Carbon-13 nuclear magnetic resonance studies on the microstructure of the copolymer of vinylidene cyanide and methyl methacrylate

Yôichi Maruyama, Yong Sung Jo, Yoshio Inoue* and Riichirô Chûjô
Department of Polymer Chemistry, Tokyo Institute of Technology, 12-1 Ô-okayama 2-chôme, Meguro-ku, Tokyo 152, Japan

and Sigeru Tasaka and Seizo Miyata
Department of Material Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan
(Received 19 September 1986; revised 16 October 1986; accepted 4 November 1986)

The microstructure of radically polymerized vinylidene cyanide–methyl methacrylate copolymer was studied by 125 MHz ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy and was compared with that of vinylidene cyanide–vinyl acetate copolymer. The latter shows high piezoelectricity, while the former has low piezoelectricity. It was found that the microstructures of both copolymers were not largely different from each other; namely, both have highly alternating sequences with a non-stereoregular structure. Possible origins of piezoelectricity were discussed for these copolymers based on the ^{13}C n.m.r. data.

(Keywords: poly(vinylidene cyanide-*co*-methyl methacrylate); carbon-13 nuclear magnetic resonance; tacticity; configuration; microstructure; piezoelectricity)

INTRODUCTION

Since large piezoelectricity was found in poly(vinylidene fluoride)[1] (PVDF), piezoelectric properties have been extensively studied for several polymers. Moreover, the copolymer of vinylidene fluoride and trifluoroethylene was proved to have piezoelectricity as large as that of PVDF[2]. The piezoelectricity of these crystalline fluoropolymers depends strongly on structural factors, especially on the orientation of the molecular axis, crystallinity[3,4], crystal defects[5,6], morphology[7], etc.; their properties have been clarified by X-ray diffraction[8]. For example, β-PVDF (all *trans*, planar zigzag phase) has polar crystals showing large piezoelectric *d* constant ($\sim 25\,\mathrm{pC\,N^{-1}}$), whereas α-PVDF (3/1 helical phase) shows no piezoelectricity, due to the existence of non-polar crystals[9,10]. In 1980 Miyata *et al.*[11] found large piezoelectricity in poly(vinylidene cyanide-*co*-vinyl acetate), P(VDCN/VAc). Unlike the fluoropolymers, the cyanide copolymer is amorphous, so that structural information was unavailable from X-ray analysis. Recently, the microstructure of this copolymer has been analysed successfully by n.m.r. spectroscopy. In particular, the ^{13}C n.m.r. spectrum of P(VDCN/VAc) could explain the amorphous character[12]. Poly(vinylidene cyanide-*co*-methyl methacrylate), P(VDCN/MMA), is also an amorphous copolymer. The differences of monomer structure between these two copolymers are that the methoxycarbonyl group is substituted for the acetyl group, and the methyl group attaches at the α-carbon. Since the C–C≡N dipole moment, which would considerably contribute to piezoelectricity, is also present in P(VDCN/MMA), comparable piezoelectricity to that of P(VDCN/VAc) is expected. But a piezoelectric *d* constant of only $\sim 0.2\,\mathrm{pC\,N^{-1}}$, which amounts to one thirty-fifth *d* of P(VDCN/VAc), is observed[13]. The difference in piezoelectric behaviour between P(VDCN/VAc) and P(VDCN/MMA) can be elucidated by the difference in sequence distribution, configuration or conformation, and so on. According to the previous n.m.r. study for P(VDCN/VAc), an alternating arrangement of VDCN and VAc seems to facilitate its dipole rotation by attenuating the dipolar interaction between cyanide groups, resulting in large piezoelectricity. In the present work, the primary structure (such as monomer composition, monomer sequence distribution, and stereochemical configuration) is determined and compared with that of P(VDCN/VAc) by ^{13}C n.m.r. method. Furthermore, the origin of the piezoelectricity in these vinylidene cyanide copolymers will be discussed.

EXPERIMENTAL

Materials

The copolymer of vinylidene cyanide (VDCN) and methyl methacrylate (MMA) synthesized by radical polymerization with equal initial mole fractions was given by Mitsubishi Petrochemical Co. Ltd.

^{13}C nuclear magnetic resonance measurements

^{13}C n.m.r. spectra were recorded at 125 MHz and 25 MHz on Jeol GX-500 and Jeol PS-100 high-resolution spectrometers, respectively. Measurements were made in

---

* To whom correspondence should be addressed.

0032–3861/87/071087–06$03.00

a solution of perdeuterated dimethyl sulphoxide (Me_2SO-d_6) at 67°C with a sample concentration of 7 wt%.

The 25 MHz ^{13}C n.m.r. spectra were measured for determining the chemical shifts with respect to internal tetramethylsilane. In order to distinguish the methylene carbon resonance from the quaternary carbons, the method of so-called water eliminated Fourier transform (WEFT) was applied. The corresponding pulse sequence was 40 μs (180°)–0.2 s–20 μs (90°)–10 s. The 125 MHz ^{13}C n.m.r. spectra used in this experiment could provide all the quantitative results concerning monomer sequence distributions and stereochemical configuration. The glass sample tube used at 125 MHz was of 10 mm outside diameter. The sweep width in the FT mode amounted to 25 000 Hz and the corresponding data points were 16 000. A pulse angle of 45° and a pulse repetition time of 10 s were chosen. The validity of the above repetition time at 125 MHz was confirmed by the fact that the relative intensities for the configurationally different peaks in cyanide carbon resonance were identical at 25 MHz and 125 MHz. Spectra were obtained after accumulation of 16 600 scans. The peak intensities were measured by the cutting and weighing method.

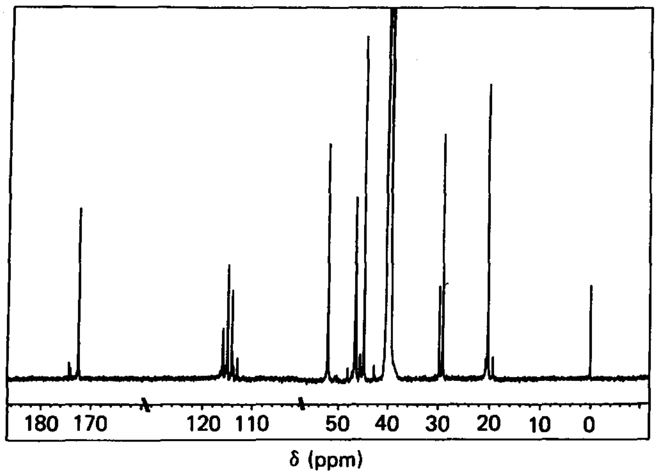


Figure 1 125 MHz ^{13}C n.m.r. spectrum of vinylidene cyanide-*co*-methyl methacrylate copolymer in Me_2SO-d_6 at 67°C

RESULTS AND DISCUSSION

Figure 1 shows the 125 MHz ^{13}C n.m.r. spectrum of P(VDCN/MMA) in Me_2SO-d_6 solution at 67°C. The assignments of various resonance peaks have been made by comparison with those of poly(methyl methacrylate) and P(VDCN/VAc). For the assignments of peaks split due to the compositional distribution, reference was made to the ^{13}C n.m.r. spectrum of P(VDCN/MMA) sample (MMA/VDCN = 9/1). In order to assign the methylene and quaternary resonances explicitly, WEFT mode was used. In *Figure 2*, the fast relaxing resonance was assigned to the methylene carbons, because they are protonated, whereas the quaternary carbon is not. All the assignments are summarized in *Table 1* and will be discussed in detail later.

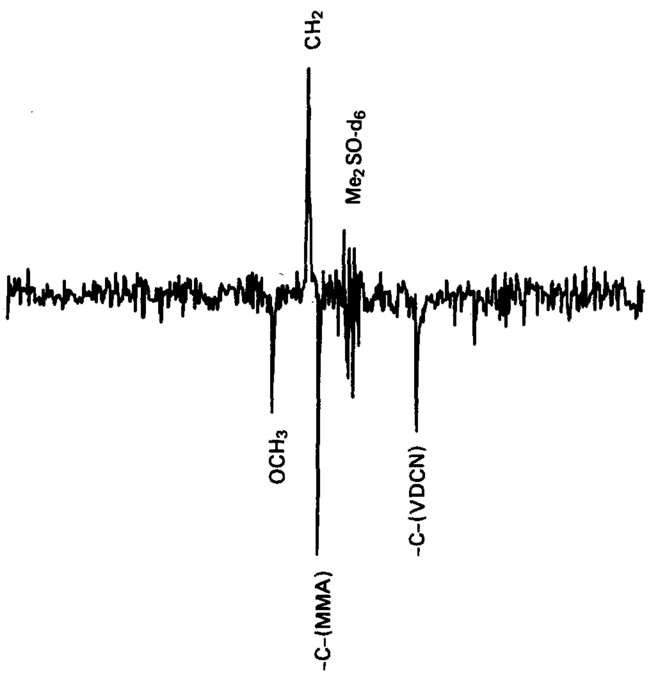


Figure 2 25 MHz ^{13}C n.m.r. fast relaxing signal of the methylene carbon

Table 1 Chemical shift assignments of vinylidene cyanide-*co*-methyl methacrylate copolymer

Carbon	Chemical shift[a]	Assignment
C=O	174.3, 174.0 172.5, 172.3	(MMA–MMA–VDCN) (VDCN–MMA–VDCN)
C≡N	116.6–115.8 115.7–114.7 114.6–113.8	(MMA–VDCN–MMA)
	113.9–113.5 113.1–112.7	(MMA–VDCN–VDCN)
	113.3	(VDCN–VDCN–VDCN)
OCH_3	52.2, 52.1 52.0	
CH_2	48.0 47.3–46.0 45.5, 45.4	(MMA–MMA) (MMA–VDCN) (VDCN–VDCN)
$-\overset{\vert}{\underset{\vert}{C}}-$ (MMA)	44.8, 44.7, 44.6	
$-\overset{\vert}{\underset{\vert}{C}}-$ (VDCN)	29.7 29.0, 28.9	(VDCN–VDCN–VDCN) + (VDCN–VDCN–MMA) (MMA–VDCN–MMA)
CH_3	20.6, 20.5, 20.2 19.1	(VDCN–MMA–VDCN) (VDCN–MMA–MMA)

[a] Chemical shift is given with respect to internal tetramethylsilane

From the result that each resonance of this copolymer is very sharp and simple, we conclude roughly that the monomeric units of VDCN and MMA are almost all arranged in head-to-tail fashion and most monomer sequences are alternating. According to Gilbert *et al.*[14], the product of the reactivity ratios for two monomers, VDCN and MMA, in a polymerization is equal to 1.4×10^{-3}. This magnitude suggests a strong tendency of P(VDCN/MMA) to form an alternating copolymer, supporting the simple ^{13}C n.m.r. spectrum.

In order to discuss the compositional sequence quantitatively, we denote the monomer sequence and the mole fractions of the two monomers by (MMA) and (VDCN), while those of the three dyads are given by (MMA–VDCN), (MMA–MMA) and (VDCN–VDCN). A similar notation is employed for the six triads, e.g. (MMA–MMA–MMA), (MMA–VDCN–MMA), etc.

First, the monomer composition, the copolymerization parameters and the monomer sequence distribution can be determined. For this purpose, the assignment of the compositional triads for each MMA- and VDCN-centred sequence is essential. *Figure 3* shows the expanded resonance for the methyl carbon region that represents all the possible MMA-centred triads. In this region there are three distinct peaks, (a), (b) and (c). For P(VDCN/MMA), however, no peak corresponding to homotriad (MMA–MMA–MMA) was observed, whereas the chemical shifts of the methyl carbon resonances for poly(methyl methacrylate) in Me$_2$SO-d$_6$ are 21.234 (mm), 18.686 (mr) and 16.745 (rr). Taking into consideration that this copolymer tends to be alternating, peaks (a) and (b) of large peak intensity can be assigned as (VDCN–MMA–VDCN) triads, while peak (c) is (MMA–MMA–VDCN).

Now we consider the copolymerization mechanism. From the compositional results with respect to the MMA-centred triads, we can calculate the conditional probability P_{21} that an MMA–VDCN unit comes about as a result of an MMA growing chain end adding to VDCN:

$$P_{21}=\frac{\text{(VCDN–MMA–VDCN)}+\text{(VDCN–MMA–MMA)}/2}{\text{(VDCN–MMA–VDCN)}+\text{(MMA–MMA–VDCN)}+\text{(MMA–MMA–MMA)}} \quad (1)$$

Assuming k_{22} to be the kinetic constant for the formation of an MMA–MMA unit and k_{21} that of MMA–VDCN, we have

$$P_{21}=k_{21}(\mathrm{M}_1)/[k_{21}(\mathrm{M}_1)+k_{22}(\mathrm{M}_2)] \quad (2)$$

$$P_{22}=k_{22}(\mathrm{M}_2)/[k_{21}(\mathrm{M}_1)+k_{22}(\mathrm{M}_2)]=1-P_{21} \quad (3)$$

where (M$_1$) and (M$_2$) represent the respective mole fractions of VDCN and MMA monomer feeds in the reactant mixture. So from (2) and (3) we obtain MMA reactivity ratio r_2:

$$r_2=\frac{k_{22}}{k_{21}}=\frac{(\mathrm{M}_1)}{(\mathrm{M}_2)}\left(\frac{1}{P_{21}}-1\right) \quad (4)$$

Introducing P_{21} into (4), r_2 can be calculated and the number-average sequence length of MMA, N_2, being the reciprocal of P_{21}, also obtained:

$$N_2=1/P_{21} \quad (5)$$

Generally speaking, this equation seems to be unsuitable for this copolymer with a conversion of 18%, since this equation holds good for low conversion (ordinarily less than 10%). But as described later, this material has such a large alternating character that it is proper to regard (M$_1$)/(M$_2$) as unity throughout the whole copolymerization process. We can therefore determine r_2 reasonably from (4). The calculated values of P_{21}, N_2 and r_2 are given in *Table 2*. As expected, all of these parameters show that VDCN monomer is preferentially attached to the MMA growing chain end.

Next, compositional information concerning the VDCN-centred triads can be obtained from the resonance of cyanide carbon region. *Figure 4* shows the expanded resonance for the cyanide carbon region. With respect to the compositional triads, the cyanide carbon resonances are classified into (a,b,c), (d,e) and (f). Similarly to MMA-centred triads, (a,b,c) can be assigned to (MMA–VDCN–MMA) triads. A comparison with P(VDCN/VAc) leads one to assign peak (f) as (VDCN–VDCN–VDCN) triad, and the residual peaks (d) and (e) can be assigned to (VDCN–VDCN–MMA). It is considered that splittings into (a,b,c) or (d,e) peaks originate from the configurational effect and more fine splittings are due to pentad structure. The VDCN homotriad is negligible because the VDCN homosequence is subject to chain scission by atmospheric moisture at room temperature[15]. In the same manner as the case of MMA-centred triads, copolymerization parameters with respect to the VDCN unit can be determined directly from the compositional distribution of VDCN-centred triads by using the relationships:

$$P_{12}=\frac{\text{(MMA–VDCN–MMA)}+\text{(MMA–VDCN–VDCN)}/2}{\text{(MMA–VDCN–MMA)}+\text{(VDCN–VDCN–MMA)}+\text{(VDCN–VDCN–VDCN)}} \quad (6)$$

$$r_1=\frac{(\mathrm{M}_2)}{(\mathrm{M}_1)}\left(\frac{1}{P_{12}}-1\right) \quad (7)$$

and

$$N_1=1/P_{12} \quad (8)$$

These parameters are summarized together with those determined by Gilbert *et al.*[14] using the Mayo–Lewis copolymerization equation in *Table 2*, and are almost in agreement with our ^{13}C n.m.r. data. From the fact that both conditional probabilities (or the two number-average sequence lengths) are close to unity and the monomer reactivity ratios are almost zero, we know that this copolymer shows a highly alternating character.

Using the above compositional distribution of VDCN- and MMA-centred triads, we can calculate the monomer composition of the copolymer. These six possible triads make it possible to give the calculated compositions for the three dyads, i.e. (VDCN–VDCN), (MMA–MMA)

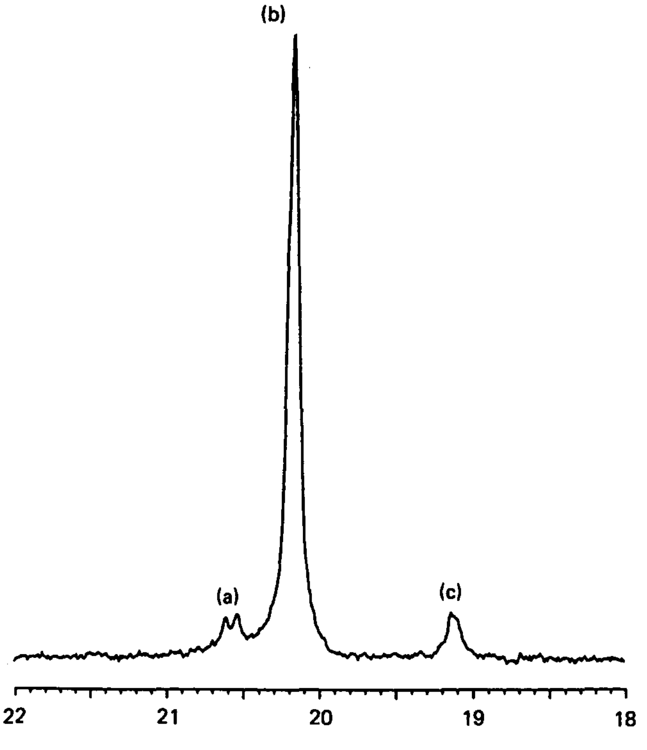


Figure 3 Expanded resonance of the methyl carbon region of *Figure 1*

Table 2 Copolymerization parameters in vinylidene cyanide-*co*-methyl methacrylate copolymer

P_{12}	0.932	0.970 (0.929–0.976)[a]
P_{21}	0.966	0.956 (0.901–0.966)
r_1	0.073	0.031 (0.023–0.077)
r_2	0.036	0.046 (0.035–0.11)
N_1	1.073	1.031 (1.025–1.076)
N_2	1.036	1.046 (1.110–1.035)

[a] Data from ref. 14

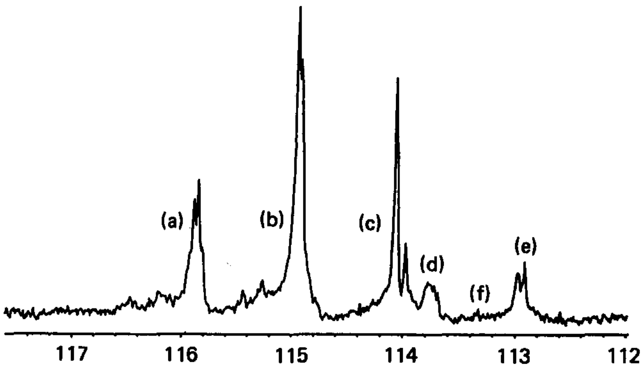


Figure 4 Expanded resonance of the cyanide carbon region of *Figure 1*

and (MMA–VDCN). The composition of (VDCN–VDCN) and (MMA–MMA) can be calculated from the resonance of cyanide and methyl carbons, respectively:

$$(\text{VDCN–VDCN}) = (\text{VDCN–VDCN–VDCN}) + (\text{MMA–VDCN–VDCN})/2 \qquad (9)$$

$$(\text{MMA–MMA}) = (\text{MMA–MMA–MMA}) + (\text{VDCN–MMA–MMA})/2 \qquad (10)$$

Thus the composition of the (MMA–VDCN) dyads can be readily calculated:

$$(\text{VDCN–MMA}) = 1 - (\text{VDCN–VDCN}) - (\text{MMA–MMA}) \qquad (11)$$

Finally, monomer compositions of (MMA) and (VDCN) are easily calculated from the dyad composition in a similar way:

$$(\text{VDCN}) = (\text{VDCN–VDCN}) + (\text{MMA–VDCN})/2 \qquad (12)$$

$$(\text{MMA}) = (\text{MMA–MMA}) + (\text{MMA–VDCN})/2 \qquad (13)$$

In principle, the resonance of the methylene carbons also provides the same information for dyads. *Figure 5* shows the expanded resonance of the methylene and quaternary carbon region. The resonance of the methylene carbons is split into three main peaks that are assigned to (MMA–MMA), (VDCN–MMA) and (VDCN–VDCN) from low to high field. The observed values are 0.039, 0.899 and 0.062, respectively, which are in good agreement with the fractions calculated from MMA- and VDCN-centred triads. Using the monomer composition as well as the conditional probabilities for cross-propagation, P_{12} and P_{21}, we can calculate the mole fractions for all six triads, for example:

$$(\text{MMA–VDCN–MMA}) = (\text{MMA})P_{21}P_{12} \qquad (14)$$

and

$$(\text{MMA–MMA–VDCN}) = (\text{MMA})(1 - P_{21})P_{21} + (\text{VDCN})P_{12}(1 - P_{21}) \qquad (15)$$

The calculated mole fractions for the six compositional triads are summarized in *Table 3* together with the calculated values for P(VDCN/VAc) which was already

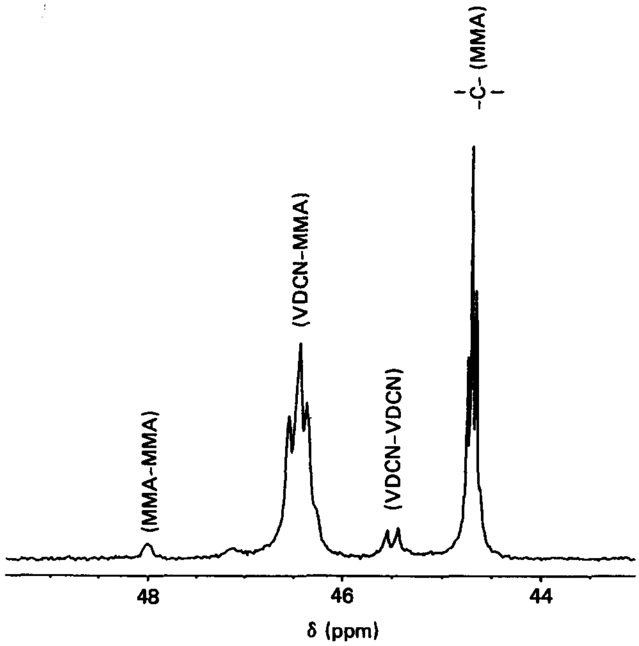


Figure 5 Expanded resonance of the methylene carbon region of *Figure 1*

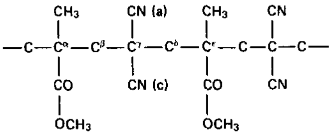
Table 3 Calculated fractions of triads in the vinylidene cyanide–methyl methacrylate copolymer and the vinylidene cyanide–vinyl acetate copolymer

P(VDCN/MMA)		P(VDCN/VAc)[a]	
VDCN–VDCN–VDCN	0.002	VDCN–VDCN–VDCN	0.002
VDCN–VDCN–MMA	0.064	VDCN–VDCN–VAc	0.055
MMA–VDCN–MMA	0.435	VAc–VDCN–VAc	0.442
MMA–MMA–MMA	0.001	VAc–VAc–VAc	0.006
MMA–MMA–VDCN	0.033	VAc–VAc–VDCN	0.096
VDCN–MMA–VDCN	0.465	VDCN–VAc–VDCN	0.400

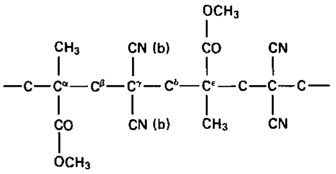
[a] Data from ref. 12

published in ref. 12. The sum of alternating triads, e.g. (MMA–VDCN–MMA) + (VDCN–MMA–VDCN), is 0.900 for P(VDCN/MMA), showing a large alternating character. On the other hand, the sum for P(VDCN/VAc) is 0.842, so it can be said that the alternating character which is necessary to buffer the dipolar interaction between the C—C≡N dipoles in vinylidene cyanide is dominant in P(VDCN/MMA) as compared with P(VDCN/VAc), which shows a large piezoelectricity.

To analyse the configuration, a concept of ε-tacticity defined by Jo *et al.*[12] is used. If we assume VDCN–MMA as the repeating unit in the alternating sequence, two configurationally different structures in the dyad sense are possible:



$$-\mathrm{C}-\underset{\substack{\mathrm{CO}\\ \mathrm{OCH_3}}}{\overset{\mathrm{CH_3}}{\mathrm{C}^{\alpha}}}-\mathrm{C}^{\beta}-\underset{\mathrm{CN\,(c)}}{\overset{\mathrm{CN\,(a)}}{\mathrm{C}^{\gamma}}}-\mathrm{C}^{\delta}-\underset{\substack{\mathrm{CO}\\ \mathrm{OCH_3}}}{\overset{\mathrm{CH_3}}{\mathrm{C}^{\varepsilon}}}-\mathrm{C}-\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{C}}}-\mathrm{C}- \qquad \mathrm{I}$$



$$-\mathrm{C}-\underset{\substack{\mathrm{CO}\\ \mathrm{OCH_3}}}{\overset{\mathrm{CH_3}}{\mathrm{C}^{\alpha}}}-\mathrm{C}^{\beta}-\underset{\mathrm{CN\,(b)}}{\overset{\mathrm{CN\,(b)}}{\mathrm{C}^{\gamma}}}-\mathrm{C}^{\delta}-\underset{\mathrm{CH_3}}{\overset{\substack{\mathrm{OCH_3}\\ \mathrm{CO}}}{\mathrm{C}^{\varepsilon}}}-\mathrm{C}-\underset{\mathrm{CN}}{\overset{\mathrm{CN}}{\mathrm{C}}}-\mathrm{C}- \qquad \mathrm{II}$$

Formulae I and II represent segments of the copolymer chain. Here, the configuration of formula I is defined as ε-isotactic, and the configuration in formula **II** as ε-syndiotactic. The relative configuration of the chain in formula I is defined as m_ε (ε-meso) and that in formula **II** as r_ε (ε-racemic). As described earlier in *Figure 4*, splitting of the cyanide carbon resonance of the (MMA–VDCN–MMA) triad into three peaks (a), (b) and (c), is caused by the ε-tactic arrangement. Considering that the cyanide carbons (a) and (c) are magnetically non-equivalent while cyanide carbons (b) are magnetically equivalent, the resonance pattern of the cyanide carbon should be split into three peaks. Although the assignments of (a) and (c) carbons are not yet clearly verified, it is considered that the resonance of carbon (c) appears at a higher field than that of carbon (a), which may be similar to the case of styrene–methyl methacrylate copolymer, where the co-isostatic peak has been assigned at higher field than the co-syndiotactic peak[16,17]. Apparently, the peak at intermediate field is assigned as the resonance of carbon (b). ε-Isotacticity is calculated from the following equation:

$$\sigma_\varepsilon = \frac{(a) + (c)}{(a) + (b) + (c)} \qquad (16)$$

where (a), (b) and (c) are the relative intensities of the corresponding cyanide carbon resonances. The calculated value is 0.495, indicating that P(VDCN/MMA) is completely atactic. This is also evidence that this copolymer is amorphous in the solid state. As seen in *Figure 5*, the methylene carbon and quaternary carbon resonances are also split into three peaks due to the configurational heptad and the pentad, respectively. Each of the three peaks arises from ε-tacticity, namely ε-syndiotactic ($r_\varepsilon r_\varepsilon$), ε-heterotactic ($m_\varepsilon r_\varepsilon + r_\varepsilon m_\varepsilon$) and ε-isotactic ($m_\varepsilon m_\varepsilon$). If one assumes a terminal Bernoullian control model with a single parameter σ_ε as a stereospecific polymerization mechanism, their 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 0.495 determined by cyanide carbon resonance, this ratio is calculated as 1:2.04:1.04, which would be expected to be in good agreement with the observed ratio for methylene and quaternary regions. However, the peaks of methylene and quaternary carbons overlap each other, so that we could not obtain the corresponding ratio of those intensities. The difference of height for both side peaks is attributed to the fact that the space between the peak at lowest field and that at intermediate field is not the same as that between the peak at highest field and that at intermediate field.

In conclusion, the monomer composition, monomer sequence distribution and configuration for P(VDCN/MMA) can be determined by ^{13}C n.m.r. It becomes apparent that the microstructures described above for P(VDCN/MMA) and P(VDCN/VAc) do not different from each other. The other possible reason that P(VDCN/MMA) does not show large piezoelectricity may be the conformational effect. According to the stable conformation of P(VDCN/MMA), the dipole moment of the carbonyl group may cancel that of the cyanide group. Also there is the problem concerning molecular mobility of the C–CN dipole, which cannot rotate owing to steric hindrance of α-methyl group during the poling process. Further study concerning these problems is now in progress in our laboratory.

ACKNOWLEDGEMENT

This work was partly supported by a Grant-in-Aid for Scientific Research (1986), no. 61470099, from the Ministry of Education, Science and Culture of Japan.

REFERENCES

1 Kawai, H. *Jpn. J. Appl. Phys.* 1969, **8**, 975
2 Uchidari, M., Iwamoto, T., Iwata, K. and Tamura, M. *Rep. Prog. Polym. Phys. Jpn.* 1979, **22**, 345
3 Ohigashi, H. *J. Appl. Phys.* 1976, **47**, 949
4 Douglass, D. C., McBriety, V. J. and Wang, T. T. *J. Chem. Phys.* 1982, **77**, 5826
5 Takahashi, Y., Koyama, M. and Tadokoro, H. *Macromolecules* 1976, **9**, 870
6 Drey-Aharon, H., Sluckin, T. J., Taylor, P. L. and Hophinger, A. *J. Phys. Rev.* 1980, **B21**, 3700
7 Lando, J. B. and Doll, W. W. *J. Macromol. Sci.–Phys.* 1968, **B2**, 205
8 Hasegawa, R., Takahashi, Y., Chatani, Y. and Tadokoro, H. *Polym. J.* 1972, **3**, 600
9 Lovinger, A. J., Davis, G. T., Furukawa, T. and Broadhurst, M. G. *Macromolecules* 1982, **15**, 323
10 Davis, G. T., Furukawa, T. and Broadhurst, M. G. *Macromolecules* 1985, **18**, 1850
11 Miyata, S., Yoshikawa, M., Tasaka, S. and Ko, M. *Polym. J.* 1980, **12**, 857

12 Jo, Y. S., Inoue, Y., Chûjô, R., Saito, K. and Miyata, S. *Macromolecules* 1985, **18**, 1850

13 Tasaka, S., Miyasato, K., Yoshikawa, M., Miayata, S. and Ko, M. *Ferroelectrics* 1984, **57**, 267

14 Gilbert, H., Miller, F. F., Averill, S. J., Carlson, E. J., Folt, V. L., Heller, H. J., Stewart, F. D., Schmidt, R. F. and Trumbull, H. J. *J. Am. Chem. Soc.* 1956, **78**, 1669

15 Gilbert, H., Miller, F. F., Averill, S. J., Schmidt, R. F., Stewart, F. D. and Trumbull, H. L. *J. Am. Chem. Soc.* 1954, **76**, 1074

16 Hirai, H., Koinuma, H., Tanabe, T. and Takeuchi, K. *J. Polym. Sci., Polym. Chem. Edn.* 1979, **17**, 1339

17 Ebdon, J. R., Huckerby, T. N. and Khan, I. *Polymer* 1983, **24** (*Commun.*), 162