〈研究論文(學術)〉

폴리에틸렌테레프탈레이트-코-에틸렌이소프탈레이트의 고리해중합

류동일 · 이웅의 · 신윤숙*

전남대학교 공과대학 섬유공학과, *전남대학교 가정대학 의류학과
(1997년 11월 18일 접수)

Cyclo-depolymerization of Poly(ethylene Terephthalate-co-ethylene Isophthalate)s

Dong Il Yoo, Eung Eui Lee and Youn Sook Shin*

*Department of Textile Engineering and *Department of Clothing & Textiles,*
Chonnam National University, Kwangju, 500-757, Korea
(Received November 18, 1997)

Abstract—Oligomeric extracts of poly(ethylene terephthalate-co-ethylene isophthalate)s [(PET/EI] are analyzed by high performance liquid chromatography(HPLC) and nuclear magnetic resonance spectroscopy (NMR). Existence of separated peaks for small cyclics of trimer and tetramer gives the existence of structural isomeric forms. NMR confirms that cyclization of PET/EI occurs more easily at the site of isophthaloyl unit.

1. Introduction

Condensation polymers, such as polyesters, polyamides and polysiloxanes, contain small amount of cyclic oligomer as a result of equilibrium reaction. Due to commercial and technical importance, researches concerning the cyclic oligomer of poly-condensates are mainly on PET. Related studies on the cyclic oligomer of PET are concentrated on cyclization mechanism[1~3], separation and identification[4~9], synthesis[10,11], equilibrium reaction[5]. The effect of cyclics onto the crystallization process of polymer is also investigated[12~14]. It is well established that cyclization probability is strongly influenced by the rigidity of repeating monomeric unit[15,16].

This study aims to investigate on the cyclio-depolymerization of copolyesters having various content of repeat monomeric unit by means of HPLC and NMR. We made copolyesters that ET unit is one which does not readily form a cyclic oligomer and EI unit is one which readily forms a cyclic oligomer of relatively low molecular weight.

2. Experimental

Homopolymers and copolymers of ethylene isophthalate(EI) and ethylene terephthalate(ET) re-

peat units were obtained by conventional two step condensation polymerization[17].

Cyclic oligomer of PET was extracted by using dioxane for 24 hr. Cyclic oligomer extraction of PEI and the other copolymers was carried out by using acetone for 24 hr. As predominant components of the extracts from copolymers are cyclics[6~9], the extracts of PET, PET/EI and PEI are abbreviated as CET, CET/EI and CEI, respectively.

[EI]₂, which is a crystalline sublimate, evolves on the wall of polymer tube during polymerization of PEI[18]. The sublimate was collected and purified by recrystallizing in monochlorobenzene(MCB) and dimethylformamide(DMF) subsequently.

Pure [ET]₃, which is also crystalline and major component of CET, was isolated from the mixture of cyclic oligomers by recrystallization in MCB and DMF subsequently.

HPLC analysis was performed by using a Pye Unicam LC-XP series Liquid Chromatograph. Separation of oligomeric components was achieved through a Technosphere5sil(15cm×4.6mm) normal phase column along with a UV detector at 254nm. Hexane/dioxane(70/30, in volume ratio) was used at the flow rate of 1.5ml/min. ^{1}H NMR spectra in CDCl₃ or a mixture of CDCl₃/trifluoroacetic acid(TFA) were obtained by using GE 300 MHz spectrometer. A Du Pont DSC 910 equipped with a Thermal Analyser 2000 was used for thermal analysis. Mass spectrum of [EI]₂ was taken by using chemical ionization method with a Kratos Mass Spectrometer.

3. Results and discussion

3.1 Standard materials : [EI]₂ and [ET]₃

There are a lot of analytical data for [ET]₃ which is crystalline and major component of CET. However, little attention was paid on CEI, especially on [EI]₂[18]. NMR spectrum of [EI]₂ in Fig. 1 shows four different types of protons. CDCl₃/TFA is

chosen for [EI]₂, which is crystalline and insoluble in many other solvents. Protons of C₂ and C₅ of the phenyl ring show spin-spin coupling of triplet at 8.964 and 7.696, respectively. The protons of C₄ and C₆ of the phenyl ring show equivalent chemical shift at 8.341 and there coupling between two protons(C₂ and C₅) produces quartet. The coupling constants of J₂₄(or J₂₆) and J₄₅(or J₆₅) are 1.6 and 7.8 Hz, respectively. Coupling between protons of C₂ and C₅, which is expected negligibly small, is not detected from 300 MHz NMR. And the protons at ethylene unit show singlet at 4.809. The spectrum shown in Fig. 1 gives integral of 1 : 2 : 1 : 4 and the absence of other peaks due to chain end group, thereby the cyclic form of meta substitution is identified. Mass spectrum of [EI]₂ indicates molecular ion(M+1) peak of [EI]₂ as shown in Fig. 2. Table 1 gives Tm and the heat
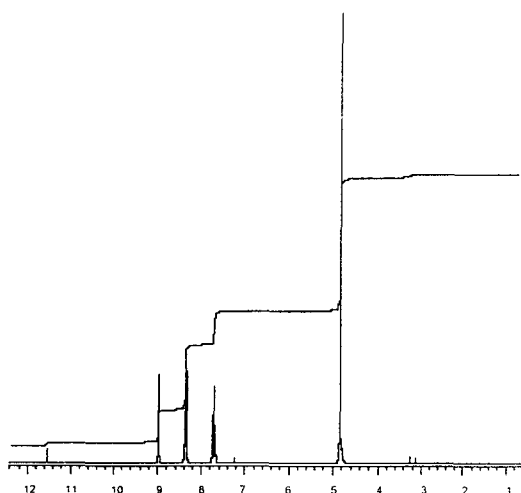

Fig. 1 NMR spectrum of [EI]₂.

Table 1. DSC data of [EI]₂ and [ET]₃

Oligomer	Tm(℃)		ΔH(J/g)
	Measured	Literature	
[EI]₂	335.9	325–327[18]	136.4
[ET]₃	323.4	314-316[1], 319[2], 318[4], 318.2[19]	94.5

of fusion(ΔH) of [EI]$_2$ and [ET]$_3$ obtained by DSC. Tm obtained in this study gives higher value than the data reported by other researchers.
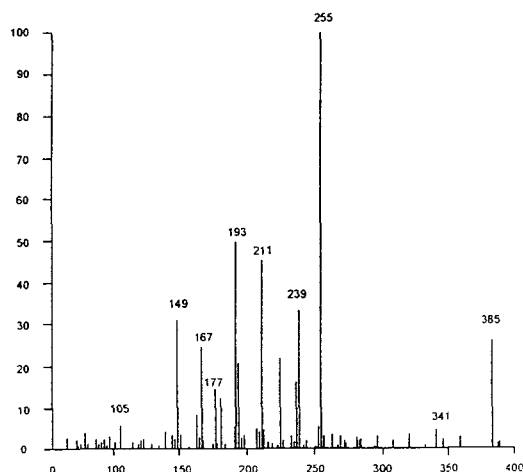

Fig. 2 Mass spectrum of [EI]$_2$.

3.2 HPLC and NMR of cyclic oligomer in copolyesters

Chromatograms of CET and CEI are shown in Figs. 3~4, respectively. As internal standard materials, [ET]$_3$ and [EI]$_2$ are used and all the components isolated are assigned by the help of former studies concerning HPLC of CET[6~9]. From the chromatograms of Fig. 3~4, log(retention time) against repeat unit of the cyclics are plotted as shown in Fig. 5. Linear slopes are obtained that they are homologous series of cyclics. The cyclics of CET and CEI plotted in Fig. 5 are homologues of [ET]$_n$ and [EI]$_n$. The retention times of [ET]$_n$ are different from those of [EI]$_n$. Other components between [ET]$_n$ homologues of Fig. 3 are assigned as cyclics containing diethylene glycol unit.

Fig. 6 shows some chromatograms with the change of ET composition. The cyclization theory by Jacobson and Stockmayer[16] confirms that most probable isomers can be formed at any monomer composition of PET/EI system. Among the possible

isomeric forms of cyclic n-mer, [(EI)$_x$(ET)$_y$] (x+y=n), the isomers of small size are reolved into some isolated peaks. The chromatograms of CET/EI(20/80) and (40/60) also show separated peaks for small isomeric forms, i.e., cyclic trimer and tetramer. However, it is not resolved for the cyclics larger than tetramer because of restricted column efficiency and the similarity of hydrodynamic volumes.
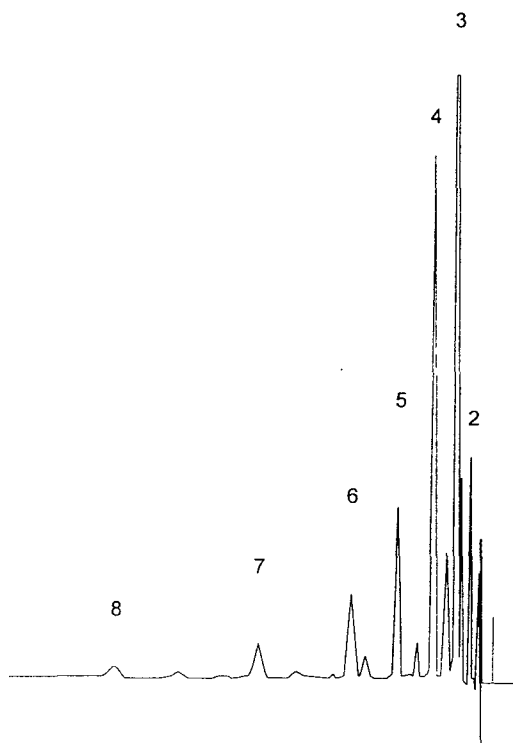

Fig. 3 HPLC chromatogram of CET.

Table 2 gives the composition of PET/EI and CET/EI, which is the integration ratio of terephthaloyl to isophthaloyl unit calculated from NMR data. The composition of PET/EI is quite the same as monomer feed ratio. For the monomer feed ratio 80/20 and 70/30, EI unit of CET/EI is richer than that of PET/EI. This deviation indicates that cyclization of PET/EI occurs more easily at the site of EI unit.
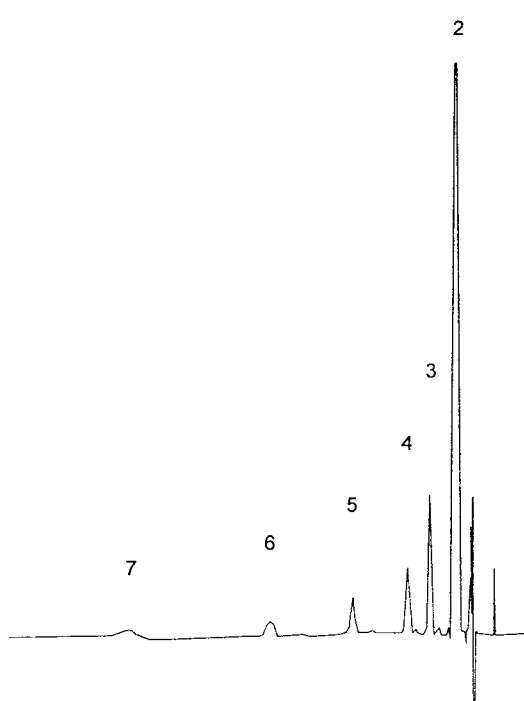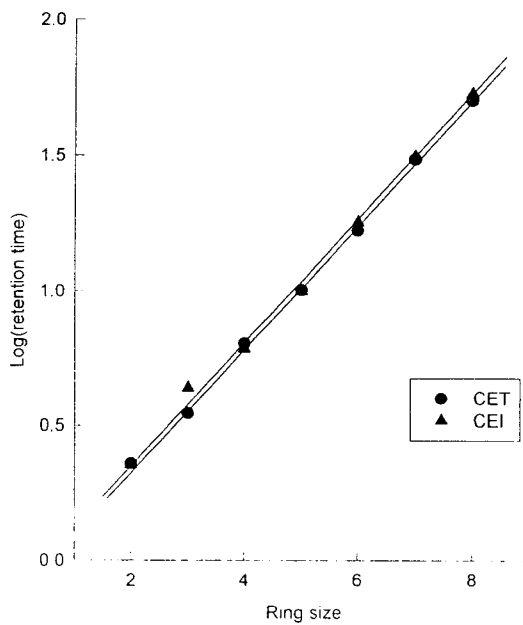
Fig. 4 HPLC chromatogram of CEI.

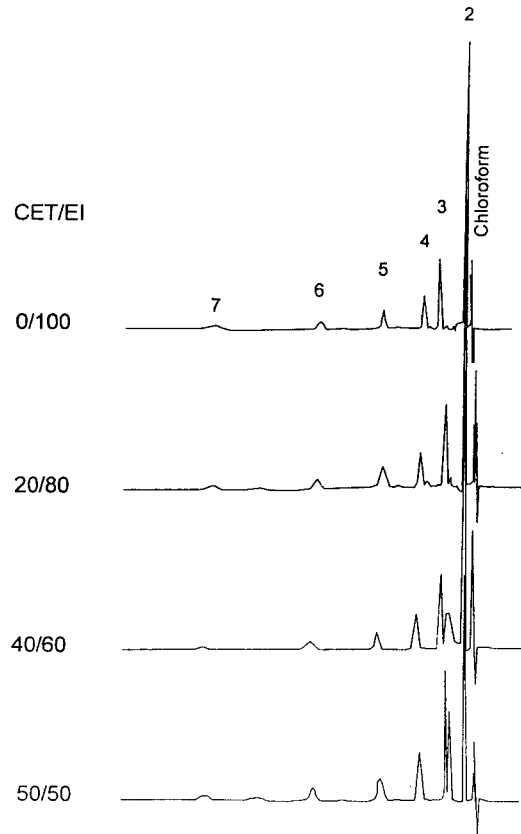Fig. 5 Logarithmic retention time vs. repeat unit of CET and CEI.

Fig. 6 HPLC chromatograms of CET/EI with the increase of ET composition.

Table 2. Composition of PET/EI and CET/EI calculated by NMR data

Monomer feed ratio	PET/EI	CET/EI
100/0	100/0	100/0
80/20	79/21	64/36
70/30	73/23	60/40
50/50	50/50	50/50
20/80	22/78	20/80
0/100	0/100	0/100

References

1. I. Goodman and B.F. Nesbitt, *J. Polym. Sci.*, 48, 423(1960).

류동일·이응의·신윤숙

2. L.H. Peebles, M.W. Huffman, and C.T. Ablett, *J. Polym. Sci. A-1,* **7,** 479(1969).
3. W.S. Ha and Y.K. Choun, *J. Polym. Sci. : Polym. Chem. Ed.,* **17,** 2103(1979).
4. H. Zahn and P. Kusch, *Text. Ind.,* **69,** 880 (1967).
5. D.R. Cooper and J.A. Semlyen, *Polymer,* **14,** 185(1973).
6. J.P. Luttringer, H. Majer, and R. Reinert, *Melliand Textilber.,* **60,** 160(1979).
7. W.R. Hudgins WR, K. Theurer, and T. Mariani, *J. Appl. Polym. Sci. : Appl. Polym. Symp.,* **34,** 145(1978).
8. A.L. Cimeocioglu, S.H. Zeronian, K.W. Alger, M.J., Collins, G.C. East, *J. Appl. Polym. Sci.,* **32,** 4719(1986).
9. G. Wick and H. Zeitler, *Angew. Makromol. Chem.,* **112,** 59(1983).
10. E. Meraskentis and H. Zahn, *J. Polym. Sci., B.,* 4, 1890(1966).
11. E. Meraskentis and H. Zahn, *Chem. Ber.,* **103,** 3034(1970).
   개 2Yu, H. Bu, and Y. Jin, *Makromol. Chem.,* **187,** 2461(1986).
13. D.I. Yoo and W.S. Ha, *J. Kor. Soc. Text. Eng. Chem.,* **24,** 309(1987).
14. D.I. Yoo and W.S. Ha, *J. Kor. Fiber. Soc.,* **27,** 435(1990).
15. W. Kuhn, *Kolloid-Z.,* **68,** 2(1934).
16. H. Jacobson and W.H. Stockmayer, *J. Chem. Phys.,* **18,** 1600(1950).
17. W.R. Sorenson and T.W. Campbell, *"Preparative Methods of Polymer Chemistry",* p. 131, Interscience, New York, 1968.
18. C.E. Berr, *J. Polym. Sci.,* **15,** 591(1955).
19. S. Shiono, *J. Polym. Sci. : Polym. Chem. Ed.,* **17,** 4123(1979).