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고체상태에서의 CPMAS NMR 분광법을 이용한 랜덤 공중합체의 결정구조 연구

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Crystal Structure Study of Random Copolymers by CPMAS Solid-State NMR Spectroscopy

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초 록 폴리(에틸렌 테레프탈레이트-co-1,4-사클로헥실렌 디메틸렌 테레프탈레이트), P(ET-CT), 공중합체의 결정구조를 CPMAS NMR 분광법을 이용하여 해석하였다. 결정화 시료에서 메틸렌기에 의한 공명 피크를 CT와 ET 성분으로 분리시켜 분석한 결과, 0-20 몰%의 CT 조성을 갖는 공중합체는 bulky한 CT 성분이 PET 결정격자에서 배제되고 66-100 몰%의 CT 조성을 갖는 공중합체는 PCT 결정격자 내부에 ET 성분이 부분적으로 혼입되는 것을 확인할 수 있었다. 이와 같은 결정구조의 공중합 조성 의존성은 ET와 CT의 반복단위 길이와 결정격자의 크기가 다르기 때문인 것으로 추정된다.

Abstract The crystal structures of poly(ethylene terephthalate-co-1,4-cyclohexylene dimethylene terephthalate), P(ET-CT), copolymers were studied by CPMAS solid-state NMR spectroscopy. With the estimation of methylene resonance peaks, the bulkier CT component of the copolymer in the range of 0-20 mol% CT is excluded from the ET crystal lattice, whereas smaller ET component of the copolymer in the range of 66-100 mol% CT can be partially included into the CT crystal lattice. These different crystallization behavior can be explained with the difference in chain bulkiness and crystal lattice dimension between two copolymer components.

Introduction

In the crystallization of crystalline/crystalline random copolymers, there is a possibility to find some degree of isomorphism due to co-crystallization between similar repeating units [1]. The crystallization of copolymer units can occur, when steric hindrance and thermodynamic instability are considerably small. Previous experimental observations and their theoretical discussions confirmed the possibility that in some copoymers all or limited amounts of the copoymer units could be included in the crystalline lattice[2-13].

Different species which crystallize from solution or melt over a certain range of composition with a common crystal lattice are said to form mixed crystals. Mixed crystal formation is often only possible for species which crystallize in pure state with equal shape. Thus, this phenomenon has been called isomorphism. There are two different classes of isomorphism in macromolecules: isomorphism of whole chains and isomorphism of repeating units only. Repeating unit isomorphism is more common in macromolecules than chain isomor-

phism[7]. Natta distinguished two different types of repeating unit isomorphism in crystalline/crystalline copolymers[1]. Type 1: Homopolymers of the two repeating units have crystals with similar structure. In this case a continuous change in lattice parameters from one homopolymer towards the other is expected for the copolymer as a function of crystallization. For example, trans/cis isomeric copolymers of poly(1,4-cyclohexylene dimethylene terephthalate), PCT[8] follows this type. Type 2: Homopolymers of the two repeating units have different crystal structures. In this case a repeating unit is substituted into a crystal structure different from its own homopolymer. Such substitution is strictly called isodimorphism. At some intermediate composition the copolymer changes from one crystal structure (with changed lattice parameters due to substitution) to other (also with changed lattice parameters due to substitution). Frequently both crystals may be found side by side in intermediate concentration range. Various copolymers follow this type, such as poly(3-hydroxy butyrate-co-3-hydroxy valerate)[2], poly(ethylene terephthalate-co-adipate), poly(ethylene terephthalate-co-sebacate)[9-12], poly(ethylene terephthalate-co-benzoate)[13], poly(ethylene terephthalate-co-ethylene isophthalate)[14], and so on.

In this study, the copolymer composition of random copolymers in crystal state are analyzed by Cross Polarized Magic Angle Spinning (CPMAS) solid-state NMR spectroscopy. The solid-state NMR is expected to provide an useful means for discriminating chemically equivalent carbons distributed among different environments in copolymers, including more than two types of crystalline lattices and a noncrystalline phase[15].

Experimental

Samples

Poly(ethylene terephthalate-co-1,4-cyclohexylene dimethylene terephthalate), P(ET-CT) copolymer samples were used in this study. All samples were kindly supplied by Eastman Kodak and Sun Kyong Industries. The composition and the fraction of diad sequence distribution were already analyzed by ^{1}H NMR and ^{13}C NMR spectroscopies[16] and listed in Table 1.

Table 1. The copolymer composition and the fraction of diad sequence distribution in P(ET-CT) copolymers.

Composition (ET/CT)	Inherent viscosity	Fraction of diad sequence		
		Pec	Pee	Pcc
PET, 100/0	0.74	–	1	–
COP 95/5	0.80	0.071	0.908	0.021
80/20	0.65	0.298	0.638	0.063
66/34	0.75	0.433	0.444	0.123
34/66	0.75	0.381	0.173	0.446
20/80	0.75	0.342	0.053	0.605
PCT, 0/100	0.89	–	–	1

(ec, ee and cc indicate ET-CT and CT-ET, ET-ET and CT-CT sequences, respectively)

Samples were dried at 100℃ under vacuum for 24 hours, hot pressed to form a thin film, and quenched in liquid nitrogen. The film samples were isothermally crystallized at the temperature below melting temperature.

Measurement

The solid state high-resolution ^{13}C NMR spectra were observed at 67.9MHz on a GSX-270 spectrometer equipped with CPMAS ac-

cessories. A sample was packed in a ceramic cylindrical rotor with polyimide end caps. All NMR spectra were acquired with high-power dipolar decoupling(DD) of about 60kHz and MAS at 5.0-5.5kHz. CPMAS NMR spectra were measured with a 2-ms contact time, a 5-s pulse repetition time, a 27kHz spectral width, 8k data points, and 1000 accumulations. ^{13}C chemical shifts were calibrated indirectly by the methyl resonance of solid hexamethyl benzene(17.4 ppm relative to TMS).

Wide-Angle X-ray Diffraction(WAXD) was measured for evaluation of the crystallinity using a diffractor(Rigaku Rad B) at 40 kV and 20 mA. Ni-filtered Cu Kα radiation (the wave length:0.154nm) was used.

Analysis

The degree of crystallinity was determined by X-ray method evaluating the contributions of crystalline reflections and amorphous halo [16].

The relative peak intensities of NMR resonance peaks were determined with a curve resolution program. With this program a sum of Lorentzian curves of different peak sites and different peak intensities can be accurately obtained by an optimal fit. The optimized individual peak intensities were estimated from experimental chemical shifts, experimental peak intensities and line widths.

Results and Discussion

Figure 1 shows ^{13}C NMR spectra of COP-(34/66) sample in crystalline phase(a) and in solution phase(b). The solution spectrum of the copolymer is contrasted to the CPMAS spectrum of the crystalline phase in both the number of resonances and the line widths of resonance. In solid state, the rapid interconversion between many molecular conformations usually precluded[15]. As a result, the split peaks due to the copolymer sequence distribution or trans/cis isomers of CT unit in solution phase cannot be observed in solid state. Almost all carbon resonances from both repeating units overlap with each other. The largest chemical shift difference between ET and CT units is observed for the methylene carbon resonance. Thus the methylene carbon

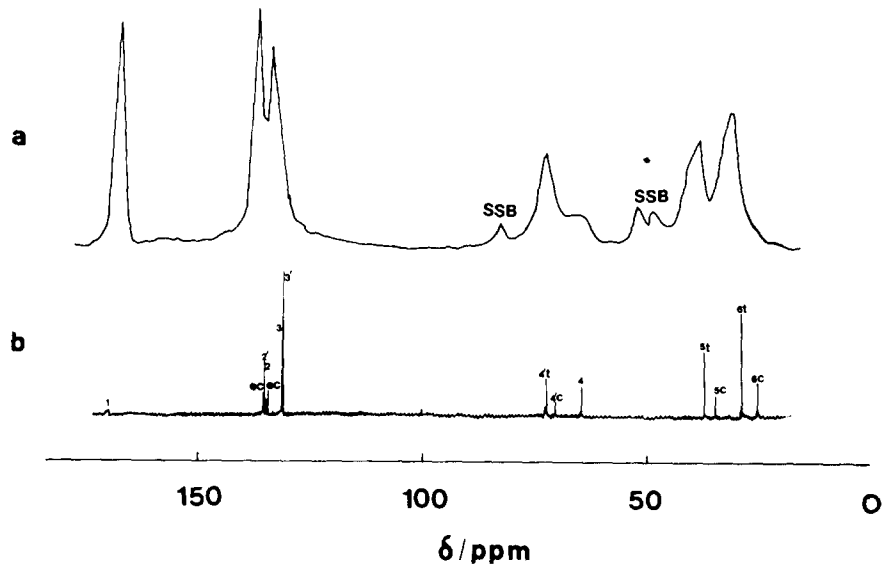

Fig. 1. CPMAS NMR spectra of COP(34-66).
a) CPMAS spectrum in crystalline state, b) ^{13}C spectrum in solution state.
(ssb: spin side band, ec: ET-CT or CT-ET sequences, t: trans and c: cis isomers.)

resonances of all samples were analyzed to estimate the copolymer composition in the crystalline peaks.

Figure 2 shows CPMAS NMR spectra for three quenched samples. The chemical shifts and line widths of methylene resonances were determined by curve resolution program and the results are listed in Table 2. These results show that both of the chemical shifts and peak widths are independent of the composition for amorphous peaks of each repeating unit within experimental error.

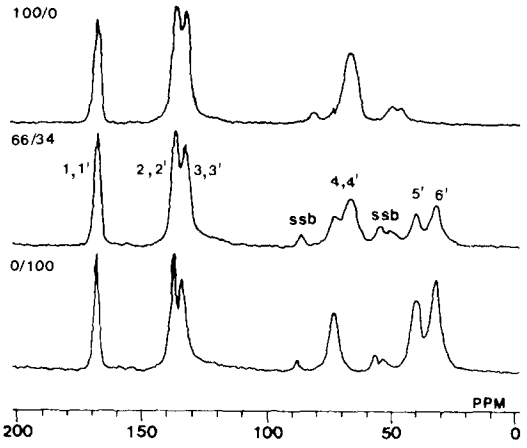

Fig. 2. CPMAS NMR spectra for quenched samples.

Table 2. Chemical shifts and line widths of methylene carbon resonances for quenched smaples.

Composition	Chemical shifts(ppm)		line width(Hz)	
ET/CT	ET	CT	ET	CT
100/0	63.75	–	384	–
66/34	63.85	70.38	383	308
0/100	–	70.69	–	273

Table 3 shows the crystallization temperature condition and the crystallinity(Xc) by X ray analysis for the samples crystallized from the molten state for the 100 minute that is enough time to reach a saturated state of the crystallization. In the CPMAS spectra for the crystallized samples as seen in Figure 3, each of the ET and CT methylene resonances was resolved into two peaks by the curve resolution program. The two peaks represent the contributions from the crystalline and amorphous phases, respectively. In this procedure, the chemical shifts and the peak widths of amorphous peaks were assumed to be similar to that of the quenched samples. The fitted spectra of COP (20/80) are shown in Figure 4, including the experimental spectrum. The calculated spectrum could reproduce well the experimental spectrum for all samples. The chemical shifts and relative peak intensities of the crystalline and amorphous phases are listed in Table 4.

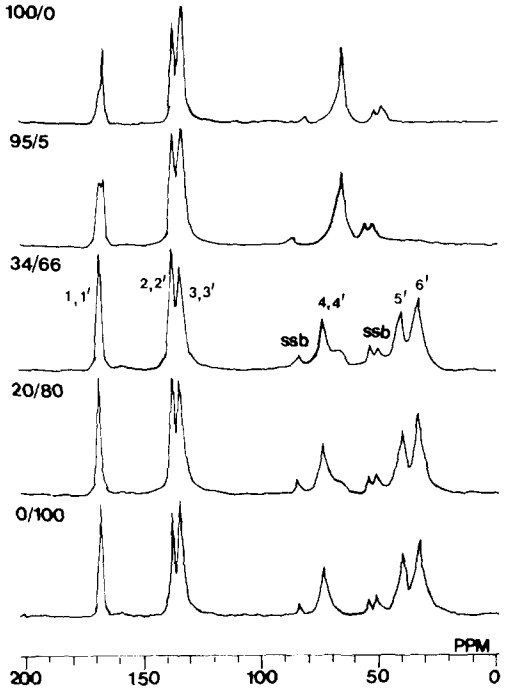

Fig. 3. CPMAS NMR spectra for crystallized samples.

In above CP results, the relative peak intensities do not reflect exact composition because the CP efficiency depends on the ^{1}H–^{13}C dipole interaction[2]. The dipole interaction in the crystalline region, for example, generally larger than that in the amorphous region. The CP efficiencies of different repeating units in the

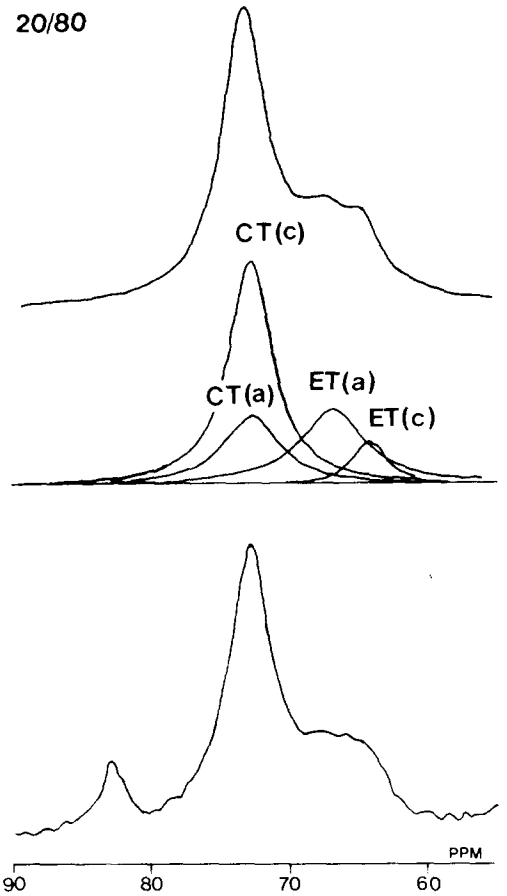

Fig. 4. Methylene resonance peaks of COP(20/80).
a: amorphous, c: crystalline.
1: experimental, 2: separated, 3: summed.

Table 3. The crystallization temperature condition (Tc) and the crystallinity(Xc) of the P(ET-CT) samples.

ET/CT	Tc(℃)	Xc
100/0	230	0.462
95/5	230	0.425
80/20	195	0.358
66/34	—	—
34/66	225	0.341
20/80	245	0.382
0/100	250	0.432

same crystalline lattice, however, can be assumed to be the same because of effective ^1H spin diffusion. Thus, the composition of CT unit in the crystalline phase(X^c) could be estimated from the relative peak intensities of the crystalline phase. The estimated X^c values of crystallized samples are also shown in Table 4.

Figure 5. shows the plots of the mole fraction of CT unit in crystal phase(X^c) against the mole fraction of CT unit in solution phase (X_{CT}). The straight line means that the mole fraction of CT unit in crystal phase equals to that of CT unit in solution phase. In other words, this represents that a uniform inclusion of the one copolymer component into the other

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

	Chemical shift (ppm)				Relative intensity				
ET/CT	CT(c)	CT(a)	ET(a)	ET(c)	CT(c)	CT(a)	ET(a)	ET(c)	X^c
100/0	—	—	64.93	62.09			0.435	0.565	.000
95/5	—	70.22	64.78	62.17	—	0.041	0.494	0.465	.000
80/20	—	70.55	64.56	62.0	—	0.152	0.439	0.409	.000
34/66	70.93	70.90	64.93	62.26	0.487	0.152	0.439	0.409	.873
20/80	70.84	70.10	64.19	61.57	0.334	0.195	0.247	0.071	.912
0/100	70.79	70.12	—	—	0.382	0.618	—	—	1.00

((a) and (c) represent the crystalline and the amorphous phase, respectively. X_c is the mole fraction of CT unit in crystal)

copolymer crystal is possible and that a typical isomorphism by co-crystallization can occur[1, 7]. CT component in the range of 0-20 mol% CT is excluded from the ET crystal lattice, whereas ET component in the range of 66-100 mol% CT can be partially included into the CT crystal lattice. Isomorphism by a partial incoporation of ET unit with CT crystal can be

explained with the difference in the repeating unit length and unit cell dimension.

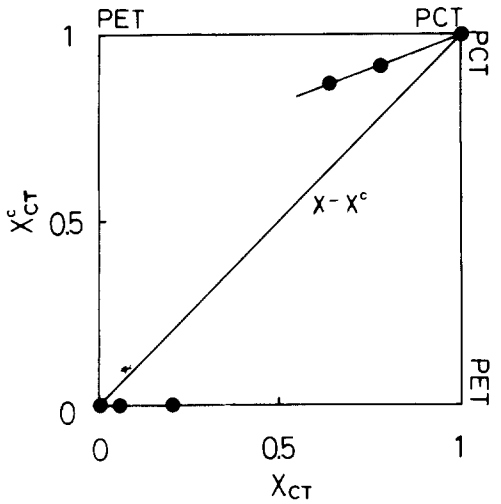

Fig. 5. Plot of the CT mole fraction in crystal state against the CT mole fraction in solution state.

Table 5 Crystal lattice constants of unit cell and other realted parameters in PET[18] and PCT [17].

Constants	PET	trans/cis PCT
a(nm)	0.448	0.637/0.602
b	0.585	0.663/0.601
c	1.075	1.420/1.307
α(degree)	99.5	89.4/89.1
β	118.4	132.9/127.0
γ	111.2	114.4/112.5
type	triclinic	triclinic/triclinic
Vc(cu.A)	219	359/350
Mw/mol	192.2	274.3/274.3
d_c(g/cm^3)	1.515	1.265/1.303
d_a	1.335	1.190/1.209
k*	0.745	0.705/0.705

(*packing density, $k = nV_a/V$, where n is the number of atoms per unit cell, V_a is the volume of the atoms defined by its constant radius, and V is the unit cell volume.)

Figure 6 shows the unit cells of PET and PCT, and the constants related to crystal lattice are listed in Table 5. PCT crystal is made from vertical stereo packing of benzene rings with cyclohexane rings[8,17], whereas PET crystal is made from nearly planar packing of bazene rings[18]. The perfect crystal and packing density of PCT are smaller than those of PET, because CT chain is bulkier and stiffer than ET chain. Accordingly, the difference between both repeating units in character gives rise to different crystallization behavior and crystal

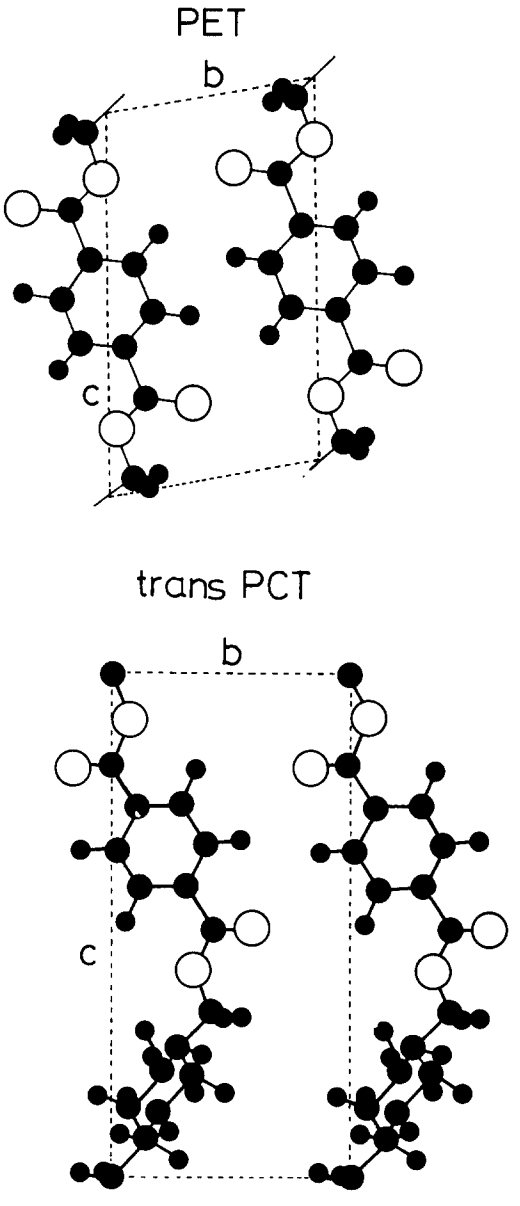

Fig. 6. Unit cells of PET and PCT

structure of the copolymer. The different dependence of crystallization behavior upon the copolymer composition, whether the one copolymer component can be co-crystallized in the other copolymer crystal or not, can be directly associated with the difference in lattice dimension and chain bulkiness between two copolymer components. In the copolymer in composition range of 66 to 100 mol% CT, it is considered that the bulkier and longer CT units can co-crystallized by incoporation with smaller and shorter ET units to some extent. In contrast, bulkier CT unit is excluded from ET crystal of the copolymer in the range of 0 to 20 mol% CT.

Figure 7 shows schematic diagrams of a inclusion model based on X-ray analysis[16]. This model can suggest a new type of isomorphism due to the accordance of the critical crystallizable sequence length between both repeating units. According to X-ray results[16], the critical crystallizable sequence length

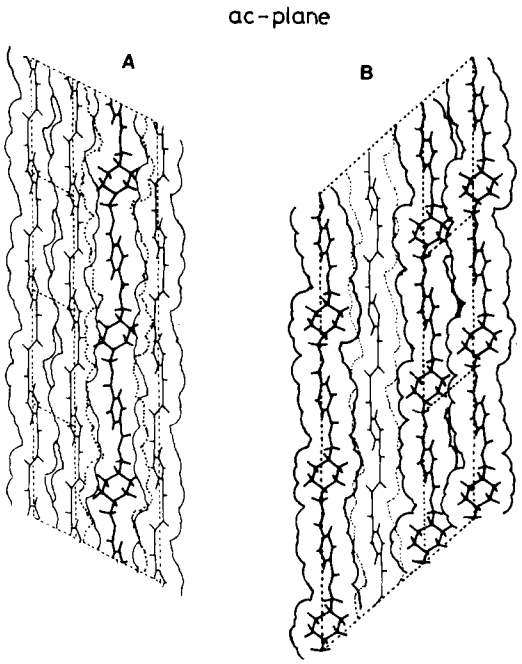

Fig. 7. Schematic diagrams of inclusion model.
A: PCT chain in PET crystal lattice,
B: PET chain in PCT crystal lattice.

along chain axis in PCT crystal with three CT units(42.6 Å) was roughly accord to that in PET crystal with four ET units(43 Å). As seen in Figure 7, there is a very small steric hindrance when ET chain is incorporated with CT crystal lattice. On the contrary, there is too large steric hindrance for bulkier CT chain to be included into ET crystal lattice. Other strucrural studies[16,19] also confirm this isomorphism due to a partial incorporation of the copolymer component in P(ET-CT) system. For an example, the composition dependence of the crystal lattice constants[16] and of the depression behavior in the equilibrium melting temperatures[19] is very similar to that of CPMAS NMR results.

Conclusion

The crystal structures of random P(ET-CT) copolymers were studied by CPMAS solid state NMR spectroscopy. The compositions of both ET and CT repeating units in crystalline phase were estimated from the methylene carbon resonances, using the curve resolution program.

The bulkier CT component of the copolymer in the range of 0-20 mol% CT is excluded from the ET crystal lattice, whereas smaller ET component in the range of 66-100 mol% CT can be partially included into the CT crystal lattice. These different crystallization behavior can be explained with the difference in chain bulkiness and crystal alttice dimension between two copolymer components. Accordingly, a new type of isomorphic model based on the accordance of the critical crystallizable sequence lengths of ET and CT units could be suggested.

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