^{13}C n.m.r. studies on the microstructure of poly(vinylidene cyanide/vinyl benzoate) and poly(vinylidene cyanide/styrene)

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The microstructure of vinylidene cyanide–vinyl benzoate and vinylidene cyanide–styrene copolymers, both of which were prepared by radical copolymerization, were studied by 125 MHz ^{13}C n.m.r. spectroscopy. The former shows high piezoelectricity, while the latter has low piezoelectricity. It was found that the compositional sequence distribution and tacticity of both copolymers were not largely different from each other, namely, both were highly alternating copolymers with a non-stereoregular structure. Possible origins of piezoelectricity were suggested for vinylidene cyanide copolymers.

(Keywords: poly(vinylidene cyanide-*co*-vinyl benzoate); poly(vinylidene cyanide-*co*-styrene); ^{13}C n.m.r.; tacticity; microstructure; piezoelectricity)

INTRODUCTION

Since the high piezoelectricity has been found on crystalline poly(vinylidene fluoride) (PVDF)[1], the piezoelectric property has been extensively studied for several polymers. The copolymers of vinylidene fluoride and trifluoroethylene, which were also crystalline, were proved to have piezoelectricity as high as that of PVDF[2]. The piezoelectricity of these crystalline fluoro polymers depends strongly on the structural factors, especially on the orientation of molecular axis, crystallinity[3,4], crystal defect[5,6], morphology[7] and so on. Their properties have been clarified by X-ray diffraction[8]. It is well known that crystalline polymers having large dipole moments in the side chains can exhibit high piezoelectricity if the main chain has an all-*trans* conformation (planar zigzag structure) and if the crystal plays a spontaneous polarization. For example, β-type PVDF (planar zigzag phase) has polar crystals showing large piezoelectric d constant of about 25 pCN whereas α-PVDF (3/1 helical phase) shows no piezoelectricity due to the existence of non-polar crystals[9,10]. In 1980, fairly good piezoelectric activity was found in a vinylidene cyanide–vinyl acetate copolymer, P(VDCN/VAc)[11]. Different from the fluoro polymers, this copolymer is amorphous, so that X-ray analysis could give little structural information. Recently, the microstructure of P(VDCN/VAc) and a vinylidene cyanide–methyl methacrylate copolymer, P(VDCN/MMA), which does not show large piezoelectricity, were analysed successfully by n.m.r. spectroscopy. In particular, ^{13}C n.m.r. spectra of P(VDCN/VAc)[12] and P(VDCN/MMA)[13] could explain the amorphous character. It was found that the microstructures of both copolymers were not largely different from each other except for the chemical structure of monomer units, i.e. both were copolymers having highly alternative and configurationally random sequences. Another vinylidene cyanide copolymer, namely, vinylidene cyanide–vinyl benzoate copolymer, P(VDCN/VBe)[14], was shown to have piezoelectricity as high as that of P(VDCN/VAc), while the vinylidene cyanide–styrene copolymer, P(VDCN/St), does not show large piezoelectricity[15]. The differences in the structure of monomer units between P(VDCN/VBe) and P(VDCN/St) are that the benzoate group is substituted for the phenyl group in the former. Since the side-chain cyanide groups having large dipole moment, which would largely contribute to the piezoelectricity are also present in P(VDCN/St), high piezoelectricity comparable to that of P(VDCN/VBe) is expected for P(VDCN/St). The molecular microstructures of piezoelectric polymers have been considered as one of the most important factors in determining the piezoelectric activity, so the difference in piezoelectric behaviour between P(VDCN/VBe) and P(VDCN/St) can be elucidated as the difference in sequence distribution, tacticity or conformation, etc.

In this paper, the primary structures such as monomer composition, monomer sequence distribution and tacticity of P(VDCN/VBe) and P(VDCN/St) are determined and compared with each other on the basis of ^{13}C and ^{1}H n.m.r. analyses. Furthermore, the origin of the piezoelectricity in these copolymers will be discussed.

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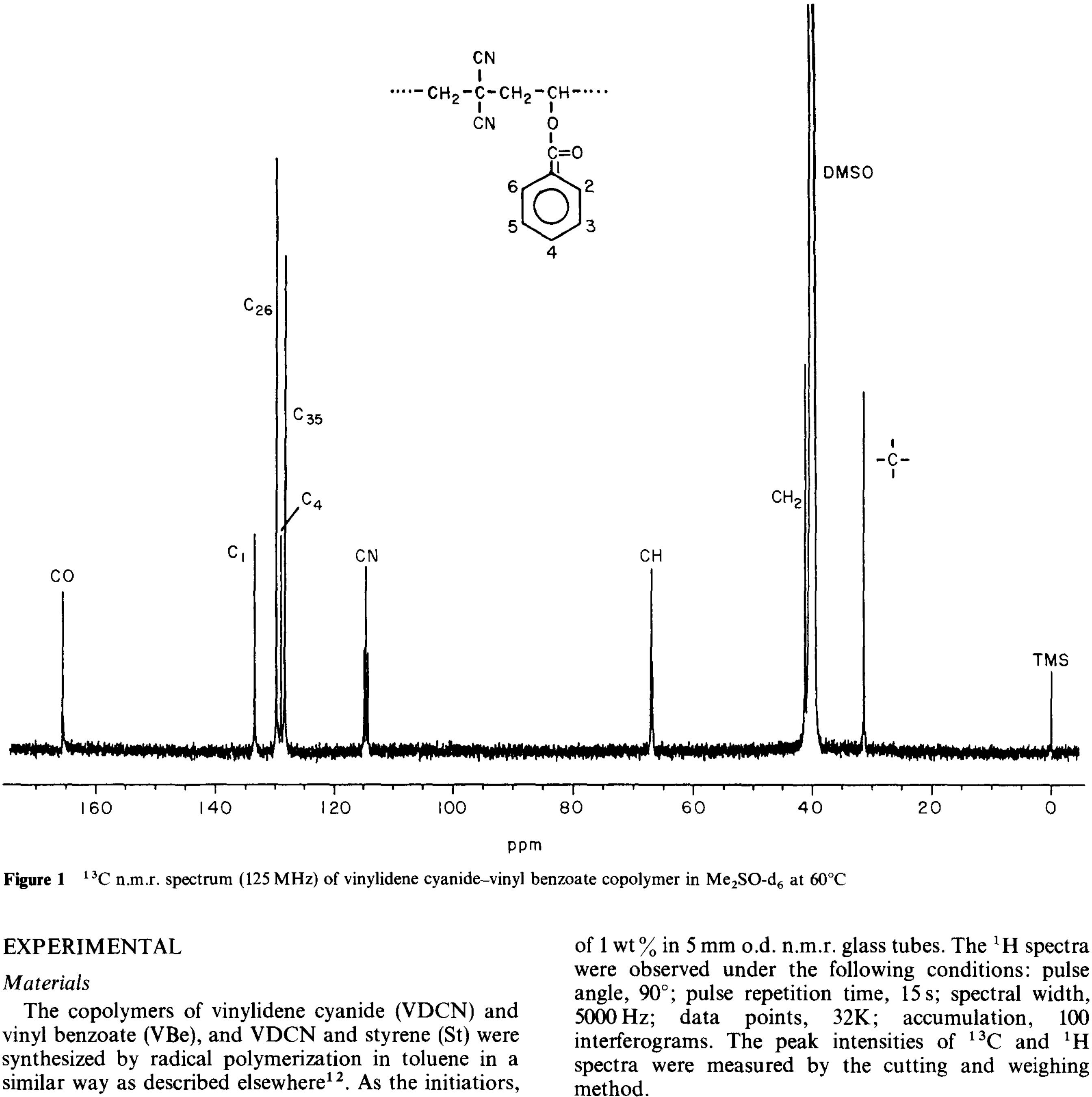


Figure 1 ^{13}C n.m.r. spectrum (125 MHz) of vinylidene cyanide–vinyl benzoate copolymer in Me_2SO-d_6 at 60°C

EXPERIMENTAL

Materials

The copolymers of vinylidene cyanide (VDCN) and vinyl benzoate (VBe), and VDCN and styrene (St) were synthesized by radical polymerization in toluene in a similar way as described elsewhere[12]. As the initiatiors, AIBN (at 70°C) and lauroyl peroxide (at 13°C) were used for the preparations of P(VDCN/VBe) and P(VDCN/St), respectively.

N.m.r. measurements

^{13}C and ^1H n.m.r. spectra of copolymers were recorded on a Jeol GX-500 high resolution n.m.r. spectrometer. ^{13}C n.m.r. spectra were observed at 125 MHz and 65°C in 7 wt% solutions in perdeuterated dimethyl sulphoxide (Me_2SO-d_6) in 10 mm o.d. glass tubes. Chemical shifts were referenced to internal tetramethylsilan and indicated as ppm. The sweep width in the *FT* mode amounted to 25 000 Hz and the corresponding data points were 16K. A pulse angle of 45° and a pulse repetition time of 8.7 s were chosen. *FT* spectra of P(VDCN/VBe) and P(VDCN/St) were obtained after accumulation of 15 820 and 22 040 interferograms, respectively.

^1H n.m.r. spectra (500 MHz), which were used to determine monomer composition, were measured in solution of Me_2SO-d_6 at 83°C with sample concentration of 1 wt% in 5 mm o.d. n.m.r. glass tubes. The ^1H spectra were observed under the following conditions: pulse angle, 90°; pulse repetition time, 15 s; spectral width, 5000 Hz; data points, 32K; accumulation, 100 interferograms. The peak intensities of ^{13}C and ^1H spectra were measured by the cutting and weighing method.

RESULTS AND DISCUSSION

Figures 1 and *2* show the 125 MHz ^{13}C n.m.r. spectrum of P(VDCN/VBe) and P(VDCN/St), respectively, in Me_2SO-d_6 solution. The various resonance peaks have been assigned by comparison with those of P(VDCN/VAc)[12], polystyrene[16,17] and styrene/acrylonitrile copolymer[18]. All the assignments are summarized in *Tables 1* and *2*, and the details will be desribed later.

From the results that each peak in the spectra of these copolymers is very sharp and simple, we may conclude that almost all monomeric units are arranged only in head-to-tail placements. According to Gilbert *et al.*[19], the products of the reactivity ratios for VDCN/VBe and VDCN/St copolymerization are equal to 8.0×10^{-4} and 5.0×10^{-6}, respectively. These magnitudes suggest the strong tendency of P(VDCN/VBe) and P(VDCN/St) to become overwhelmingly alternating copolymers, supporting the simple appearance of their ^{13}C n.m.r. spectra.

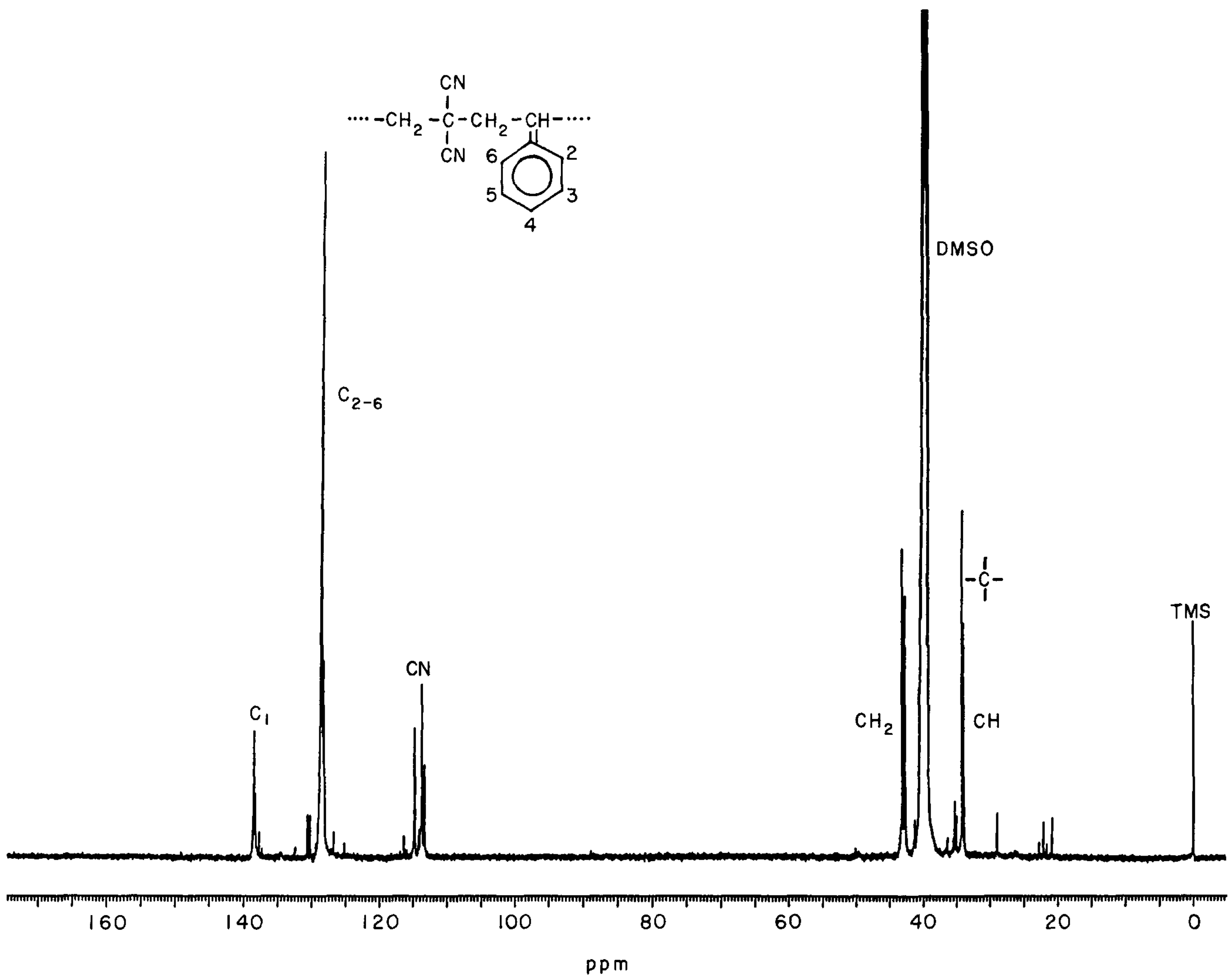


Figure 2 ^{13}C n.m.r. spectrum (125 MHz) of vinylidene cyanide–styrene copolymer in Me_2SO-d_6 at 65°C

Table 1 Chemical shift assignments of P(VDCN/VBe)

Carbon	Chemical shift*	Assignment
CO	165.5, 165.45, 165.4	(VDCN–VBe–VDCN)
	165.3	(VBe–VBe–VBe)
	165.2	(VBe–VBe–VDCN)
C_6H_5	133.4, 129.7, 128.9, 128.2	(VDCN–VBe–VDCN)
	133.6, 129.4, 128.6	(VBe–VBe–VDCN)
	129.3	(VBe–VBe–VBe)
CN	114.8	(VBe–VDCN–VBe) ε-isotactic
	114.5	ε-syndiotactic
	114.2	ε-isotactic
CH	67.0, 66.9, 66.7	(VDCN–VBe–VDCN)
CH_2	41.0	(VBe–VDCN)
$-\overset{\vert}{\underset{\vert}{C}}-$	31.4	(VDCN–VDCN–VBe)
	31.24, 31.22, 31.18	(VBe–VDCN–VBe)
	30.9	(VDCN–VDCN–VDCN)

* Chemical shift is given with respect to internal tetramethylsilan

Table 2 Chemical shift assignments of P(VDCN/St)

Carbon	Chemical shift*	Assignment
C_1	138.7, 138.5, 138.3	(VDCN–St–VDCN)
C_{2356}	129.0–128.4	
C_4	128.3–128.1	
CN	114.8	(St–VDCN–St) ε-isotactic
	113.8–113.7	ε-syndiotactic
	113.4–113.3	ε-isotactic
	114.2, 113.9	(VDCN–VDCN–St)
	114.1	(VDCN–VDCN–VDCN)
CH_2	43.1, 42,72, 42.68	(St–VDCN)
$-\overset{\vert}{\underset{\vert}{C}}-$	34.2	(St–VDCN–St)
CH	33.95, 33.92, 33.88	(VDCN–St–VDCN)
	33.8	(St–St–VDCN)

* Chemical shift is given with respect to TMS

In order to discuss the compositional sequence distributions quantitatively, we denote the monomer sequence and the mole fractions of the monomers for P(VDCN/VBe) and P(VDCN/St) by (VDCN), (VBe) and (St), while those of the three dyads are given by (VDCN–VDCN), (VDCN–VBe) and (VBe–VBe) for P(VDCN/VBe), and (VDCN–VDCN), (VDCN–St) and (St–St) for P(VDCN/St). Similar notations are employed for the six triads, e.g. (VDCN–VBe–VBe), (VDCN–VDCN–VBe), (VDCN–VDCN–VDCN), etc.

First, the monomer composition, the copolymerization parameters and the monomer sequence distribution can be determined. *Figure 3* shows the expanded resonance for the quaternary carbon region of P(VDCN/VBe)

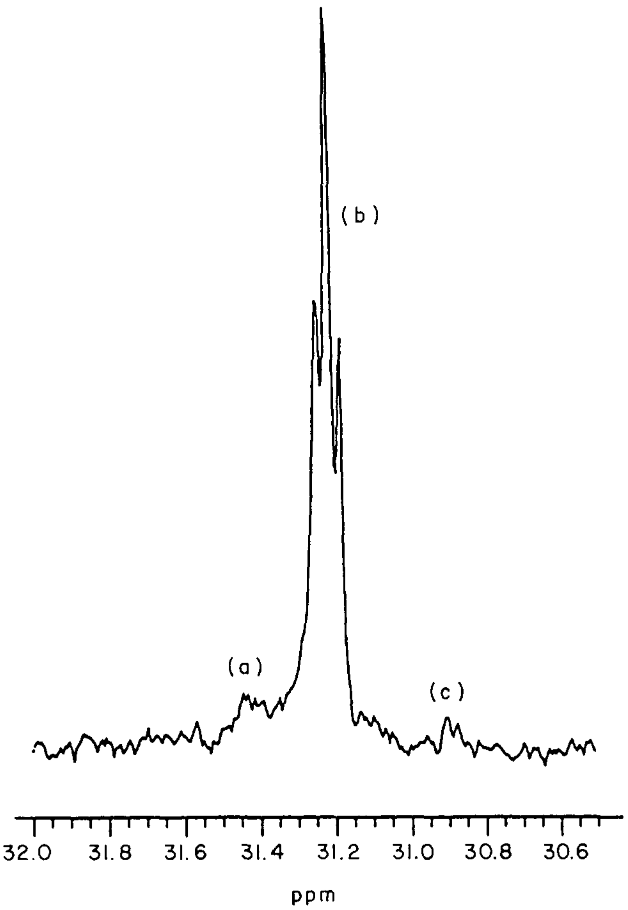


Figure 3 Expanded spectrum of the quaternary carbon resonance region of *Figure 1*

which represents the splittings due to all the possible VDCN-centred triads. These triads appear more than expected for the three compositional VDCN triads, indicating the existence of the effect both of sequence distribution and tacticity. With respect to the compositional triads, the quaternary carbon resonance in *Figure 3* is classified into (a), (b) and (c) corresponding to the VDCN-centred triads, i.e. (VDCN–VDCN–VBe), (VBe–VDCN–VBe) and (VDCN–VDCN–VDCN), respectively, for taking into consideration that these copolymers tend to be alternating. Three splits in the resonance (b) is considered to originate from the effect of tactic structure that will be discussed later. In the same method with P(VDCN/VBe), we could obtain the compositional information concerning the VDCN-centred triads in P(VDCN/St) from the cyanide carbon resonances.

From the results of composition with respect to the VDCN-centred triads, we can calculate conditional probability P_{12}, representing that the VDCN–VBe or VDCN–St unit comes about as a result of the VDCN-growing chain end adding VBe or St:

$$P_{12}=\frac{(\text{X–VDCN–X})+(\text{X–VDCN–VDCN})/2}{(\text{X–VDCN–X})+(\text{X–VDCN–VDCN})+(\text{VDCN–VDCN–VDCN})} \tag{1}$$

where X indicates VBe or St. Assuming k_{11} to be the kinetic constant of forming the VDCN–VDCN unit and k_{12} to be that of VDCN–X, we have

$$P_{12}=\frac{k_{12}(M_2)}{k_{11}(M_1)+k_{12}(M_2)} \tag{2}$$

where (M_1) and (M_2) are representing the respective mole fractions of VDCN and X monomer feeds in the reactant mixture, and their ratio must be fixed during polymerization[12,13]. From equation (2) we obtain the VDCN reactivity ratio, r_1:

$$r_1=\frac{k_{11}}{k_{12}}=\frac{(M_2)}{(M_1)}\left(\frac{1}{P_{12}}-1\right) \tag{3}$$

Introducing P_{12} into equation (3), r_1 can be calculated and the number-average sequence length of VDCN, N_1, being the reciprocal of P_{12}, is also obtained:

$$N_1=\frac{1}{P_{12}} \tag{4}$$

The calculated values of P_{12}, N_1 and r_1 of P(VDCN/VBe) and P(VDCN/St) are given in *Table 3*. As expected, all of these parameters of the two copolymers show that the VBe or St monomer is preferentially attached to the growing chain end of the VDCN unit in the propagation reaction.

The compositional information concerning the VBe-centred triads can be obtained from the resonance of phenyl carbon region for P(VDCN/VBe). *Figure 4* shows the expanded resonances for the phenyl carbon region. The strong resonances are split clearly into four peaks from the difference of the magnetic surroundings, and each peak is assigned to the (VDCN–VBe–VDCN) triad. With respect to the residual compositional triads, the weak phenyl carbon resonances are classified into (a) and (b), corresponding to (VBe–VBe–VDCN) and (VBe–VBe–VBe), respectively. Concerning the St-centred triads of P(VDCN/St), we can obtain this information from the resonance of the methine carbon region. For P(VDCN/St), any peak corresponding to homotriad (St–St–St) could not be observed.

In the same manner as the case of VDCN-centred triads, copolymerization parameters with respect to the VBe and St monomer unit can be determined directly from the compositional distributions of VBe- and St-centred triads, respectively, by using the relationships:

$$P_{21}=\frac{(\text{VDCN–X–VDCN})+(\text{X–X–VDCN})/2}{(\text{VDCN–X–VDCN})+(\text{X–X–VDCN})+(\text{X–X–X})} \tag{5}$$

$$r_2=\frac{(M_1)}{(M_2)}\left(\frac{1}{P_{21}}-1\right) \tag{6}$$

Table 3 Copolymerization parameters in P(VDCN/VBe) and P(VDCN/St)

	P(VDCN/VBe)	P(VDCN/St)
P_{12}	0.936	0.949
P_{21}	0.962	0.951
r_1	0.068	0.054
r_2	0.040	0.052
$\bar{N}_1$	1.068	1.054
$\bar{N}_2$	1.040	1.052

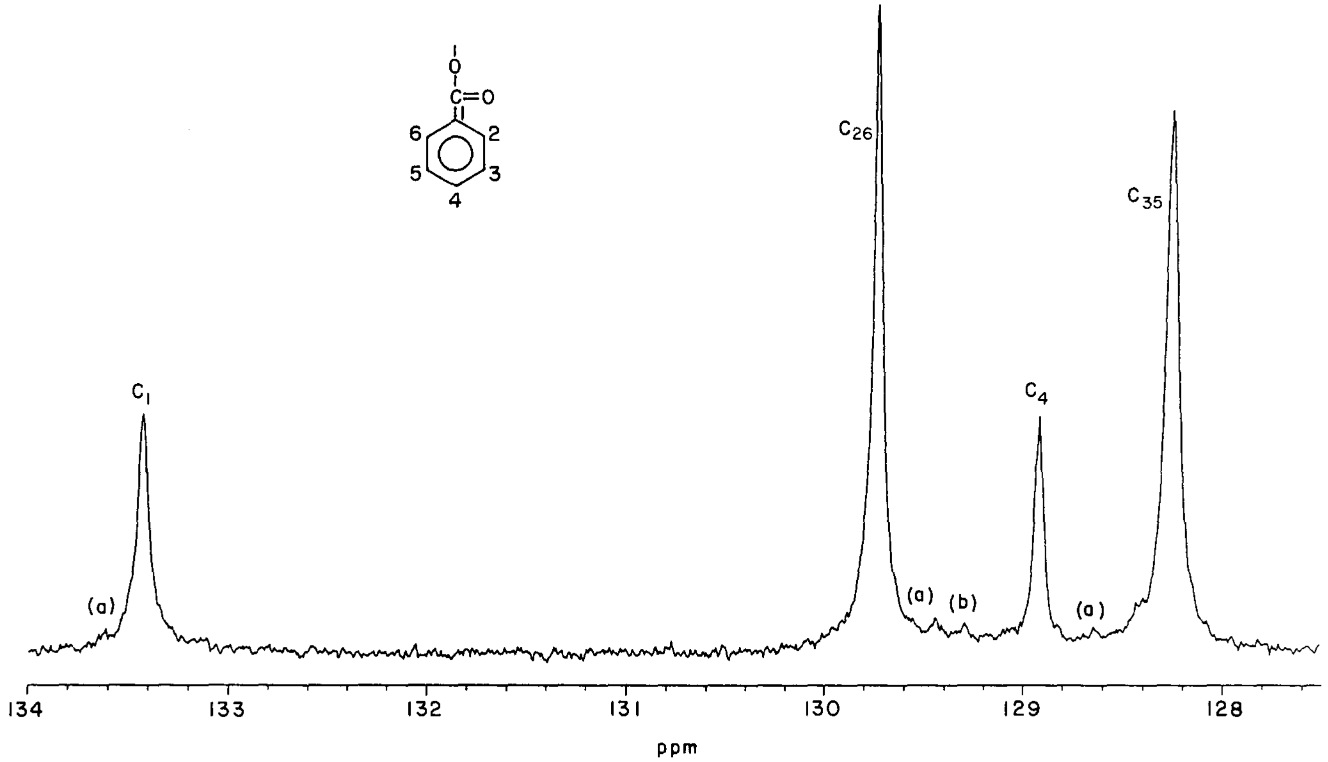


Figure 4 Expanded spectrum of the phenyl carbon resonance region of *Figure 1*

$$N_2 = \frac{1}{P_{21}} \tag{7}$$

where X again indicates VBe or St. The calculated values of P_{21}, N_2 and r_2 of P(VDCN/VBe) and P(VDCN/St) are given in *Table 3* with the values of P_{12}, N_1 and r_1. From the fact that the values of two conditional probabilities P_{12} and P_{21} and also those of the two number-averaged sequence lengths are close to unity, and the monomer reactivity ratios are almost zero for respective copolymers, we know that two copolymers have a highly alternating character and the sequence distributions of both are not largely different from each other.

Using the above triad compositional distributions, we can calculate the monomer compositions of copolymers. The compositions of six possible triads make it possible to calculate those of three dyads, i.e. (VDCN–VDCN), (VBe–VBe) and (VDCN–VBe). For P(VDCN/VBe), the compositions of (VDCN–VDCN) and (VBe–VBe) can be calculated from the resonance of quaternary and phenyl carbons, and also for P(VDCN/St) the compositions of (VDCN/VDCN) and (St–St) can be calculated from the resonances of cyanide and methine carbons, respectively, as follows:

$$\text{(VDCN–VDCN)} = \text{(VDCN–VDCN–VDCN)} + \text{(X–VDCN–VDCN)}/2 \tag{8}$$

$$\text{(X–X)} = \text{(X–X–X)} + \text{(X–X–VDCN)}/2 \tag{9}$$

where X indicates VBe of St. Thus the compositions of the (VDCN–X) dyads can be readily calculated:

$$\text{(VDCN–X)} = 1 - \text{(VDCN–VDCN)} - \text{(X–X)} \tag{10}$$

In principle, the resonance of the methylene carbons also provides the same information directly for dyads, but the splits due to the difference of compositional distributions in the methylene resonances for both copolymers were not observed. Monomer compositions of (VDCN) and (X) are easily calculated from the dyad compositions in a similar way:

$$\text{(VDCN)} = \text{(VDCN–VDCN)} + \text{(VDCN–X)}/2 \tag{11}$$

$$\text{(X)} = \text{(X–X)} + \text{(VDCN–X)}/2 \tag{12}$$

The calculated values of these were 0.513 and 0.487 for P(VDCN/VBe), and 0.502 and 0.498 for P(VDCN/St), respectively.

The monomer compositions are also able to be estimated from ^{1}H n.m.r. spectra. *Figure 5* shows the 500 MHz ^{1}H n.m.r. spectrum of P(VDCN/VBe) in $Me_2SO\text{-}d_6$ solution. From the comparison between the intensities of the methine and methylene proton resonances, the monomer composition (VBe) can be readily determined by using the relationship:

$$\text{(VBe)} = 2I(\text{CH})/I(\text{CH}_2) \tag{13}$$

or from the phenyl and methylene proton resonances:

$$\text{(VBe)} = 2I(\text{C}_6\text{H}_5)/5I(\text{CH}_2) \tag{14}$$

where I(CH), $I(CH_2)$ and $I(C_6H_5)$ represent the peak intensities of the methine, methylene and phenyl proton resonances, respectively. The results are (VBe) = 0.480 from equation (13) and 0.498 from equation (14), which are in good agreement with that from ^{13}C n.m.r. measurement. The information of monomer composition could not be obtained for P(VDCN/St) due to overlapping of the methine and methylene peaks.

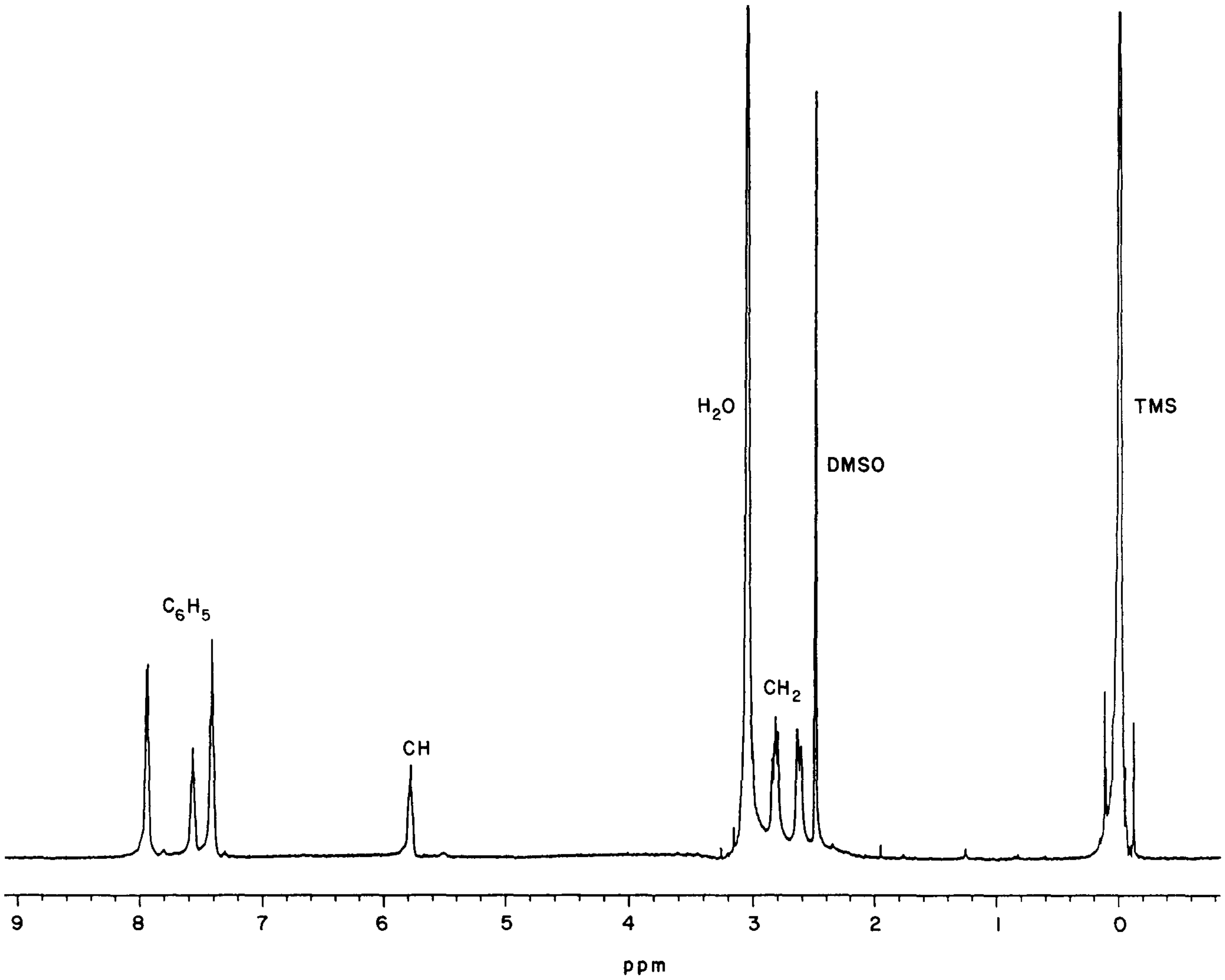


Figure 5 ^1H n.m.r. spectrum (500 MHz) of vinylidene cyanide–vinyl benzoate copolymer in $Me_2SO\text{-}d_6$ at 83°C

Table 4 Calculated and observed fractions of VDCN, VBe and St-centred triads in P(VDCN/VBe) and P(VDCN/St)

P(VDCN/VBe)			P(VDCN/St)		
	Fraction			Fraction	
Triad	Calc.	Obs.	Triad	Calc.	Obs.
(VDCN–VDCN–VDCN)	0.002	0.01	(VDCN–VDCN–VDCN)	0.001	0.01
(VDCN–VDCN–VBe)	0.061	0.04	(VDCN–VDCN–St)	0.048	0.03
(VBe–VDCN–VBe)	0.437	0.45	(St–VDCN–St)	0.451	0.46
(VBe–VBe–VBe)	0.001	0.01	(St–St–St)	0.001	0.00
(VBe–VBe–VDCN)	0.036	0.03	(St–St–VDCN)	0.045	0.05
(VDCN–VBe–VDCN)	0.463	0.46	(VDCN–St–VDCN)	0.454	0.45

Using the monomer compositions as well as the conditional probabilities for the cross propagation P_{12} and P_{21}, the mole fractions for all six triads can be calculated, for example,

$$(\text{VBe–VDCN–VBe}) = (\text{VBe})P_{21}P_{12} \qquad (15)$$

and

$$(\text{VBe–VBe–VDCN}) = (\text{VBe})(1-P_{21})P_{21} + (\text{VDCN})P_{12}(1-P_{21}) \qquad (16)$$

The calculated mole fractions for the six compositional triads of P(VDCN/VBe) and P(VDCN/St) are summarized in *Table 4*. The sum of alternating triads (VBe–VDCN–VBe) + (VDCN–VBe–VDCN) is 0.900 for P(VDCN/VBe) and that of (St–VDCN–St) + (VDCN–St–VDCN) is 0.905 for P(VDCN/St), so it can be argued that the alternating character, which is considered to buffer the dipole interaction between C–C≡N dipoles in the vinylidene cyanide of P(VDCN/VBe) and P(VDCN/St), are not largely different from each other.

To analyse the tacticity, a concept of ε-tacticity defined in a previous paper[12] is used. If we consider the

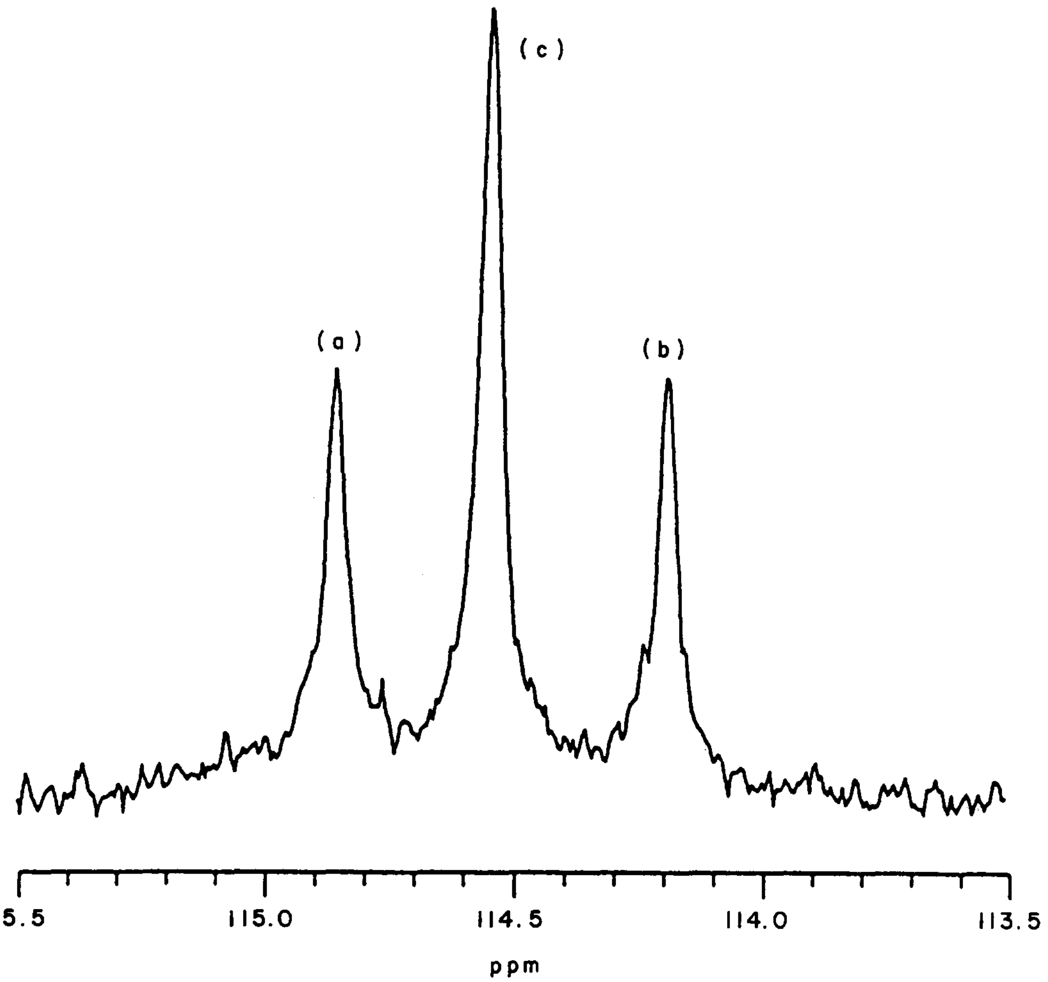
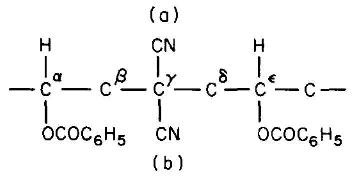
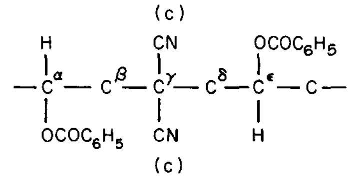


Figure 6 Expanded spectrum of the cyanide carbon resonance region of *Figure 1*

VDCN–VBe as a repeating monomer unit in the alternating sequence of P(VDCN/VBe), two different segment structures in a dyad sense are possible, i.e. formulae I and II,



$$-\overset{H}{\underset{OCOC_6H_5}{C^{\alpha}}}-C^{\beta}-\overset{\overset{(a)}{CN}}{\underset{\underset{(b)}{CN}}{C^{\gamma}}}-C^{\delta}-\overset{H}{\underset{OCOC_6H_5}{C^{\epsilon}}}-C- \qquad \text{I}$$



$$-\overset{H}{\underset{OCOC_6H_5}{C^{\alpha}}}-C^{\beta}-\overset{\overset{(c)}{CN}}{\underset{\underset{(c)}{CN}}{C^{\gamma}}}-C^{\delta}-\overset{OCOC_6H_5}{\underset{H}{C^{\epsilon}}}-C- \qquad \text{II}$$

Here, the tacticities in formulae I and II are defined as ε-isotactic and ε-syndiotactic, respectively. The relative tactic enchainment in formula I is defined as m_ε (ε-meso), and that in formula II as r_ε (ε-racemo). The above argument is also adaptable to P(VDCN/St).

Figure 6 shows the expanded resonance for the cyanide carbon region of P(VDCN/VBe). The splitting of the cyanide carbon resonance of the (VBe–VDCN–VBe) triad into three peaks (a), (b) and (c) is caused by the ε-tactic enchainment. In formulae I and II, considering that the cyanide carbons (a) and (b) are magnetically non-equivalent while cyanide carbons (c) are magnetically equivalent, the appearance of three peaks in the cyanide carbon resonance is reasonable. Three peaks (a), (b) and (c) are assigned to the carbons denoted by (a), (b) and (c) in formulae I and II, respectively. Although the assignments of (a) and (b) carbons are not yet clearly verified, it is considered that the resonance of carbon (b) appears at higher field region than that of (a), which may be similar to the case of P(VDCN/VAc) and styrene–methyl methacrylate copolymer where the coisotactic peak has been assigned at higher field compared with the cosyndiotactic one[12,20,21]. Apparently, the peak at intermediate field is assigned as the resonance of carbons (c). As shown in *Figure 2*, the cyanide carbon resonance of P(VDCN/St) also split into three peaks similar to that of P(VDCN/VBe). The ε-isotacticity σ_ε is calculated from the following equation:

$$\sigma_\varepsilon = \frac{(a)+(b)}{(a)+(b)+(c)} \qquad (17)$$

where (a), (b) and (c) are the relative intensities of the corresponding cyanide carbon resonances. The calculated values of σ_ε for P(VDCN/VBe) and P(VDCN/St) are 0.504 and 0.510, respectively. These values represent that both copolymers are completely atactic, and is evidence that both copolymers are amorphous in the solid state.

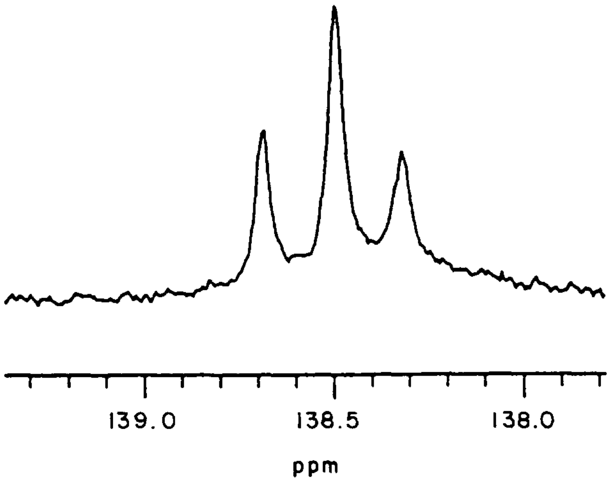


Figure 7 Expanded spectrum of the phenyl C_1 carbon resonance region of *Figure 2*

Figure 7 shows the expanded resonance for the phenyl C_1 carbon region of P(VDCN/St), that also splits into three peaks due to the ε-tactic triad. Although the assignments are not fully clarified, the peaks are tentatively assigned to ε-isotactic ($m_\varepsilon m_\varepsilon$), ε-heterotactic ($m_\varepsilon r_\varepsilon + r_\varepsilon m_\varepsilon$), and ε-syndiotactic ($r_\varepsilon r_\varepsilon$) from low to high field. If one assumes a terminal Bernoullian control model with a single parameter σ_ε as a stereospecific polymerization mechanism, the ε-tactic probability ratio is expected to be $(1-\sigma_\varepsilon)^2{:}2\sigma_\varepsilon(1-\sigma_\varepsilon){:}\sigma_\varepsilon^2$. Using the σ_ε value of 0.510 determined from the cyanide carbon resonance of P(VDCN/St), this ratio is calculated to be 0.240:0.500:0.260, which will be in good agreement with the observed one of 0.24:0.50:0.26. The split of the peak due to the difference of tactic structure can be also seen in the resonances of methylene and methine carbons for P(VDCN/St), and in those of carbonyl, methine and quaternary carbons for P(VDCN/VBe).

In conclusion, the monomer composition, monomer sequence distribution and tacticity for P(VDCN/VBe) and P(VDCN/St) can be determined by ^{13}C n.m.r. spectra. It becomes clear that the characteristics of the microstructures of P(VDCN/VBe) and P(VDCN/St) are not largely different from each other. Thus the reason why P(VDCN/VBe) shows but P(VDCN/St) does not show high piezoelectricity, should be found in some factors other than the microstructures. One of the most probable factors is the chain conformation which depends not only on the chemical structure but also on the microstructure[22,23]. Another probable factor is the chain flexibility, since the C–CN dipoles of the VDCN unit are necessary to rotate to array them in one direction during the poling process for the attainment of high piezoelectricity[24]. Further study concerning these problems is now in progress in our laboratory.

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