N.m.r. studies of microstructure and conformation of piezoelectric poly(vinylidene cyanide-*co*-vinyl formate)

Yoshio Inoue*, **Yoshihisa Ohta and Minoru Sakurai**
Department of Biomolecular Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

and Riichiro Chujo
Department of Material Engineering, The Nishi Tokyo University, Uenohara, Kita-Tsuru-gun, Yamanashi 409-01, Japan

and Iwao Seo and Manabu Kishimoto
Mitsubishi Petrochemical Co. Ltd, 8-3-1 Chuo, Ami-cho, Ibaraki 300-03, Japan
(Received 17 February 1993; revised 25 June 1993)

The microstructure and conformation of highly piezoelectric poly(vinylidene cyanide-*co*-vinyl formate), prepared by radical copolymerization, were studied by ^{13}C and two-dimensional ^{1}H *J*-resolved n.m.r. spectroscopy, respectively. This copolymer was found to have a highly alternating and stereochemically atactic sequence and a predominantly *trans*-rich conformation about the main-chain methylene–methine bond in deuterated dimethyl sulfoxide solution. These structural characteristics do not differ greatly from those of other previously reported piezoelectrically active vinylidene cyanide copolymers with vinyl acetate, vinyl benzoate, and vinyl pivalate or from those of piezoelectrically less active vinylidene cyanide copolymers with styrene and methyl methacrylate.

(Keywords: P(VDCN/VFo); alternating copolymer; piezoelectricity)

INTRODUCTION

Several copolymers of vinylidene cyanide (VDCN), such as those with vinyl acetate (P(VDCN/VAc))[1,2], vinyl benzoate (P(VDCN/VBe))[2], vinyl pivalate (P(VDCN/PiV))[3], and linear-chain fatty acid vinyl esters[4], are known to exhibit fairly high piezoelectric activity in the amorphous state after drawing followed by simultaneous poling/annealing treatments at high temperature but just below the glass transition temperature (T_g). It has been found from n.m.r. analyses that these copolymers have highly alternating and configurationally atactic sequences[5–8]. The side-chain cyanide groups, which have large dipole moments, are probably the main contributors to the high piezoelectric activity of these copolymers[9,10]. However, the piezoelectric activity of poly(VDCN-*co*-methyl methacrylate) (P(VDCN/MMA))[2] and poly(VDCN-*co*-styrene) (P(VDCN/St))[6] is quite low even after the drawing and poling/annealing treatments, even though both of these copolymers have the side-chain cyanide groups and highly alternating and stereochemically atactic sequences[6,11]. Thus, these copolymers are essentially similar to each other with respect to microstructural characteristics. The atactic structure can explain only the amorphous nature of these VDCN copolymers.

Two-dimensional *J*-resolved (2D-*J*) ^{1}H n.m.r. studies[12,13] have indicated that piezoelectrically active P(VDCN/VAc), P(VDCN/VBe), and P(VDCN/PiV) and less active P(VDCN/St) take a predominantly *trans*-rich conformation around the main-chain methylene–methine bond in solution. The three-dimensional nuclear Overhauser effect (NOE)/*J*-resolved ^{1}H n.m.r. spectrum also indicated that P(VDCN/VAc) exists in a predominantly *trans* conformation[14].

Recent studies involving enthalpy relaxation[15,16], dielectric relaxation[17,18], solid-state ^{13}C n.m.r. relaxation[19], and molecular mechanics calculations[20,21] have indicated that the main chains of the piezoelectrically more active VDCN copolymers are more flexible than those of the piezoelectrically less active copolymers. The main-chain flexibility of VDCN copolymers should depend on the side-chain bulkiness of the comonomer units. Poly(VDCN-*co*-vinyl formate) (P(VDCN/VFo)) is expected to have higher chain flexibility, and so exhibit higher piezoelectric activity, because the side chains of its comonomer units are smaller than those of other previously investigated VDCN copolymers. In the work described in this paper, P(VDCN/VFo) was synthesized and its microstructure and conformation in solution were

---

* To whom correspondence should be addressed

0032-3861/94/04/0718-05

determined on the basis of ^{13}C and ^{1}H n.m.r. analyses. The results are herein compared with those for other VDCN copolymers.

EXPERIMENTAL

The sample of P(VDCN/VFo) used here was synthesized by radical copolymerization of VDCN and VFo monomers in toluene at 40°C using lauroyl peroxide as the initiator, in a similar way to that described elsewhere[5]. The experimental details of the measurements of ^{13}C n.m.r.[6] and two-dimensional *J*-resolved ^{1}H n.m.r. spectra[12,13] are essentially identical to those reported in previous papers.

RESULTS

As expected from its chemical constituents, P(VDCN/VFo) film after drawing/poling treatments at a temperature just below its T_g (136°C) exhibits a high piezoelectric strain constant d_{31} of about 8 pC N^{-1} at 20°C, which is comparable to but slightly higher than that of P(VDCN/VAc) ($T_g = 170$°C) film[2,10]. The details of the physical properties including piezoelectricity, will be reported elsewhere.

Microstructure

Figure 1 shows the ^{13}C n.m.r. spectrum of P(VDCN/VFo) in deuterated dimethyl sulfoxide (Me_2SO-d_6) solution. The assignments of the resonances to each different carbon atom are also shown in the figure. The sharpness and simpleness of each resonance strongly suggest that almost all monomeric units are arranged only in head-to-tail placements, as found previously for other VDCN copolymers. *Figure 2* shows the magnified spectrum of the cyanide carbon resonance, indicating the three main resonances and several weak peaks. The features of this area are quite similar to those found for other VDCN copolymers[5–8]. As previously reported, VDCN copolymers have highly alternating sequences, and the three main peaks appearing in *Figure 2* are reasonably assigned to the VDCN units included in the (VFo–VDCN–VFo) alternating triad sequence. The weak peaks should arise mainly from the central VDCN units in the (VDCN–VDCN–VFo) and (VFo–VDCN–VDCN) triad sequences. Some of the weak peaks may also arise from the (VDCN–VDCN–VDCN) sequence, but its fraction must be very small as the homo-VDCN sequence may be subjected to chain scission by atmospheric moisture at ambient temperature[22].

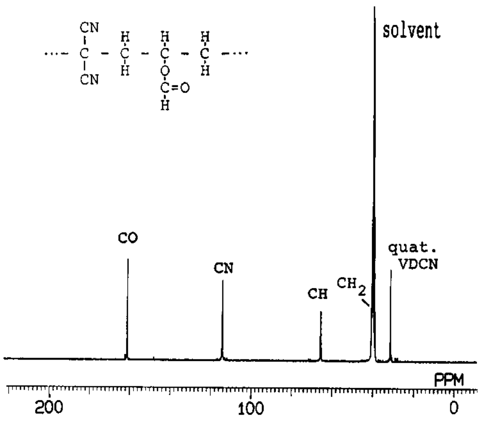


Figure 1 ^{13}C n.m.r. (67.9 MHz) spectrum of poly(vinylidene cyanide-*co*-vinyl formate) in Me_2SO-d_6 solution at 100°C

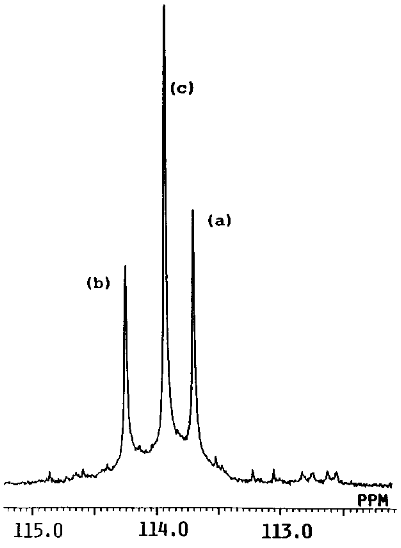
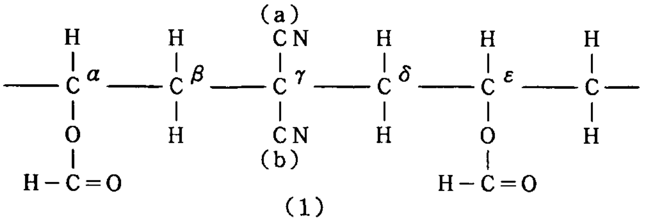


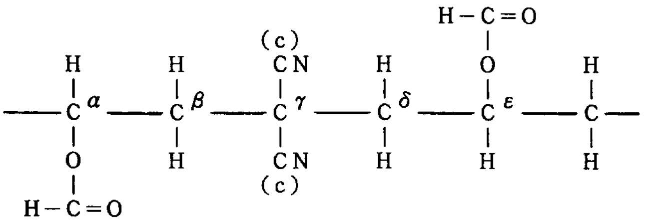
Figure 2 Cyanide resonance region of the ^{13}C n.m.r. spectrum of poly(vinylidene cyanide-*co*-vinyl formate). The labels (a) to (c) correspond to the labels given in formulae (1) and (2)

The three peaks in the main cyanide resonance arising from the (VFo–VDCN–VFo) sequence reflect the stereochemical effect of the tactic structure[5–8]. When the sequence (VDCN–VFo) is considered to be a repeating monomeric unit in the alternating chain of P(VDCN/VFo), the following two different dyad tactic structures are possible.



$$-CH(OCH{=}O)^{\alpha}-CH_2^{\beta}-C^{\gamma}(CN^{(a)})(CN^{(b)})-CH_2^{\delta}-CH(OCH{=}O)^{\varepsilon}-CH_2-$$

(1)



$$-CH(OCH{=}O)^{\alpha}-CH_2^{\beta}-C^{\gamma}(CN^{(c)})(CN^{(c)})-CH_2^{\delta}-CH(OCH{=}O)^{\varepsilon}-CH_2-$$

(2)

Here, the tactic structures of formulae (1) and (2) are defined as ε-isotactic (ε-*meso* or m_ε) and ε-syndiotactic (ε-*racemo* or r_ε), respectively[5]. In formulae (1) and (2), the cyanide carbons denoted by (a) and (b) are considered to be magnetically non-equivalent, while those denoted by (c) are equivalent. Hence, the appearance of three peaks in the cyanide carbon resonance is very reasonable. Apparently, the resonance of carbons (c) should appear at an intermediate-field region between the resonances of carbons (a) and (b). That is, the outside two peaks are assignable to the two carbons denoted by (a) and (b) in formula (1), and the centre peak is assignable to the carbons denoted by (c), as shown in *Figure 2*. The assignments (a) and (b) shown in *Figure 2* are tentative and are exchangeable.

The amount of the ε-isotactic structure present, denoted by σ_ε, is calculated from the relative intensities of the three peaks using

$$\sigma_\varepsilon=\frac{[a]+[b]}{[a]+[b]+[c]} \tag{1}$$

where [*a*], [*b*], and [*c*] are the relative intensities of the corresponding three main cyanide carbon resonances. The σ_ε value, estimated after subtraction of the intensity contributions from the weak resonances based on the computer-aided curve resolution[7,23], is 0.514. This result indicates that this copolymer is also completely atactic, as found for many VDCN copolymers.

Figure 3 shows the expanded spectrum of the methine carbon resonance region of P(VDCN/VFo), which is also split into three main peaks owing to the ε-tactic triad in the (VFo–VDCN–VFo–VDCN–VFo) alternating sequence. The three main peaks are tentatively assigned to ε-isotactic ($m_\varepsilon m_\varepsilon$ at 65.43 ppm), ε-heterotactic ($m_\varepsilon r_\varepsilon + r_\varepsilon m_\varepsilon$ at 65.29 ppm) and ε-syndiotactic ($r_\varepsilon r_\varepsilon$ at 65.15 ppm) species. Since this region of the spectrum includes contributions from the methine carbons of VFo units in (VDCN–VFo–VFo) and (VFo–VFo–VDCN) sequences, the observed resonances were resolved into their component peaks with Lorentzian line shapes using the method mentioned above. The result of curve resolution is shown in *Figure 3a*. From this curve resolution, the probability ratio of the triad tactic structures, namely $m_\varepsilon m_\varepsilon{:}(m_\varepsilon r_\varepsilon + r_\varepsilon m_\varepsilon){:}r_\varepsilon r_\varepsilon$, is estimated to be 0.262:0.484:0.254. When a terminal Bernoullian control model with a single parameter σ_ε can be assumed as a stereospecific polymerization mechanism, the ratio $m_\varepsilon m_\varepsilon{:}(m_\varepsilon r_\varepsilon + r_\varepsilon m_\varepsilon){:}r_\varepsilon r_\varepsilon$ is expected to be $\sigma_\varepsilon^2{:}2\sigma_\varepsilon(1-\sigma_\varepsilon){:}(1-\sigma_\varepsilon)^2$. Using $\sigma_\varepsilon = 0.514$ as determined from the cyanide carbon resonance, this triad ratio is calculated to be 0.264:0.500:0.236, which is in good agreement with the observed ratio. This result also indicates that P(VDCN/VFo) is an atactic polymer.

Figure 4 shows the expanded spectrum for the backbone quaternary carbon region of P(VDCN/VFo), indicating clearly six main peaks due to the six possible ε-tactic tetrad structures in (VDCN–VFo) alternating sequences. It is not easy to resolve these peaks as the chemical shift differences are too small and also included are contributions from the quaternary carbons located in the non-alternating sequences.

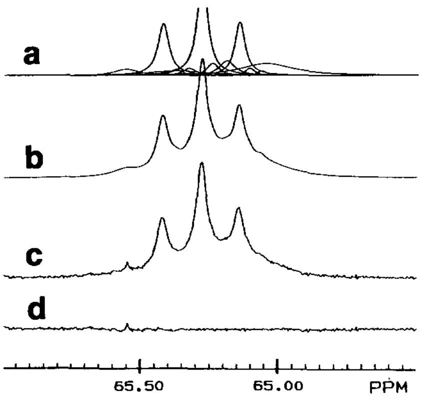


Figure 3 Methine resonance region of the ^{13}C n.m.r. spectrum of poly(vinylidene cyanide-*co*-vinyl formate): (a) result of curve resolution; (b) reproduced spectrum from (a); (c) observed spectrum; (d) difference spectrum ((c)−(b))

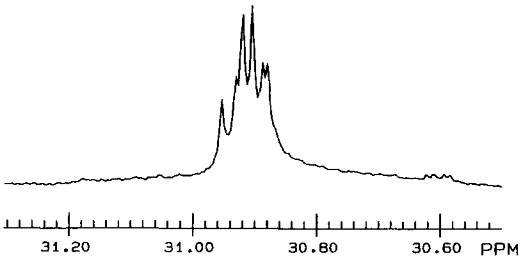


Figure 4 Quaternary carbon resonance region of the ^{13}C n.m.r. spectrum of poly(vinylidene cyanide-*co*-vinyl formate)

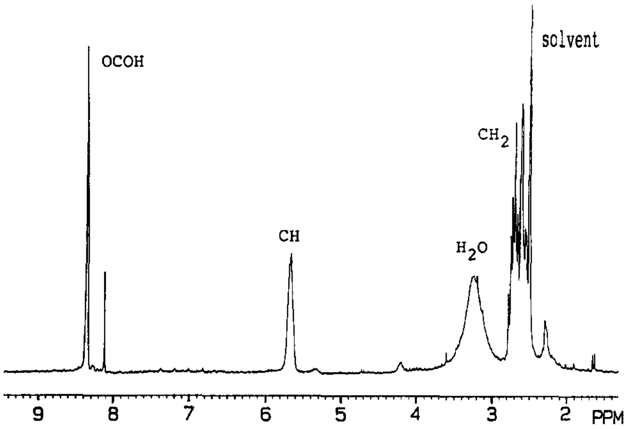


Figure 5 ^{1}H n.m.r. (270 MHz) spectrum of poly(vinylidene cyanide-*co*-vinyl formate) in Me$_2$SO-d$_6$ solution at 86.5°C

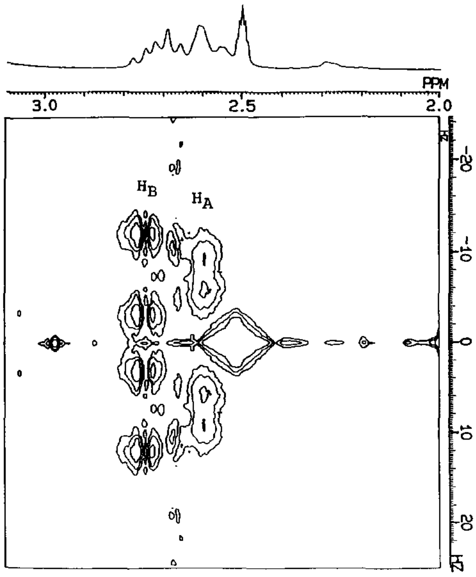


Figure 6 Contour plot of the methylene proton resonance region of the 2D-*J* ^{1}H n.m.r. spectrum of poly(vinylidene cyanide-*co*-vinyl formate)

Chain conformation

In *Figure 5* is shown the ^{1}H n.m.r. spectrum of P(VDCN/VFo) in Me$_2$SO-d$_6$ solution. The contour plot of the methylene proton resonance region of the 2D-*J* ^{1}H n.m.r. spectrum is shown in *Figure 6*. The methylene proton resonance splits into two components, corresponding to two magnetically non-equivalent protons H_A and H_B, which are assigned in the same way as before for P(VDCN/VAc)[12], P(VDCN/PiV)[13],

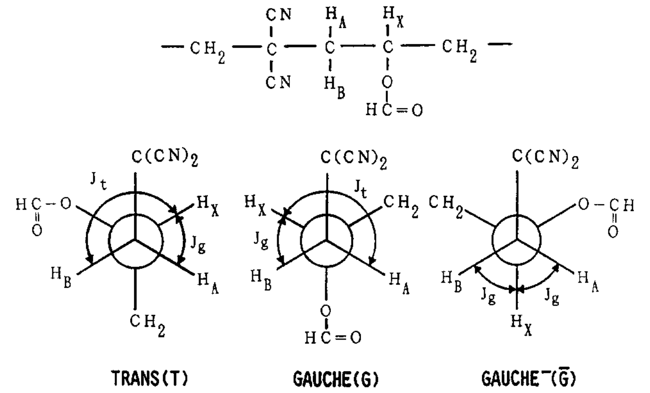


Figure 7 Newman projections illustrating the stable conformers along the $H_AH_BC–CH_X$ bond in the alternating sequence of poly(vinylidene cyanide-*co*-vinyl formate)

P(VDCN/VBe)[13], and P(VDCN/St)[13], i.e. the higher-field and lower-field components are assigned to H_A and H_B, respectively. The assignments of the H_A and H_B resonances are confirmed for P(VDCN/VAc) by the conformational analysis on the basis of molecular mechanics calculations[20]. The respective resonances of H_A and H_B in the 2D-*J* spectrum exhibit two further split signals differing in chemical shifts, indicating that the methylene resonances are resolved at the level of the dyad tactic structure. Similar tactic splittings have also been observed in the 2D-*J* spectra of other previously studied VDCN copolymers[12,13]. 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 given location on the chemical shift axis[13]. It was found that the respective component peaks of the tactically split resonances have practically the same sets of coupling constants. The observed J_{AX}, J_{BX}, and J_{AB} values are 3.4 Hz, 8.9 Hz, and −15.1 Hz, respectively, in $Me_2SO\text{-}d_6$ solution at 86.5°C.

When the conformation around the methylene–methine bond in solution is assumed to be the time average of the three preferred conformers, i.e. *trans* (T), *gauche* (G), and *gauche*⁻ (Ḡ) as shown in *Figure 7*, the observed vicinal coupling constants J_{AX} and J_{BX} are expressed as follows

$$J_{AX}=X_TJ_g+X_GJ_t+X_{\bar{G}}J_g \tag{2}$$

$$J_{BX}=X_TJ_t+X_GJ_g+X_{\bar{G}}J_g \tag{3}$$

$$1=X_T+X_G+X_{\bar{G}} \tag{4}$$

where the subscripts *t* and *g* indicate *trans* and *gauche* arrangements, respectively, with respect to the $H_AH_BC–CH_X$ bond. The J_t and J_g values are assumed to be 11 and 2 Hz, which are the typical values used in the n.m.r. conformational analysis of vinyl polymers[24]. From equations (2) to (4) and using the observed values of the coupling constants, the conformer fractions X_T, X_G, and $X_{\bar{G}}$ are estimated to be 76.7, 15.5, and 7.8%, respectively, indicating that the main chain of P(VDCN/VFo) takes predominantly the *trans*-rich conformation about the $H_AH_BC–CH_X$ bond.

DISCUSSION

P(VDCN/VFo) prepared by radical copolymerization was found to be a highly alternating copolymer with a stereochemically atactic sequence and a highly *trans*-rich conformation about the main-chain methylene–methine bond in solution. These structural characteristics are quite similar to those of other previously reported piezoelectrically active and piezoelectrically less active VDCN copolymers.

In order to obtain high piezoelectric activity, the $C(CN)_2$ dipoles of the VDCN copolymers are forced to align in the film thickness direction by drawing, poling and annealing treatments under a high direct current electric field at a high temperature just below the glass transition temperature[1,2]. Accordingly, the proper degree of chain flexibility is indispensable for achieving the dipole alignment and thus high piezoelectric activity. As the side-chain size of the monomer unit of P(VDCN/VFo) is the smallest among the VDCN copolymers investigated hitherto, P(VDCN/VFo) is expected to have a higher chain flexibility and hence a higher piezoelectric activity than the other VDCN copolymers. In fact, high piezoelectric activity was found for P(VDCN/VFo) after drawing followed by simultaneous poling/annealing treatments. The higher main-chain flexibility is suggested for P(VDCN/VFo) from the conformational analysis. P(VDCN/VFo) still takes the *trans*-rich conformation about the main-chain methylene–methine bond, similar to other VDCN copolymers, but the fractions of the *gauche* and *gauche*⁻ conformers are not too small. The results of n.m.r. conformational analysis have indicated that P(VDCN/St), which is a piezoelectrically less active copolymer, takes predominantly (>80%) the *trans*-rich conformation about the methylene–methine bond and one of the three conformers, i.e. the *gauche*⁻, is significantly suppressed (practically 0%) in $Me_2SO\text{-}d_6$ solution at 86°C[13]. The suppression of one or more of the conformers must limit the flexibility of this bond and so lower the extent of alignment of the $C(CN)_2$ dipoles attainable by poling treatment. It is concluded that the difference in chain flexibility is one of the possible factors determining the difference in piezoelectric activity among VDCN copolymers.

ACKNOWLEDGEMENTS

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas, ‘Functionality Materials (1992)’, from the Ministry of Education, Science and Culture, Japan, and by the Ogasawara Foundation for the Promotion of Science and Engineering (1991).

REFERENCES

1 Miyata, S., Yoshikawa, M., Tasaka, S. and Ko, M. *Polym. J.* 1980, **12**, 857
2 Tasaka, S., Miyasato, K., Yoshikawa, M., Miyata, S. and Ko, M. *Ferroelectrics* 1984, **57**, 267
3 Okutani, T., Tasaka, S., Miyata, S. and Seo, I. *Polym. Prepr. Jpn* 1987, **36**, 1064
4 Kishimoto, M., Fujimoto, Y. and Seo, I. *Polym. Prepr. Jpn* 1989, **38**, 1012
5 Jo, Y. S., Inoue, Y., Chujo, R., Saito, K. and Miyata, S. *Macromolecules* 1985, **18**, 1850
6 Inoue, Y., Kashiwazaki, A., Maruyama, Y., Jo, Y. S., Chujo, R., Kishimoto, M. and Seo, I. *Polymer* 1988, **29**, 144
7 Inoue, Y., Kawaguchi, K., Maruyama, Y., Jo, Y. S., Chujo, R., Seo, I. and Kishimoto, M. *Polymer* 1989, **30**, 698
8 Ohta, Y., Inoue, Y., Chujo, R., Kishimoto, M. and Seo, I. *Polymer* 1990, **31**, 1581
9 Jo, Y. S., Sakurai, M., Inoue, Y. and Chujo, R. *Polymer* 1987, **28**, 1583

10 Seo, I. and Nakajima, K. *Nikkei New Mater.* 1986, 50 (24 February)

11 Maruyama, Y., Jo, Y. S., Inoue, Y., Chujo, R., Tasaka, S. and Miyata, S. *Polymer* 1987, **28**, 1087

12 Inoue, Y., Maruyama, Y., Sakurai, M., Jo, Y. S. and Chujo, R. *Polymer* 1990, **31**, 1594

13 Inoue, Y., Maruyama, Y., Kawaguchi, K., Ohta, Y., Sakurai, M., Jo, Y. S. and Chujo, R. *Polymer* 1991, **32**, 2958

14 Mirau, P. A. and Heffner, S. A. *Polymer* 1992, **33**, 1156

15 Inoue, Y., Jo, Y. S., Kashiwazaki, A., Maruyama, Y., Chujo, R., Kishimoto, M. and Seo, I. *Polym. Commun.* 1988, **29**, 105

16 Tasaka, S., Inagaki, N., Okutani, T. and Miyata, S. *Polymer* 1989, **30**, 1639

17 Furukawa, T., Date, M., Nakajima, K., Kosaka, T. and Seo, I. *Jpn J. Appl. Phys.* 1986, **25**, 1178

18 Furukawa, T., Tada, M., Nakajima, K. and Seo, I. *Jpn J. Appl. Phys.* 1988, **27**, 200

19 Jo, Y. S., Maruyama, Y., Inoue, Y., Chujo, R., Tasaka, S. and Miyata, S. *Polym. J.* 1987, **19**, 769

20 Inoue, Y., Maruyama, Y., Sakurai, M. and Chujo, R. *Polymer* 1990, **31**, 850

21 Sakurai, M., Ohta, Y., Inoue, Y. and Chujo, R. *Polym. Commun.* 1991, **32**, 397

22 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

23 Hayashi, T., Inoue, Y., Chujo, R. and Asakura, T. *Polymer* 1988, **29**, 138

24 Bovey, F. A. 'High Resolution NMR of Macromolecules', Academic Press, New York, 1972, Ch. 9