauche* states. Regardless of the interpretation of the couplings, *Figure 4*

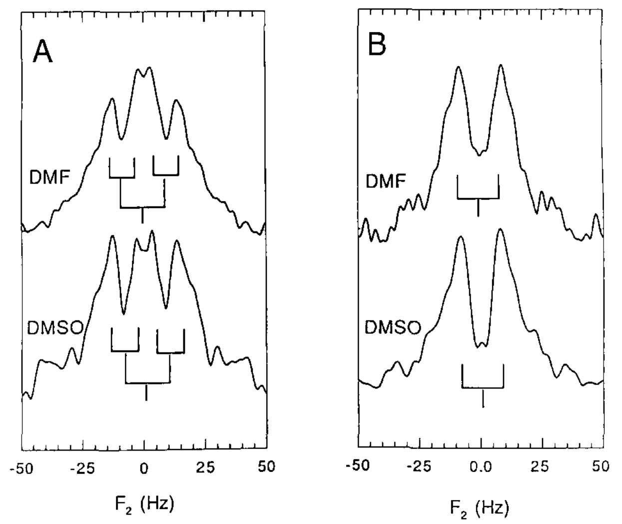


Figure 4 *J* coupling patterns obtained by 3D NOE/*J*-resolved n.m.r. spectroscopy for the methylene protons marked A and B in *Figure 3*. The results are shown for 2 wt% solutions in $DMSO_{d6}$ and DMF_{d7} solutions at 20°C

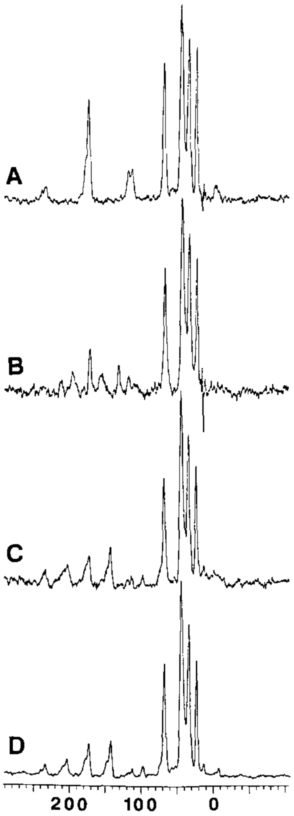


Figure 5 ^{13}C CP/MAS spectra of powdered (A, B) P(VDNCN–VAc) and in films cast from (C) DMSO and (D) DMF. All spectra were obtained with a 2 ms contact time at a spinning speed of 1.5 kHz, except (A), which was obtained with a 3 kHz spinning speed

clearly shows that similar coupling patterns (and conformations) are observed for the polymers dissolved in DMSO$_{d6}$ and DMF$_{d7}$. While both the A and B resonances show the splittings from the geminal couplings, different vicinal couplings are observed. Protons A show a 10 Hz vicinal coupling, while the couplings for the B protons are too small to be resolved in the 3D experiment. Small couplings are not observed by 3D n.m.r. if they are less than the line widths or the inverse of the acquisition time in the t_2 time dimension (3 Hz)[19,20]. The coupling constants extracted from *Figure 4* (10 and <3 Hz) are consistent with a population of rotational isomeric states that are 90% *trans*. Furthermore, since the coupling constant patterns are independent of solvent, the conformation is independent of solvent.

CP/MAS studies

CP/MAS n.m.r.[2,3] is used to compare the solid state properties of powdered P(VDNCN–VAc) with films cast from DMF and DMSO. The conformational properties are compared via the conformationally sensitive ^{13}C chemical shifts and line widths, while the molecular dynamics are measured by n.m.r. relaxation. *Figure 5A* shows the 50 MHz CP/MAS ^{13}C spectrum of powdered P(VDNCN–VAc) obtained using a 2 ms CP contact time and a 3 kHz spinning speed. The resonances are readily assigned by comparison to the solution spectra[10,11]. In addition to the expected peaks, several spinning side bands (identified by their dependence on the spinning speed) are observed for the cyano and carbonyl carbons. The remainder of the peaks are sharp and show no spinning side bands. The ^{13}C line widths in P(VDNCN–VAc) are narrower than those typically observed for vinyl atactic polymers[3]. A possible explanation for this observation is the predominance of a preferred conformation that results in similar magnetic environments for the carbon atoms. Although the line widths are similar to those observed for the crystalline peaks in semicrystalline polymers[3], X-ray diffraction studies on the powdered and film samples showed no evidence for crystallinity (not shown).

Figures 5B–D compare the ^{13}C CP/MAS spectra of powdered P(VDNCN–VAc) with films cast from DMF and DMSO. These spectra are obtained with the same CP contact time, but with a spinning speed of 1.5 kHz. The spectra of the films are obtained by cutting the cast films and stacking them in the MAS rotor. Because the film samples do not pack as evenly as the powdered samples, the maximum spinning speed (1.5 kHz) is insufficient to average the chemical shift anisotropy for the carbonyl and cyano carbons, and many spinning side bands are observed in the slower spinning samples that obscure the cyano resonance at 115 ppm. For comparison, the CP/MAS spectrum of the powdered samples at this same spinning speed is shown in *Figure 5B*, and the chemical shifts for the powdered and cast samples are compiled in *Table 1*. Inspection of *Figure 5* and *Table 1* shows that no significant chemical shift differences are observed for the powdered and cast samples. Since the ^{13}C chemical shifts are known to depend on the conformation through the *γ-gauche* effect[2,16], this result is indicative of a similar P(VDNCN–VAc) conformation in the powdered samples and in the films cast from DMF and DMSO. Furthermore, the sharp lines are consistent with a highly preferred conformation. The existence of the predominantly *trans* conformation, as found in DMF and DMSO solutions, would account for these experimental observations.

Solid state n.m.r. relaxation

The effect of the casting solvent on the molecular mobility of P(VDNCN–VAc) is investigated via n.m.r. relaxation methods[2,3]. This approach detects molecular motion by its effect on the spin-lattice (T_1) and rotating-frame spin-lattice ($T_{1\rho}$) relaxation times. For rigid systems, there is insufficient molecular motion to average the dipolar interactions and long carbon T_1s and short proton $T_{1\rho}$s are observed. The results for P(VDNCN–VAc) are interpreted in light of the relaxation times measured for other crystalline, semicrystalline and amorphous polymers[3].

Table 2 lists the proton $T_{1\rho}$ values for the powdered and cast samples. The values measured for each carbon atom are indistinguishable within experimental error, demonstrating that the sample is homogeneous on the length scale of proton spin diffusion (20 Å)[3]. The values are longer than typically found for crystalline samples[3],

Table 1 Solid state ^{13}C chemical shifts measured for P(VDNCN–VAc) powders and for films cast from DMF and DMSO

	^{13}Chemical shift (ppm)			
Sample	–CH–	–CH$_2$–	–C–	–CH$_3$
Powder	68.1	43.7	33.5	22.9
DMSO	67.6	44.0	33.9	22.9
DMF	68.1	43.8	33.7	22.8

Table 2 Proton $T_{1\rho}$ relaxation times for P(VDNCN–VAc) powders and films cast from DMSO and DMF

	$T_{1\rho}$ (ms)				
Sample	C=O	-CH-	$-CH_2-$	-C-	$-CH_3$
Powder	10.2	11.9	10.7	11.5	12.5
DMSO	10.6	10.1	10.7	10.4	10.5
DMF	8.4	9.1	9.0	9.1	9.9

Table 3 Carbon T_1 relaxation times for P(VDNCN–VAc) powders and films cast from DMSO and DMF

	T_1 (s)				
Sample	C=O	-CH-	$-CH_2-$	-C-	$-CH_3$
Powder	152	64	48	105	30
DMSO	68	40	30	52	19
DMF	63	47	39	53	27

consistent with the X-ray observations that this material is amorphous. The values are shorter than previously reported for the powdered, cast and poled samples, a feature that may be related to the effect of the residual solvent on the molecular mobility[15,28]. As noted above, we found by t.g.a. analysis that the previous procedures used for film preparation[7] did not result in complete solvent removal.

Table 3 contains the carbon T_1 relaxation times measured by CP inversion recovery[21] for the powdered and cast samples. Unlike the dipolar interactions, the *J* couplings, the carbon chemical shifts, and the proton $T_{1\rho}$ values, the carbon T_1 values depend on the casting solvent. Long T_1s are associated with rigid chains, such as those in a crystalline environment, or an environment where chain mobility is restricted by the polymer matrix. Shorter values are observed for the DMSO and DMF cast films, indicating an increase in molecular mobility in the cast films compared to the P(VDNCN–VAc) powdered samples.

DISCUSSION

D.s.c. and several n.m.r. methods are used to measure the solution and solid state properties of P(VDNCN–VAc) in an attempt to relate the microscopic and macroscopic behaviour of this copolymer. P(VDNCN–VAc) is a polymer of great interest as an amorphous yet piezoelectric material. Like many other polymers, the solid state behaviour of P(VDNCN–VAc) films depends on the sample history and the casting solvent. The piezoelectricity of P(VDNCN–VAc) is related to the dipole moments of the vinylidine cyanide groups, and therefore on chain conformation and the intermolecular orientation and reorientation of chains[6,8,12]. N.m.r. is particularly useful for these studies as the n.m.r. signals provide a measure of the molecular dynamics and the magnetic environment of the carbons and protons along the chain.

Chain conformation in P(VDNCN–VAc) is studied by several n.m.r. methods. The through-bond *J* couplings, through-space dipolar couplings and the ^{13}C chemical shifts depend on the time-averaged structure. From an n.m.r. perspective, the average conformation depends on the populations of the *trans* and *gauche* isomers that interconvert rapidly on the n.m.r. time scale[24,26]. Experimental information about the solution chain dynamics are obtained from the phase and intensity of the cross peaks in the NOESY studies[28]. While the dynamic behaviour in solution is not studied in detail, we note that the time dependence of the NOESY cross peaks for P(VDNCN–VAc) are similar to those observed for polystyrene[20], which has an effective correlation time of 0.5 ns[29] under these experimental conditions. The populations of isomers are weighted by the Boltzmann factors, and a distribution heavily weighted in the *trans* conformation is expected from molecular mechanics calculations that show that the *trans* conformation is energetically favoured[8].

The 2D NOESY and 3D NOESY/*J*-resolved studies show that the solution conformation is >90% *trans* about the methine–methylene bond, and the conformation does not depend on the solvent. This quantitative information is determined in part from the magnitudes of the *J* couplings. The couplings differ from those originally reported for P(VDNCN–VAc) from selective decoupling experiments combined with line shape simulations of the n.m.r. spectra, where a lower fraction of *trans* conformers and a solvent dependence to the *J* couplings were reported[7,14,15]. Obtaining coupling constants by this approach is hindered by the broad lines and the overlap of the methylene protons with the residual solvent lines, and these experimental difficulties may account for this discrepancy. The *J* coupling constants and conformational analysis are in closer agreement with a more recent study using 2D *J*-resolved n.m.r. spectroscopy at 85°C[27], where sharper lines are observed and the solvent lines are less overlapped with the methylene protons than shown in *Figure 2*.

The chemical shifts in the solid state carbon CP/MAS n.m.r. spectra of P(VDNCN–VAc) powders are similar to those observed for films cast from DMF and DMSO. The chemical shifts depend on the conformation through the *γ-gauche* effect[16], an empirical correlation between the chemical shift and the relative orientation of a carbon atom and its γ neighbour. The *γ-gauche* effect has been extensively used in the analysis of vinyl polymers, where conformation dependent shifts as large as 5 ppm may be expected. The chemical shifts for P(VDNCN–VAc) in powdered form and in films cast from DMF and DMSO are similar to each other, and similar to the solution spectra. In addition, the resonances are sharper than those usually observed for atactic, glassy polymers. The broad lines found in many polymers results in part from a distribution in conformations (i.e. the *γ-gauche* effect), so a predominantly *trans* conformation would provide a more uniform environment for the carbon atoms.

The carbon T_1 relaxation times are the only n.m.r. parameters that depend on the casting solvent. The relaxation is determined by the molecular mobility that has contributions from intramolecular barriers to rotation, and intermolecular barriers to reorientation that are related to the free volume in glassy polymers. The effect of free volume on the n.m.r. relaxation is obvious from the comparison of the molecular dynamics in crystalline and glassy polymers[3] or the effect of pressure on the molecular dynamics of glassy polymers[30]. Since the chemical structure and conformation is the same for the powders and films of P(VDNCN–VAc), the differences in the molecular mobility are attributed to interactions with neighbouring chains. Such differences in the molecular dynamics are expected to alter the macroscopic behaviour of polymer films. The glass transition depends on the free volume and this could account for the solvent effects observed in the d.s.c. traces in *Figure 1*. The piezoelectricity of P(VDNCN–VAc) is only observed after poling and the intermolecular interactions between chains may play an important role in the ability of the P(VDNCN–VAc) dipole moments to align under the influence of an electric field.

In summary, we have used n.m.r. methods to understand solvent effects on the macroscopic properties of P(VDNCN–VAc) films. In solutions and solids, the polymer chain conformation does not depend on the solvent, and exists in a predominantly *trans* conformation. The molecular mobility, as measured by n.m.r. relaxation, depends on the casting solvent and may be related to solvent effects on the macroscopic behaviour of P(VDNCN–VAc) films.

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