polymer papers

Nuclear magnetic resonance study on isomorphous behaviour in random copolyesters: poly(ethylene terephthalate-*co*-1,4-cyclohexenedimethylene terephthalate)

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Isomorphism of copolymers of ethylene terephthalate (ET) and 1,4-cyclohexenedimethylene terephthalate (CT) was analysed by high-resolution solid-state ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy. The ET/CT copolymer system was confirmed to have random comonomer sequence distribution. The *trans*/*cis* isomer compositions of the cyclohexene group in the CT unit were almost constant for all samples, giving a ratio of 67/33. The CT contents in the crystalline phases were determined by high-resolution solid-state ^{13}C n.m.r. spectroscopy. The crystalline phases consisted of only ET components in the composition range of 80–100 mol% ET, whereas those in the composition range of 66–100% CT adopted the incorporation of the comonomer units in the PCT crystal.

(Keywords: random copolyester; isomorphism; solid-state nuclear magnetic resonance spectroscopy)

INTRODUCTION

Binary crystalline–crystalline random copolymers show some degree of isomorphism owing to cocrystallization between two comonomer units[1–3] with similar chemical structure, similar repeat-unit length, similar volume and compatible conformation. For example, a bacterially synthesized copolyester, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (P(3HB-3HV)), forms isomorphous crystals[4,5]. 3HB and 3HV monomer units have the same main-chain skeleton. The only difference between these units is found in the side chains, namely the side chain of 3HB is a methyl group while that of 3HV is an ethyl group. The conformations of P(3HB)[6,7] and P(3HV)[8] homopolymers in the crystalline state are a 2_1 helix with fibre periods of 0.596 and 0.556 nm, respectively. Therefore, this copolymer system fulfils the requirements for isomorphism.

Of the requirements for isomorphism in a binary AB-type random copolymer that consists of two crystallizable components, similarity in the main-chain structure between the two comonomer units seems to be the most important. In cocrystallization for a copolymer system in which the two comonomer units possess side chains having slightly different sizes, such as methyl and ethyl groups, and have similar monomer repeat-unit lengths, the crystal lattice dimensions perpendicular to the fibre axis are varied with incorporation of the comonomer unit. On the other hand, for two comonomer units with different repeat-unit lengths but with similar side chains, cocrystallization of the two comonomer units produces translational misfit along the chain. Axial defects are unfavourable for crystallization in a flexible polymer, because of large free-energy loss.

There is, however, a copolymer that is expected to form an isomorphous crystal even if the two comonomer units are different in repeat-unit length. For example, there is a copolymer of ethylene terephthalate (ET) and 1,4-cyclohexenedimethylene terephthalate (CT) whose repeat unit is constituted by similar chemical structures of PET except for introducing a cyclohexane ring between the methylene groups. Cocrystallization of ET and CT units is realized to some extent, and the minimum melting temperature and the minimum heat of fusion appear at an intermediate composition of about 30–40 mol% CT[9]. In this paper, the isomorphism in the P(ET/CT) system is analysed by high-resolution solid-state ^{13}C n.m.r. spectroscopy.

EXPERIMENTAL

Materials

Samples of PET, PCT and ET/CT copolymers except for Cop B as listed in *Table 1* are commercial products

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Table 1 Annealing conditions and the degree of crystallinity

Sample	Annealing temp. (°C)	Annealing time (min)	Crystallinity[a]
PET	230	100	0.46
Cop A	230	100	0.43
Cop B	195	120	0.36
Cop C	–	–	–
Cop D	225	100	0.34
Cop E	245	100	0.38
PCT	250	100	0.43

[a] Determined by X-ray diffraction

available from Eastman Kodak Co. The sample of Cop B was kindly supplied by Sun Koung Industry. The samples were dried at 100°C under vacuum for 24 h, hot-pressed to thin films and then quenched into liquid nitrogen, resulting in amorphous samples. The quenched samples were annealed at several temperatures in order to get the utmost degree of crystallinity. The annealing conditions and the ultimate crystallinity determined by X-ray analysis are listed in *Table 1*.

N.m.r. measurements

Solution-state ^{1}H and ^{13}C n.m.r. spectra were recorded on a JEOL GSX-270 spectrometer operating at 270 and 67.9 MHz, respectively. Samples were dissolved in a mixture of $CDCl_3$ and CF_3COOD (10 g l^{-1}). ^{1}H spectra were recorded at 30°C with 45° pulse, 6 s pulse repetition, 5 kHz spectral width, 16K data points and 16 accumulations. ^{13}C spectra were recorded at 30°C with 45° pulse, 8 s pulse repetition, 16 kHz spectral width, 64K data points and 1000–1500 accumulations.

High-resolution solid-state ^{13}C n.m.r. spectra were recorded at 67.9 MHz on a JEOL GSX-270 spectrometer equipped with cross-polarization magic-angle sample spinning (c.p.m.a.s.) accessories. C.p.m.a.s. n.m.r. spectra were measured with 2 ms contact time, 5 s pulse repetition, 27 kHz spectral width, 8K data points and 1000 accumulations. All spectra were acquired with high-power dipolar decoupling of ca. 60 kHz and m.a.s. at 5.0–5.5 kHz. ^{13}C chemical shifts were calibrated indirectly with the methyl resonance of solid hexamethylbenzene (17.6 ppm relative to tetramethylsilane).

N.m.r. spectral analysis. The relative peak intensities of solution-state n.m.r. spectra were determined with a curve resolution program[10]. This program includes the optimization process of the intensities, chemical shifts and linewidth of Lorentzian curves. A monolinear least-squares method was applied to optimization of the parameters. For solid-state n.m.r. spectra, the NMR-1 program supplied from New Methods Research Incorporation was utilized for the curve resolution.

X-ray. Wide-angle X-ray diffractions (WAXD) were measured using a diffractometer (Rigaku Rad B) at 40 kV and 20 mA with Ni-filtered Cu Kα radiation.

The X-ray pattern of the quenched sample showed only an amorphous halo and that of the annealed sample showed many crystalline peaks. The X-ray diffraction pattern was resolved into crystalline peaks and amorphous halo by a peak separation computer program written in our laboratory. The degree of crystallinity was determined by the area ratio of the crystalline peaks and the amorphous halo.

RESULTS AND DISCUSSION

Copolymer composition and its sequence distribution

Figure 1 shows the ^{1}H n.m.r. spectrum of Cop B. The methylene resonances are divided into three groups. The cyclohexenedimethylene (–CH_2–cyclohexyl–CH_2–) groups of the CT unit have two isomers, *cis* (equatorial–axial) and *trans* (equatorial–equatorial or axial–axial); the latter form (*trans*-CT) is more stable than the former (*cis*-CT). The three groups are associated with the methylene resonances of ET, *cis*-CT and *trans*-CT. The assignment for ET was done from comparison of the spectra of P(ET/CT)s with various compositions. The assignments of *cis*-CT and *trans*-CT were done from the analysis of ^{13}C n.m.r. spectra (described later). The resonances from the cyclohexene group of the CT unit are divided into two groups, which are also assigned to *cis*-CT and *trans*-CT, respectively. The assignments of the methylene and cyclohexene protons are shown in *Figure 1*. The copolymer compositions of ET, *cis*-CT and *trans*-CT are estimated from the relative peak intensities of the methylene and cyclohexene proton resonances as listed in *Table 2*. The *trans* and *cis* isomer compositions of the CT unit are almost constant, about 67 and 33 mol%, respectively, for all copolymers used in this study.

Figure 2 shows the ^{13}C n.m.r. spectrum of Cop B. The assignments of this spectrum are also shown in this figure. The assignments were performed based on the

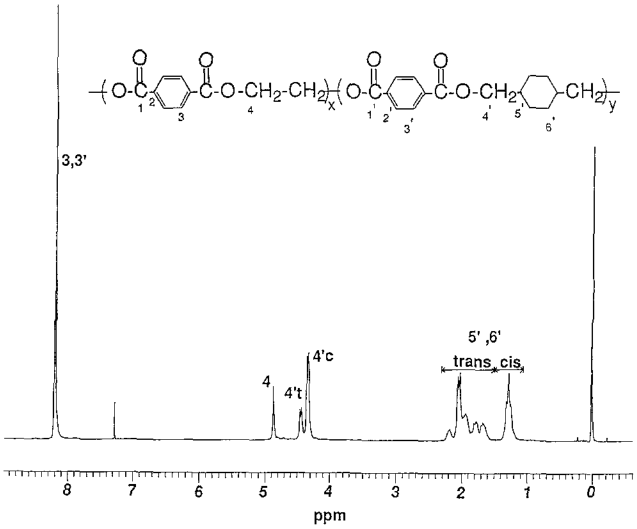

Figure 1 The 270 MHz ^{1}H n.m.r. spectrum of Cop B in $CDCl_3$/CF_3COOD mixture at 30°C

Table 2 Copolymer composition and isomer composition of CT unit

Sample	Copolymer composition[a] ET	Copolymer composition[a] CT	CT isomer composition[b] *trans*	CT isomer composition[b] cis
Cop A	0.950	0.050	0.655	0.355
Cop B	0.796	0.204	0.687	0.313
Cop C	0.657	0.343	0.644	0.356
Cop D	0.337	0.663	0.678	0.322
Cop E	0.192	0.808	0.692	0.308
PCT	0.000	1.000	0.685	0.315

[a] Mole fractions determined from the methylene proton resonances
[b] Mole fractions determined from cyclohexene proton resonances

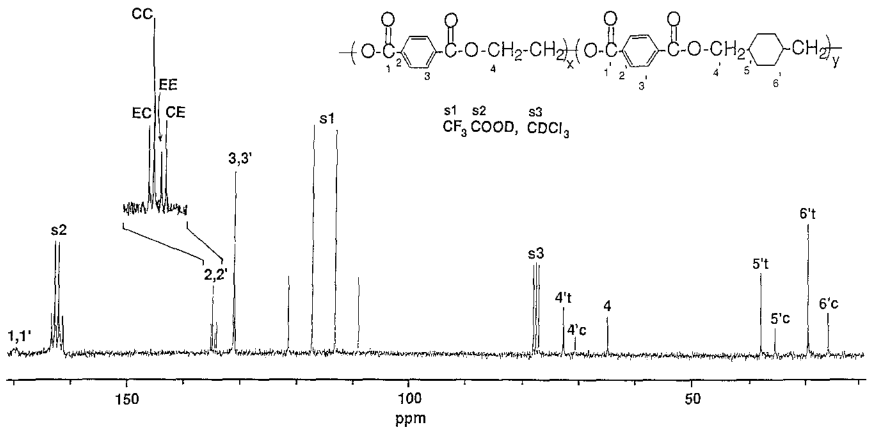

Figure 2 The 67.5 MHz ^{13}C n.m.r. spectrum of Cop B in $CDCl_3/CF_3COOD$ mixture at 30°C

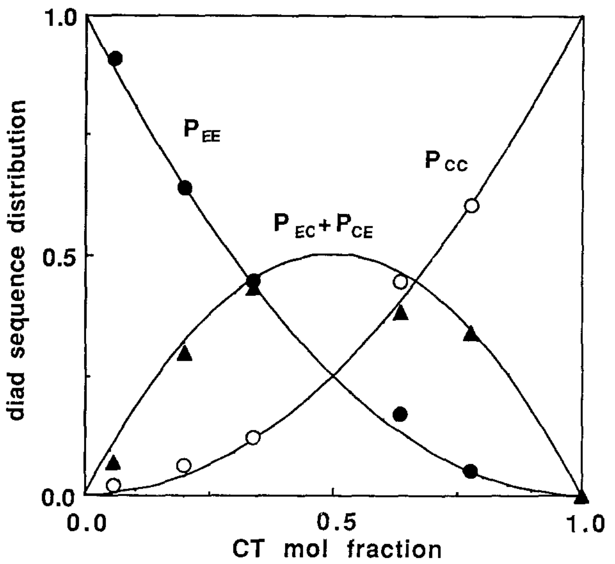

Figure 3 Diad sequence distributions of P(ET/CT) plotted against CT molar composition. Full curves indicate the calculated distribution based on Bernoullian statistics

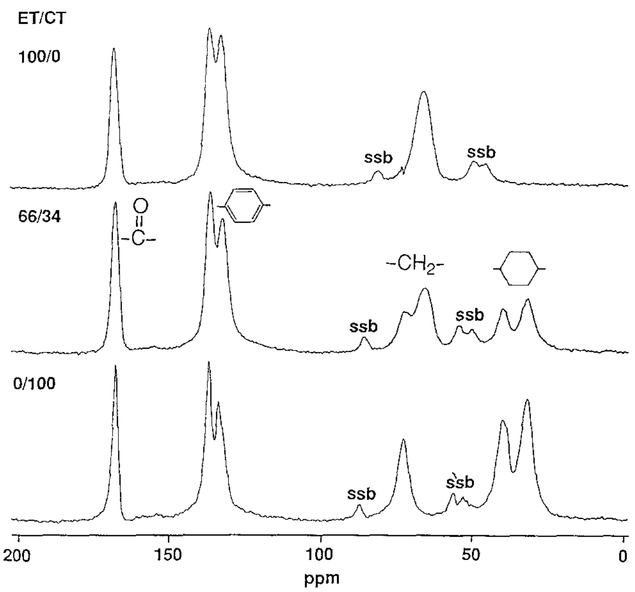

Figure 4 The 67.5 MHz c.p.m.a.s. n.m.r. spectra of the quenched (amorphous) samples

comparison of the spectra with different copolymer samples. The assignments for the methylene protons of CT isomers are described elsewhere[11]. The cyclohexene resonances show that the composition of the *trans* isomer of CT is larger than that of the *cis* isomer for all copolymer samples examined. Thus, the methylene proton resonances of CT units are assigned as shown in *Figure 1*. The benzene carbon resonances of the CT units (C2′ in *Figure 2*) split into four peaks, reflecting the diad sequence distribution. The diad sequence distributions are determined by the relative peak intensities of these resonances and are plotted against the mole fraction of CT units in *Figure 3*.

If the sequence of a copolymer is statistically random, the diad sequence distribution can be described by Bernoullian statistics, as follows:

$$F_{AA}=F_A^2$$

$$F_{AB}=F_AF_B$$

$$F_{BB}=F_B^2$$

where F_{IJ} and F_I indicate the mole fractions of I–J diad sequence and I monomer in the copolymer chains, respectively. The diad sequence distributions for the copolymer samples calculated by Bernoullian statistics are also shown in *Figure 3*. The fractions of diad sequences observed experimentally are reproduced well by the calculated ones. Thus, the P(ET/CT) samples used in this study were concluded to be statistically random copolymers.

Copolymer composition in crystalline phase

Figures 4 and *5* show 67.5 MHz c.p.m.a.s. spectra of amorphous (quenched) and crystalline (annealed) samples, respectively. These spectra are simple in comparison with the solution spectra (*Figure 2*) because of their peak broadening. The peak splittings caused by sequence distribution cannot be observed in the solid-state spectra for both amorphous and crystalline samples. Most carbon resonances from ET and CT units overlap with each other. The largest difference in the chemical shifts between ET and CT units is observed for the methylene carbon resonances. Thus, the methylene carbon resonances for all samples were used to estimate the copolymer composition in the solid state.

The chemical shifts and the peak widths of the

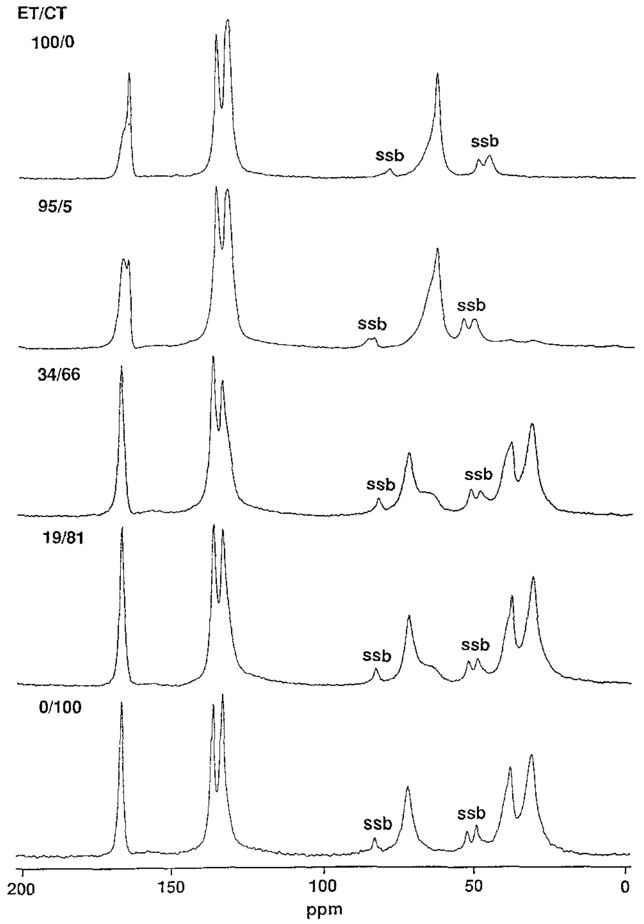

Figure 5 The 67.5 MHz c.p.m.a.s. n.m.r. spectra of the annealed (crystalline) samples

Table 3 Chemical shifts and linewidths of methylene carbon resonances for amorphous samples

	Chemical shift (ppm)		Linewidth (Hz)	
Sample	CT	ET	CT	ET
PET		64.75		380
Cop C	71.38	64.85	310	380
PCT	71.69		270	

methylene carbon resonances in the amorphous state were determined by curve resolution. For the amorphous PET and PCT, the methylene resonance shows a symmetrical shape. The methylene resonances for the copolymer samples are resolved into two components, representing the ET and CT units. These results indicate that both the shift and the width are almost independent of composition for the amorphous state as listed in *Table 3*.

The c.p.m.a.s. spectra of the methylene carbon show the unsymmetrical curves for the crystalline PET and PCT samples (homopolymers) as seen in *Figure 5*. The unsymmetrical peak could be due to overlapping of the two resonance peaks associated with the crystalline and amorphous phases. On the other hand, the c.p.m.a.s. spectra for the annealed samples comprised four resonance peaks, such as the crystalline ET, the amorphous ET, the crystalline CT and the amorphous CT. The curves were resolved into four peaks by using the NMR-1 program. The computer-fitted spectra of Cop B are shown in *Figure 6* together with the spectrum observed experimentally. The calculated spectrum reproduces well the experimental one for all samples. The chemical shifts and relative peak intensities of the crystalline and amorphous phases are listed in *Table 4*.

In general, relative peak intensities in c.p.m.a.s. spectrum do not always reflect exact copolymer compositions because the c.p. efficiency depends on the ^1H–^{13}C dipole interaction. The dipole interaction in the crystalline phase is generally larger than that in the amorphous phase. The c.p. efficiencies in the crystalline phase, however, can be assumed to be almost equal in magnitude for the different comonomer units because of effective ^1H spin diffusion. Thus, the copolymer composition in the crystalline phase (X_c) can be estimated from the relative crystalline peak intensities in the c.p.m.a.s. spectra for the copolymers. The estimated X_c values are also listed in *Table 4* and are plotted against the copolymer composition as shown in *Figure 7*. The crystalline phases in Cop A and Cop B consist of only ET component, whereas those in Cop D and Cop E adopt the incorporation of the ET segments to some extent. In other words, the simultaneous formation of both the PCT and PET crystals and/or the incorporation of ET units in the PCT crystal occur in the composition range rich in CT units.

Crystal lattice

In the ET/CT copolymer system, the minimum melting temperature and heat of fusion appear at an intermediate composition of about 30–40 mol% CT[9]. This point should represent the crystal lattice transition. The crystal lattice for the copolymers in the composition range rich in ET units is made up by PET crystal. In the composition region rich in CT units, the crystal lattice comprises only

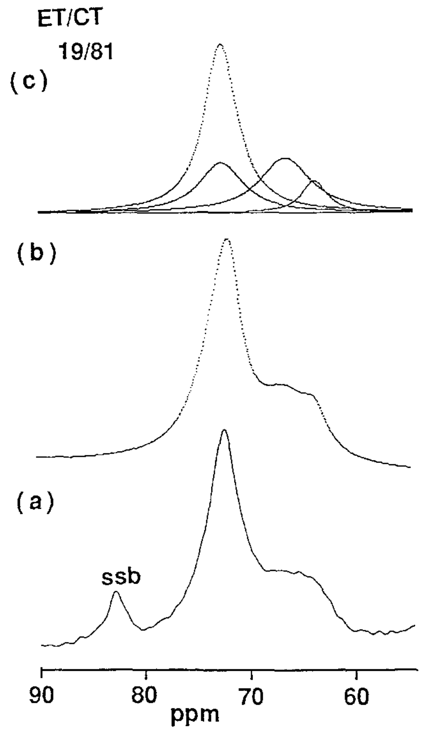

Figure 6 Experimental and calculated methylene resonances of the annealed Cop E in 67.5 MHz c.p.m.a.s. n.m.r. spectra: (a) experimental spectrum; (b) calculated spectrum; (c) component curves of calculated spectrum

Table 4 Chemical shifts and peak intensities of methylene carbon resonances for crystalline samples

	Chemical shift[a] (ppm)				Intensity[a]				
Sample	CT(a)	CT(c)	ET(a)	ET(c)	CT(a)	CT(c)	ET(a)	ET(c)	X_c
PET			65.93	63.09			0.435	0.565	0.000
Cop A	71.22		65.78	63.17	0.041		0.494	0.465	0.000
Cop B	71.55		65.56	63.09	0.152		0.439	0.409	0.000
Cop D	71.90	71.93	65.93	63.26	0.195	0.487	0.247	0.071	0.873
Cop E	71.10	71.84	65.19	62.57	0.385	0.334	0.249	0.032	0.912
PCT	71.12	71.79			0.618	0.382			1.00

[a] (c) and (a) represent the crystalline and amorphous phases, respectively

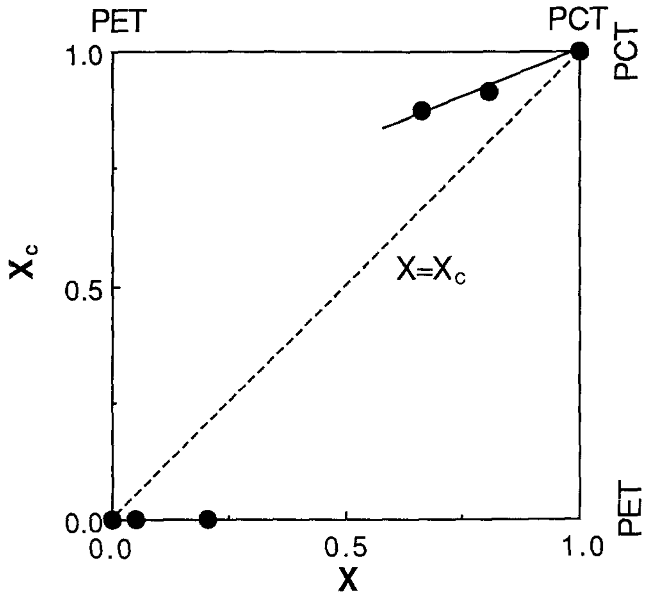

Figure 7 Plots of the mole fraction of CT units in the crystalline phase as a function of copolymer composition of CT mole fraction

PCT crystal. The simultaneous formation of both PCT and PET crystals in an ET/CT copolymer should not occur. Thus, the PCT crystal adopted the incorporation of ET units to some extent. X-ray analysis of the crystal lattices will follow these results[14].

In general, cocrystallization in a binary AB-type crystalline–crystalline random copolymer system requires similar chemical structure, similar repeat-unit length, similar volume and compatible conformation between the two comonomer segments in the crystal lattice. Among these requirements for cocrystallization, the similarity in the main-chain structure between the two comonomer units seems to be the most important. For example, the 3HB and 3HV units of P(3HB-3HV) cocrystallize because of their same main-chain skeleton.

On the other hand, cocrystallization will be hardly realized between two comonomer units with different repeat-unit length but with similar side chains such as ET/CT copolymer, because of their translational misfit (defects) along the chain direction. However, cocrystallization between ET and CT units is possible to some extent, as discussed above. So, a new concept is required for cocrystallization in the ET/CT copolymer system. According to the unit-cell dimensions, the sequence length of four ET repeat units (4.30 nm) is almost identical with that of three CT repeat units (4.26 nm)[12,13]. Therefore, it is possible to cocrystallize between three CT repeat units and four ET repeat units, exhibiting copolymer isomorphism owing to similar sequence length rather than similar repeat-unit length. More detailed crystallographic discussions will be published in a separate paper[14].

REFERENCES

1 Perez, E., VanderHart, D. L., Crist, B. and Howard, P. R. *Macromolecules* 1987, **20**, 78
2 Perez, E., Bello, A., Perena, J. M., Benavente, R., Martinez, M. C. and Aguilar, C. *Polymer* 1989, **30**, 1508
3 Allerga, G. and Bassi, I. W. *Adv. Polym. Sci.* 1969, **6**, 549
4 Kamiya, N., Sakurai, M., Inoue, Y., Chujo, R. and Doi, Y. *Macromolecules* 1991, **24**, 2178
5 Yoshie, N., Sakurai, M., Inoue, Y. and Chujo, R. *Macromolecules* 1992, **25**, 2046
6 Cornivert, J. and Marchessault, R. H. *J. Mol. Biol.* 1972, **71**, 735
7 Yokouchi, M., Chatani, Y., Tadokoro, H., Teranishi, K. and Tani, H. *Polymer* 1973, **14**, 267
8 Yokouchi, M., Chatani, Y., Tadokoro, H. and Tani, H. *Polym. J.* 1974, **6**, 248
9 Yoo, H. Y., Umemoto, S., Kikutani, T. and Okui, N. *Polymer* 1994, **35**, 117
10 Hayashi, T., Inoue, Y., Chujo, R. and Asakura, T. *Polymer* 1988, **29**, 138
11 Benavente, R. and Perena, J. M. *Rev. Plast. Mod.* 1989, **394**, 585
12 Boye, C. A. *J. Polym. Sci.* 1961, **55**, 275
13 Fakirov, S., Fisher, E. W. and Schmidt, G. F. *Makromol. Chem.* 1975, **176**, 2459
14 Yoo, H. Y., Umemoto, S., Kikutani, T. and Okui, N. in preparation