

Chemical Structure Study on Copolyterephthalates Based on Ethylene Glycol and 1, 4-Cyclohexane Dimethanol by High Resolution NMR Analysis

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고분해능 NMR 분석법에 의한 에틸렌글리콜과 1, 4-시클로헥산디메탄올의 테레프탈산 공중합체의 화학구조 연구

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Abstract: Chemical structure of poly(ethylene terephthalate-co-1, 4-cyclohexylene dimethylene terephthalate), P(ET-CT) copolyesters was investigated by High Resolution NMR analysis. The copolymer composition and isomeric ratio were determined by methylene resonance peaks which were separated into three peaks corresponding to ET, trans CT and cis CT units, respectively. The copolymer sequence distribution was evaluated from the carbon resonance peaks connected to carbonyl groups in benzene, indicating diad distribution. According to statistics model, these copolyesters are almost random copolymers. The copolymer sequence distribution could be simulated and its averaged length was calculated by random copolymer statistics.

요 약: 에틸렌글리콜과 1, 4-시클로헥산디메탄올의 테레프탈산 공중합체인, poly(ethylene terephthalate-co-1, 4-cyclohexylene dimethylene terephthalate), P(ET-CT)의 화학 구조를 고분해능 NMR 분석을 통하여 조사하였다. ¹H NMR 분석에서 메틸렌기에 의한 chemical shift가 ET, 트랜스 CT, 및 시스 CT로 분리됨에 따라 공중합조성 및 이성질체의 비율을 구할 수 있었다. ¹³C NMR 분석에서 카르보닐기에 연결된 벤젠기의 탄소가 diad로 분리됨에 따라 공중합 연쇄 분포(copolymer sequence distribution)를 구한 결과, P(ET-CT) 공중합체는 랜덤공중합체임이 판명되었다. 아울러 랜덤 통계식을 이용하여 공중합 연쇄의 분포 및 평균길이를 구할 수 있었다.

1. Introduction

Poly(1, 4-cyclohexylene dimethylene terephthalate), PCT is the condensation product of dimethyl terephthalate and 1, 4-cyclohexane dimethanol[1].

It differs from the repeating unit of poly(ethylene terephthalate), PET by the presence of the cyclohexane ring between methylene groups. The presence of this ring affects chemical structure and gives rise to trans/cis isomerism as well as to conformational isomers[2]. Poly(ethylene terephthalate-co-1, 4-cyclohexylene dimethylene terephthalate), P(ET-CT) copolyesters have been developed and used as new thermoplastics processable within a wider processing temperature window[3-5], since these copolyesters with different composition have slower crystallization rate and lower melting temperature. In spite of successful application of P(ET-CT) copolyesters in industrial fields, there are a few studies for these copolyesters, for example crystallization behavior[6], chemical structure[7], and dynamic mechanical properties[8]. There is no such study upon this copolyester system over the entire copolymer composition range and, thus, information for this copolymer system is very limited.

The evaluation of chemical structure, such as the copolymer composition and sequence distribution, is inevitable before investigating the effect of chemical structure on crystallization behavior, on higher order structure, and on various physical properties. This is why a small variation of chemical structure brings about considerable changes in crystallization behavior and morphology of polymers. Block copolymers may easily contain crystallizable repeating sequences of sufficient length to build up crystallinity. Random copolymers, in contrast, show a sharp reduction in crystallinity with increasing the copolymer composition[9]. However, it is well-known that High Resolution NMR spectroscopy is a potential method to analyze different chemical composition and structural irregularities, such as tacticity, branching and the copolymer sequence distribution, within a reasonable accuracy[10-14].

This study deals with the quantitative analysis of the copolymer composition by ^1H NMR spectroscopy and the characterization of the copolymer sequence distribution by ^{13}C NMR spectroscopy in P(ET-CT) copolyesters. Statistical evaluation for the copolyesters is also carried out, and the average copolymer sequence length which will be discussed with the crystallizable sequence length in next study is calculated by random statistics.

2. Experimental

Samples of PET, PCT, and P(ET-CT) copolyesters with five different compositions were kindly supplied by Eastman Kodak and Sun Kyung Industries, as shown in Table 1.

Samples were dried at 100 under vacuum for 24 hours, hot-pressed, and quenched quickly in liquid nitrogen. All quenched samples except COP-2 and COP-3 dissolved in a mixture of deuteriochloroform (CDCl_3) and deuterio trifluoroacetic acid (CF_3COOD), because they were insoluble in CDCl_3 . COP-2 dissolved in CF_3COOD and COP-3 dissolved in CDCl_3 . These conditions are determined according to solubility and also listed in Table 1. Concentration of each solution is about 10 g/L.

The ^1H NMR spectra were observed at 30°C on a JEOL GSX-270 spectrometer operating with 270 MHz, 6-s pulse repetition, 4 KHz spectral width, 32 K data points, 16 accumulations. The proton noise-decoupled ^{13}C NMR spectra were observed with 125 MHz, 6-s pulse repetition, 1300 Hz spectral width,

Table 1. P(ET-CT)* Copolyester Samples

Polymer sample	Inherent viscosity	Solvent
PET	0.74	$\text{CF}_3\text{COOD} + \text{CDCl}_3$
COP-1	0.80	"
COP-2	0.65	CF_3COOD
COP-3	0.75	CDCl_3
COP-4	0.75	$\text{CF}_3\text{COOD} + \text{CDCl}_3$
COP-5	0.75	"
PCT	0.89	"

* Poly(ethylene terephthalate-co-1, 4-cyclohexylene terephthalate).

64K data points, and 1000–1500 accumulations.

The relative peak intensities of ^1H and ^{13}C NMR were determined with a curve resolution program. With this program, a sum of Lorentzian curves by an optimal fit. The optimized individual peak intensities were estimated from experimental chemical shifts, experimental total peak intensities, and line widths.

3. Results and Discussion

Fig. 1 shows ^1H NMR spectrum of COP-4. The chemical shifts are observed, from higher to lower chemical shift direction, with the peaks of a phenylene, three methylene, and two cyclohexylene groups. Comparing methylene resonances of both homopolyesters and copolyesters, three split peaks correspond to ET, cis CT, and trans CT repeating units, respectively. On the other hand, two cyclohexylene resonances correspond to trans and cis isomers[2], though they are somewhat complicated and broad shapes with multiple peaks. The assignments of chemical shifts for all samples are listed in Table 2. Corresponding chemical shifts of all copolyesters except COP-2 and COP-3 are almost same values. The chemical shifts of COP-2 are higher, while those of COP-3 are slightly lower.

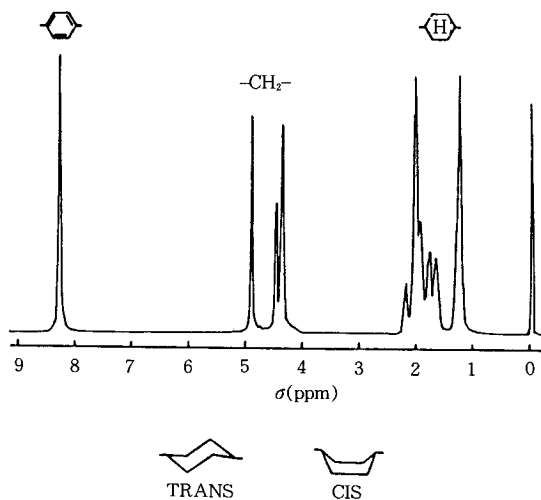


Fig. 1. ^1H NMR spectrum of COP-4.

This should be related to the difference in chemical environment depending on different solvent effect. In fact, the magnitude of deshielding effect by solvent or deshielding agent in solution state can affect a change of chemical shifts [14]. Thus, the magnitude of deshielding effect by solvent can be considered as following order: $\text{CF}_3\text{COOD} \gg \text{Mixed solution of CF}_3\text{COOD and CDCl}_3 > \text{CDCl}_3$.

As methylene groups are divided into ET, cis CT, and trans CT units, respectively, they can be used to determine the copolymer composition and the isomeric ratio of trans/cis in CT units. Of course, the isomeric ratio can also be evaluated by using the separated cyclohexane peaks. The relative peak intensities for all corresponding proton resonances are listed in Table 3. Fig. 2 elucidates that this copolyester system seems to be rather a three-component system of ET/trans CT/cis CT than a common two-component system of ET/CT. Nevertheless, this can be regarded as a binary system of ET/CT, since the values of isomeric ratio are almost

Table 2. Chemical Shifts in ^1H NMR Spectra

Polymer	C_6H_6	CH_2		C_6H_{10} CT trans/cis
		ET/trans	CT/cis	
PET	8.19	4.86/ - / -	- / -	- / -
COP-1	8.19	4.85/4.33/4.20	2.04/1.28	
COP-2	8.38	5.06/4.64/4.50	2.23/1.47	
COP-3	8.10	4.71/4.31/4.20	1.97/1.18	
COP-4	8.19	4.85/4.43/4.32	2.07/1.29	
COP-5	8.19	4.86/4.44/4.33	2.04/1.26	
PCT	8.19	- /4.42/4.32	2.04/1.28	

Table 3. Relative Peak Intensities in ^1H NMR Spectra

Polymer	CH_2		C_6H_6 CT trans/cis	Composition (ET/CT)
	ET/trans	CT/cis		
PET	100/ - / -	- / -	100/0	
COP-1	95.0/3.28/1.77	65.5/35.5	95/5	
COP-2	79.6/14.0/6.40	68.7/31.3	80/20	
COP-3	65.7/22.1/12.2	64.4/35.6	66/34	
COP-4	33.7/45.0/21.3	67.8/32.2	34/66	
COP-5	19.8/55.5/24.7	69.2/30.8	20/80	
PCT	- /68.6/31.4	68.5/31.5	0/100	

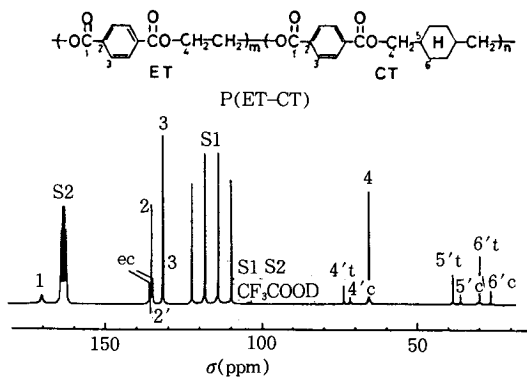


Fig. 2. Three-component diagram of ET/trans CT/cis CT for P(ET-CT) copolyesters.

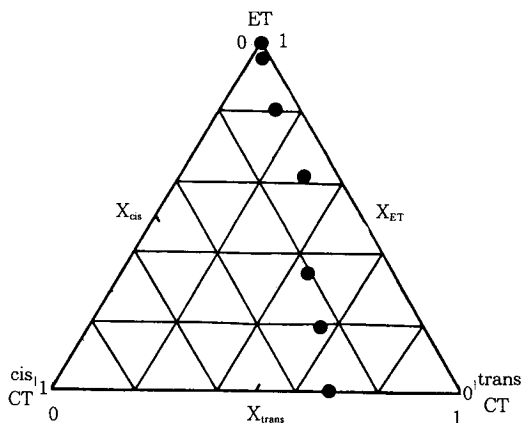


Fig. 3. ^{13}C NMR spectrum of COP-(80/20) and its assignment. (n and n' : carbon No. of ET and CT units, t and c : trans and cis, ec : diad sequences of ET-CT and CT-ET)

constant:trans/cis= about 68/32. Accordingly, the composition of the copolyesters could be determined as the last column in Table 3.

Fig. 3 shows ^{13}C NMR spectrum of COP-(80/20) and assignments of all resonances. The chemical shifts of all carbon sites are listed in Table 4. There is also no difference in chemical shifts among the copolyesters except COP-(80/20) and (66/34) which have higher and slightly lower chemical shifts due to different interactions with the solvents, like in proton resonances. The resonance peaks of

Table 4. Chemical Shifts in ^{13}C NMR Spectra
(unit : ppm)

Species Carbon No.	CO			C_6H_6			
	1	2	2'	ec*	ec*	3	3'
PET	169.3	134.6	—	—	—	131.0	—
COP-(95/5)	169.3	134.4	134.9	135.2	134.1	131.1	130.7
(80/20)	169.3	134.4	134.9	135.2	134.1	131.1	130.7
(66/34)	169.1	133.7	134.2	134.4	133.5	129.8	129.7
(34/66)	169.4	134.4	134.9	135.2	134.1	131.1	131.0
(20/80)	169.8	134.4	134.9	135.2	134.1	131.1	131.0
PCT	169.7	—	134.8	—	—	—	130.9

Species Carbon No.	CH_2			C_6H_{10}			
	4	4't	4'c	5't	5'c	6't	6'c
PET	65.1	—	—	—	—	—	—
COP-(95/5)	65.0	72.9	70.8	37.9	35.4	29.5	26.0
(80/20)	73.6	71.4	65.6	38.6	36.1	29.9	26.3
(66/34)	63.1	70.4	68.2	37.2	34.6	28.9	25.4
(34/66)	64.9	72.9	70.7	37.9	35.4	29.5	26.0
(20/80)	65.0	72.8	70.7	37.9	35.4	29.5	26.0
PCT	—	72.8	70.7	37.9	35.3	29.5	26.0

(ec* indicates the fraction of ET-CT or CT-ET sequences.)

methylene and cyclohexane are also split into ET/trans CT/cis CT and trans/cis isomers, respectively, but there is no more peak to evaluate the copolymer sequence distribution.

In contrast, benzene resonance peaks of each copolyester are separated into quartets resulting from 'diad' distribution of the copolymer sequences, namely ET-ET, ET-CT, CT-ET, and CT-CT sequences, as shown in detail in Fig. 4. This indicates that the carbon atom connected to carbonyl groups in benzene should be affected by different interaction of the diol groups neighboring. The fraction of each copolymer sequence can be evaluated with corresponding relative peak intensity, as listed in Table 5.

If a A/B-copolymer is statistically random copolymer, then the fraction of the copolymer sequence can be described by Bernoullian model[16-17].

$$P_{AA} = P_A \times P_A = P^2 \quad (1)$$

$$P_{BB} = P_B \times P_B = (1-P)^2 \quad (2)$$

$$P_{AB^*} = P_{AB} + P_{BA} = 2P(1-P) \quad (3)$$

where P_{xy} and P indicate the probability of X-Y sequences and the probability for coming of A-re-

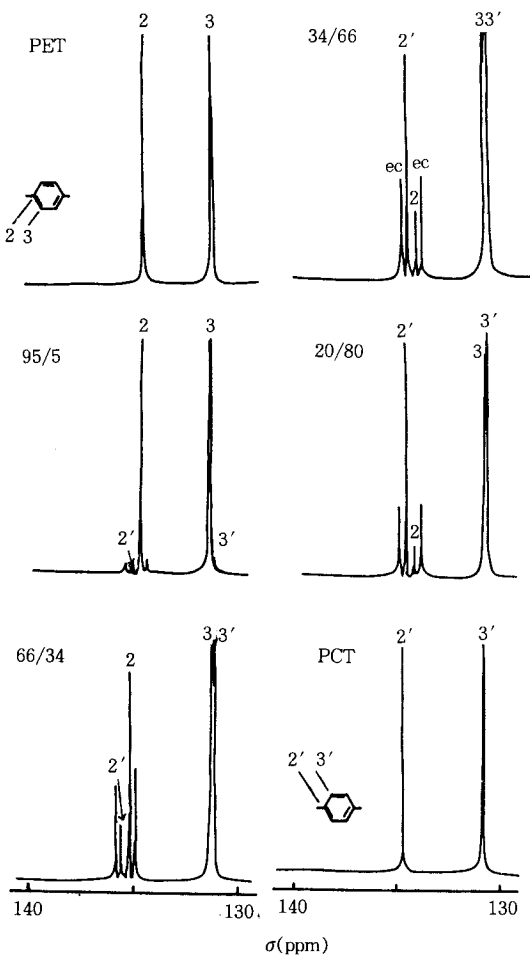


Fig. 4. Benzene resonance peaks of diad sequences.

peating unit, respectively. The probability is generally approximated with the mole fraction of repeating units. If the experimental value of the copolymer sequence fraction is greater than the calculated value of equation (3), a copolymer has rather alternating tendency, otherwise rather blocky in character.

Fig. 5 shows that P(ET-CT) copolyesters can be regarded as random copolymers, because that the experimental values are nearly coincide with the calculated values. Random copolymers generally show a sharp reduction in crystallinity and melting temperatures. This can be explained as a function

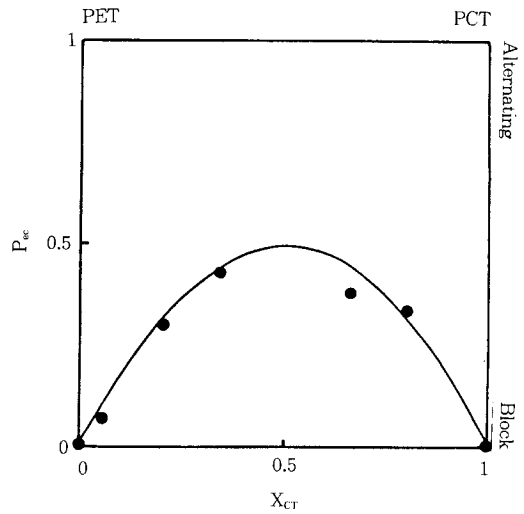


Fig. 5. Plots of the P_{ec} against the mole fraction of CT unit.

Table 5. The Fraction of Diad Sequence and Other Statistical Parameters of P(ET-CT) Copolyesters

ET/CT	P_{ee}	P_{cc}	P_{ec}	$\langle Ln \rangle_e$	$\langle Ln \rangle_c$	$\langle Lw \rangle_e$	$\langle Lw \rangle_c$
PET	1.0	—	—	P_n^*	—	P_w^*	—
95/5	0.908	0.021	0.071	17.7	1.1	29.4	1.1
80/20	0.638	0.063	0.298	4.7	1.3	8.4	1.5
66/34	0.444	0.123	0.433	3.0	1.5	4.9	2.0
34/66	0.173	0.446	0.381	1.6	2.8	2.1	4.5
20/80	0.053	0.605	0.342	1.3	4.5	1.6	7.9
PCT	—	1.0	—	P_n^*	—	P_w^*	—

* P_n and P_w indicate the degree of polymerization, e and c indicate ET and CT repeating units.

of the distribution and averaged length of the copolymer sequence. For this purpose, a statistically random copolymer can be simulated by using a randomized function. Fig. 6 is a schematic diagram of the copolymer sequence distribution for 100 repeating units in COP-(66/34). In addition, the averaged sequence length in random copolymer can also be calculated, like in a stereospecific polymer [17].

ET*CT*ET-ET-ET*CT*ET-ET*CT-CT-
 CT-CT*ET-ET*CT*ET-ET*CT*ET-ET
 CT-CT-CT*ET-ET*CT*ET*CT*ET-ET-
 ET-ET-ET*CT*ET-ET*CT*ET-ET*CT*
 ET*CT*ET-ET*CT*ET-ET-ET-ET
 ET-ET-ET*CT*ET*CT*ET-ET*CT*ET
 CT*ET-ET*CT*ET*CT*ET-ET*CT*ET-
 ET-ET*CT*ET-ET-ET-ET*CT*ET-ET*
 CT*ET-ET*CT-CT*ET*CT*ET-ET-ET*
 CT*ET*CT*ET-ET-ET-ET-ET*CT

Fig. 6. Statistical simulation diagram of a randomized copolymer sequence distribution for COP-(66/34).

$$\langle Ln \rangle_x = 1/(1-P) \quad (4)$$

$$\langle Lw \rangle_x = (1+P)/(1-P) \quad (5)$$

where n and w indicate number and weight-averaged, and P is the probability or the mole fraction of X repeating unit. The calculated averaged sequence lengths are also listed in Table 5. The averaged sequence length becomes short as increasing of the copolymer composition. The shorter the crystallizable sequence of repeating units, the lower is melting temperature or crystallinity[9]. According to other studies[18,19], the melting temperature and the heat of fusion in P(ET-CT) copolymers decrease with an increase of the minor copolymer composition. This depression behavior was explained with the average copolymer sequence length smaller than those of homo-polymers. The relationship between the averaged copolymer sequence length and the crystallizable sequence length in microcrystallites of P(ET-CT) copolyesters was discussed in detail[18].

4. Conclusion

The copolymer composition and sequence distribution of P(ET-CT) copolyesters are characterized by High-Resolution ^1H and ^{13}C NMR spectroscopies. The copolymer composition of ET/CT and trans/cis isomeric ratio in CT unit are determined by methylene resonance peaks which are separated into three peaks corresponding to ET, trans

CT, and cis CT units. The isomeric ratio is almost constant throughout the composition, giving the value of about 68/32. The copolymer sequence distribution is evaluated from benzene resonance peaks which are split into quartets, indicating diad distribution. According to the diad distribution, P(ET-CT) copolyesters are almost statistically random copolymers.

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