

## PET와 2-브로모테레프탈산 및 1,5-디아세톡시나프탈렌으로 부터 얻은 공중합체의 성질

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## Properties of Copolyesters Obtained by Post-Copolymerization of PET with 2-Bromoterephthalic Acid and 1,5-Diacetoxynaphthalene

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요 약 : PET를 2-브로모테레프탈산 및 1,5-디아세톡시나프탈렌과 반응시켜 일련의 공중합체를 합성하였다. 이들 공중합체의 열적성질과 액정성을 DSC 및 편광 현미경 분석법으로 행하였다. 공중합체 모두 두개의 Tg를 보여 주었으며, PET단위의 함량이 50 mole% 보다 적을 때는 액정성을 나타냈다. 광각 X-선 분석결과에 의하면 2-브로모테레프탈산과 1,5-나프탈렌디올 잔기의 함량이 20 mole% 만 되어도 PET의 결정구조는 완전히 파괴되었다. 공중합체를 클로로포름으로 용출하여, 가용분과 불용분을 원소분석 및 IR분석을 행하여 보니 공중합체의 조성이 불균일함을 알았다.

**Abstract :** A series of copolyesters were prepared by post-copolymerizing PET with mixtures of 2-bromoterephthalic acid and 1,5-diacetoxynaphthalene. Thermal and liquid crystalline properties of the copolymers were examined by differential scanning calorimetry and by observation on the hot-stage of a polarizing microscope. The copolyesters exhibited two Tg's. Those containing less than 50 mole % PET unit were found to be thermotropic. Wide angle X-ray analysis of the copolyesters was performed and it was found that inclusion of as low as 20 mole % of 2-bromoterephthalic acid and 1,5-naphthalenediol moieties completely destroyed PET crystalline structure. Chemical and IR spectroscopic analyses of chloroform extractable and unextractable fractions suggest that copolyesters prepared are heterogeneous in composition and consist of fractions with differing compositions.

## INTRODUCTION

Modification of poly(ethyleneterephthalate) (PET) by copolymerization with *p*-acetoxybenzoic acid<sup>1</sup> or with an equimolar mixture of terephthalic acid and 1,4-diacetoxybenzene<sup>2,3</sup> can lead to various liquid crystalline compositions. Other monomers can be included in copolymerization to further modify the properties of resulting polymers. The liquid crystalline copolyesters exhibit many unusual properties such as low melt viscosity, very high mechanical strength, anisotropy in properties, etc.

The first such report, Kuhfuss and Jackson's<sup>1</sup> on oxybenzoate modified, liquid crystalline PET copolyesters, mentioned that the copolymers were of random sequence. One recent communication,<sup>4</sup> however, described the compositions of these copolymers as heterogeneous. One of our earlier papers<sup>5</sup> also described reorganization of similar copolyesters and implied the existence of compositional variations.

In the present investigation we have prepared a series of copolyesters from PET and a mixture of 2-bromoterephthalic acid (BTA) and 1,5-diacetoxynaphthalene (DAN).

Although the monomer sequence in the copolymers must be more complex, the copolymer structures may be represented as follows, solely in an attempt to describe their overall composition and different structural units :

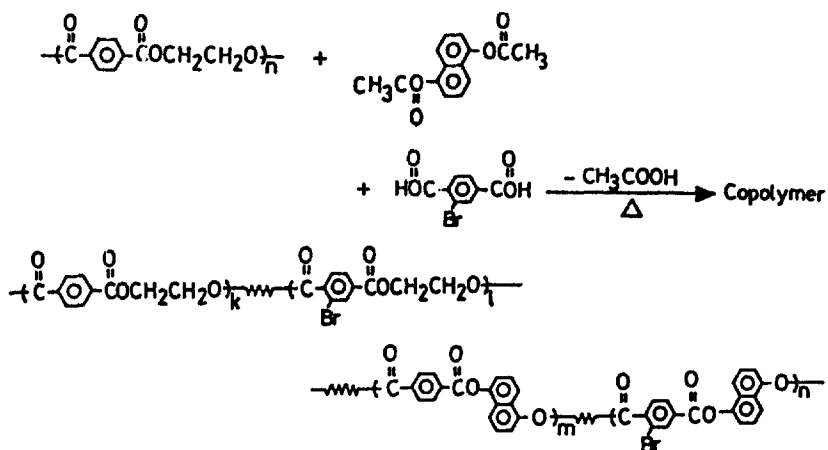
The polymers were examined by differential scanning calorimetry (DSC), on the hot-stage of a polarizing microscope and by wide-angle X-ray diffraction analysis. We also conducted an extraction study of the copolymers, using chloroform as a solvent. Compositions and properties of the extractable portions were compared with those of unextractables.

## EXPERIMENTAL

### Polymer Preparation

Since all of the polymers were prepared in the same manner, only a representative synthetic procedure used for the synthesis of 50 : 50 PET : BTA-DAN is given. The polymerization tube was charged with 1.384g of PET (0.72 mole based on repeating unit, supplied by Sam Yang Industrial Co., Chonju City, Korea), 1.765g of 2-bromoterephthalic acid (BTA) (0.72 mole, Aldrich Chemical) and 2.023g of 1,5-diacetoxynaphthalene (DAN) (0.83 mole, prepared from 1,5-naphthalenediol and acetic anhydride)<sup>6</sup>. From many trial runs, it was learned that 9-15 mole % of DAN in excess of that of BTA was necessary to compensate the loss of the compound by sublimation during polymerization.

Vacuum was applied to the vessel containing reaction mixture for one hour and then a stream of dry N<sub>2</sub> was allowed to flush the reaction tube. The reaction mixture, under a constant stream



of  $N_2$ , was placed in an oil bath at 280°C. When all of the reactants melted, the vacuum mechanical stirrer was turned on. After one hour of reaction at 280°C, the temperature was raised to 290°C and maintained at the same temperature for another hour. Then a vacuum was applied to the system and the polymerization was allowed to proceed for a half hour at 0.5 torr. Higher reaction temperatures were also tried, but this led to excessive darkening of the products. The polymer thus obtained was recovered from the reaction vessel and ground in a micromill. Table 1 shows the polymerization conditions used for the preparation of the polymers in this study.

#### Characterization

The polymer of compositions were estimated from their bromine contents, which were determined by the Microanalytical Laboratory of the University of Massachusetts, Amherst, Massachusetts, U.S. A. Their structures were further confirmed by IR spectra (Perkin Elmer 710 B). Solution viscosity numbers were measured at 30°C on 0.1g/dl solutions in a 35 : 40 : 25 mixture by weight of 1,1,2,2-tetrachloroethane : *p*-chlorophenol : phenol. A Cannon-Ubbelohde type viscometer was used.

Thermal properties were studied under a  $N_2$  atmosphere on a differential scanning calorimeter (Mettler TA 3000) at a heating rate of 10°C/min. Wide angle X-ray diffractograms were obtained at room temperature on a Rigaku Geiger Flex D-Max IIIa using Ni-filtered  $Cu-K\alpha$  radiation ( $\lambda=1.5418\text{\AA}$ ). Powdered polymers were compressed into a plaque about 1.5cm  $\times$  1.5cm  $\times$  0.1cm for X-ray studies. Optical textures and phase transitions of the polymers were observed on a polarizing microscope (Leitz, Ortholux) equipped with a hot stage (Mettler FP 52) : a small quantity of sample was heated to 350°C and the melt was quenched by a dry-ice/acetone mixture. The quenched samples were not only subjected to X-ray analysis, but also were observed at room temperature through the polarizing microscope.

#### Annealing and Chloroform Extraction

Polymers were annealed under vacuum at 220°C for 5 hours. The annealed samples also were subjected to DSC and X-ray analyses and solution viscosity measurement.

Three copolymers (2g each) were subjected to Soxhlet extraction for 2 days using chloroform. Soluble and insoluble portions were recovered

Table 1. Polymerization Conditions

PET/BTA-DAN mole %	Reactant Quantity, g( $10^{-2}$ mole)			Reaction Time, min		Reaction Temp., °C and time (min) at 0.5 torr	
	PET	BTA <sup>a</sup>	DAN <sup>b</sup>	280°C	290°C		
19/81	0.4567 (0.2376)	2.4453 (0.9979)	2.6697 (1.0930)	30	10	290	(15)
39/61	1.0170 (0.5292)	2.0424 (0.8335)	2.2298 (0.9129)	60	60	280	(30)
49/51	1.3800 (0.7181)	1.8476 (0.7540)	2.0171 (0.8258)	40	40	290	(20)
50/50	1.3841 (0.7202)	1.7648 (0.7202)	2.0230 (0.8282)	60	60	280	(30)
59/41	1.6055 (0.8354)	1.4330 (0.5848)	1.5645 (0.6405)	60	60	280	(15)
60/40	1.6818 (0.8751)	1.4296 (0.5834)	1.6387 (0.6709)	60	60	290	(40)
79/21	3.0266 (1.5749)	1.0130 (0.4134)	1.1060 (0.4528)	60	60	280	(30)
						290	(60)

<sup>a</sup> BTA : 2-bromoterephthalic acid.

<sup>b</sup> DAN : 1,5-diacetoxynaphthalene.

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by evaporation of the chloroform and were characterized separately.

## RESULTS AND DISCUSSION

### Synthetic Results and General Properties

The bromine contents of polymers and general properties before and after annealing are presented in Table 2. According to the bromine analysis results overall copolymer compositions were almost the same as those of their respective feeds. The IR spectra of the copolymers exhibited the expected absorption bands such as strong C=O stretching mode at  $1740\text{cm}^{-1}$ , the sharp naphthalenic C=C stretching absorption at  $1630\text{cm}^{-1}$ , the C-O stretching mode at  $1100\text{cm}^{-1}$ , and the aromatic C-H out-of-plane bending absorptions around  $820\text{cm}^{-1}$ .

Polymers were not soluble in conventional solvents, so solution viscosities were measured using a mixed solvent consisting of 1,1,2,2-tetrachloroethane, *p*-chlorophenol and phenol. The solution viscosity numbers (0.58-1.01) of the copolyesters were comparable to or higher than the value (0.66) for the original PET. Annealing the as-polymerized samples at  $220^\circ\text{C}$  for 5 hours under vacuum increased the solution viscosity numbers (see Table 2). The increase appears to be higher for the copolymers having a higher content of PET structural units,

probably due to the enhanced flexibility of polymer chains.

A couple of typical DSC thermograms are shown in Fig.1 Upper thermogram shows two weak endothermic transitions before melting at around  $319^\circ\text{C}$ . In fact, DSC thermograms of all of the copolyesters, with the exception of the first two listed in Table 2, were similar. These two endothermic transitions which appeared before  $T_m$ , we believe, correspond to two glass transitions: the lower temperature ones ( $61\text{-}64^\circ\text{C}$ ) are probably for ethylene glycol-structure-rich segments and the higher temperature ones ( $103\text{-}113^\circ\text{C}$ ) for 1,5-naphthalene-unit-rich segments. Therefore, the existence of two  $T_g$ s

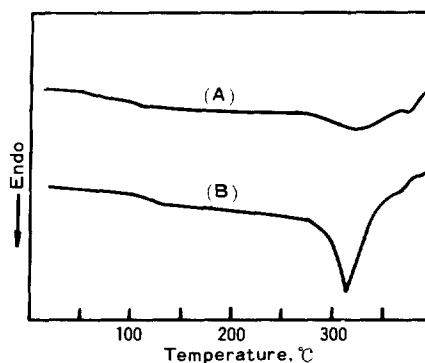


Fig. 1. DSC thermograms of as-polymerized samples (A for 49PET/51BTA-DAN and B for 19PET/81BTA-DAN)

Table 2. Bromine Content and General Properties of Polymers<sup>a</sup>

Feed, Molar Ratio	Bromine Content <sup>b</sup>	$\eta_{inh}^c$ , dl/g	$T_g^d$ and $T_g^e$ , $^\circ\text{C}$	$T_m^c$ , $^\circ\text{C}$
PET/BTA-DAN	Wt. %	as-polymerized (annealed)	as-polymerized (annealed)	as-polymerized (annealed)
0/100 <sup>d</sup>	—	1.75	115 (—)	319 (—)
19/81	19.0 (19.3)	—	113 (—)	314 (—)
39/61	16.2 (16.3)	0.83 (0.84)	61,107 (67,112)	319 (325)
49/51	14.6 (14.5)	0.58 (0.63)	64,103 (63,106)	319 (324)
50/50	14.3 (14.2)	0.76 (0.82)	64,107 (65,109)	329 (332)
59/41	12.5 (12.4)	0.67 (0.75)	61,103 (68,105)	317 (331)
60/40	12.1 (12.2)	1.01 (1.41)	62,103 (62,104)	318 (331)
79/21	7.5 (7.3)	0.64 (—)	64, 86 (—, —)	319 (—)
100/0	—	0.66 (—)	67 (—)	255 (—)

<sup>a</sup> Data in the dashed(—) compartments are not available.

<sup>b</sup> The numbers in the parentheses report the theoretical content, if all the feedstock polymerized.

<sup>c</sup> Values in the parentheses are those for the samples annealed at  $220^\circ\text{C}$  for 5 hours under vacuum.

<sup>d</sup> Data taken from reference 7.

implies that there may be compositional heterogeneity in these copolyesters. The  $T_g$ s of annealed samples were slightly higher or comparable to those of as-polymerized polymers. It is added at this point that most of the samples, regardless whether they were as-polymerized, or soluble, or insoluble samples, revealed much more distinct endotherm for higher temperature glass transitions than for the lower temperature transitions, which were often very weak. Moreover, in the most of 2nd heating DSC thermograms the lower temperature transitions became too weak to detect. This implies that the lower  $T_g$  transitions are very sensitive to thermal history of the samples.

Melting temperatures ( $T_m$ ) determined by DSC analysis also are included in Table 2. Surprisingly, the melting temperatures of all of the copolyesters were found to be about the same, around 314-319°C, which is very close to the melting temperature (319°C) of poly(1,5-naphthylene 2-bromoterephthalate). As the content of PET structural units increased, the size of the melting endotherm appearing around 319°C gradually decreased and the peak shape broadened. Therefore, the  $T_{ms}$  recorded in Table 2 for the compositions containing PET unit higher than 50 mole% should be taken only as approximations. The  $T_{ms}$  of annealed samples were slightly higher than those of as-polymerized samples. This must be partly due to perfection of crystalline structure and partly due to increase in molecular weight. For none of the polymers, however, did we observe any melting endotherms around 255°C where original PET melts. Such observations strongly suggest that the crystallinity of PET is rapidly destroyed by inclusion of relatively small quantity of comonomers. On the other hand, a new crystal structure is developed at the comonomer contents as low as 40 mole%. This persists throughout the range of higher comonomer content. This could clearly be demonstrated by comparing the wide angle X-ray diffractograms (Figures 2A-2D) of these copolymers. The X-ray diffractogram of 79 : 21 PET : BTA-DAN, Figure 2B, shows a practically amorphous nature, while that in Figure 2C shows a semi-crystalline nature for

the 19 : 81 PET : BTA-DAN ratio. The X-ray diffractogram of 19 PET / 81BTA-DAN is about the same as that of the aromatic homopolymer of BTA and DAN (Figure 2D).

In fact, Kuhfuss and Jackson<sup>1</sup> earlier also observed the exact same phenomenon in *p*-oxybenzoate-PET copolymers. The crystallinity of PET rapidly disappeared while poly(*p*-oxybenzoate) diffraction appeared as the *p*-oxybenzoate content was increased in the copolymers.

#### Thermotropic Properties and Compositional Heterogeneity

Only the polymers containing more than 50 mole% of BTA and DAN moieties exhibited nematic textures when heated above their melting points. The 50/50 copolymer definitely showed the coexistence of isotropic and birefringent phase in melts, which is another strong indication for the presence of compositional heterogeneity in such copolymers.

We subjected three of the copolyesters (PET / BTA-DAN=39/61, 49/51 and 59/41) to Soxhlet extraction using  $\text{CHCl}_3$ . The properties of soluble and insoluble fractions were compared with each other and also with those of as-polymerized samples. Table 3 summarizes the results. The

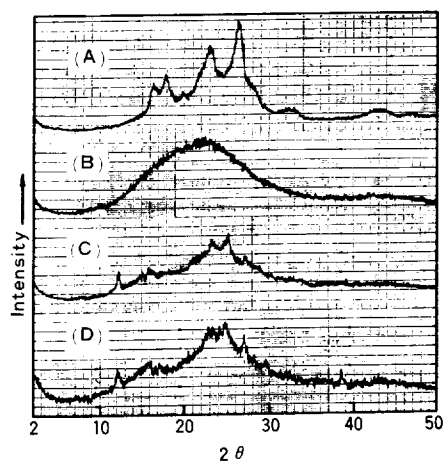


Fig. 2. X-ray diffractograms of copolyesters((A) PET : (B) 79PET / 21BTA-DAN; (C) 19PET / 81BTA-DAN; (D) BTA-DAN homopolymer<sup>7</sup>).

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**Table 3.** Properties of the Soluble and Insoluble Fractions

Copolymer	Properties	As-polymerized	Soluble	Insoluble
PET / BTA-DAN				
39 / 61	$\eta_{inh}$	0.83	0.48	0.88
	$T_g^1$ and $T_g^2, ^\circ C$	61 <sup>a</sup> ,107	46,77	120
	$T_m, ^\circ C$	319	284 <sup>a</sup>	(C)
	Wt. %	—	21	79
	Br Wt. %	16.2	20,5 <sup>b</sup>	15.1
	LC props.	YES	NO	YES
49 / 51	$\eta_{inh}$	0.58	0.32	0.70
	$T_g^1$ and $T_g^2, ^\circ C$	64 <sup>a</sup> ,103	50,79	61,112
	$T_m, ^\circ C$	319	292 <sup>a</sup>	347
	Wt. %	—	26	74
	Br Wt. %	14.6	17.2	13.0
	LC props.	YES	NO	YES
59 / 41	$\eta_{inh}$	0.67	0.63	0.70
	$T_g^1$ and $T_g^2, ^\circ C$	61,103	46,96	83,120
	$T_m, ^\circ C$	317	282 <sup>a</sup>	361
	Wt. %	—	63	37
	Br Wt. %	12.5	14.2	10.1
	LC props.	NO	NO	YES

<sup>a</sup> Endotherms were too weak and broad to exactly define transition temperatures. Therefore, the values of transitions given are only approximations.

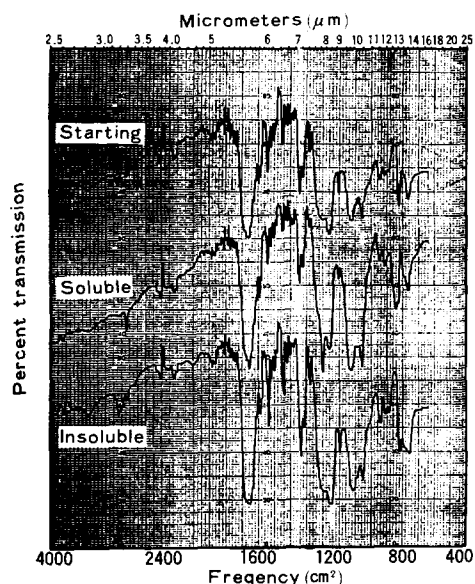
<sup>b</sup> No experimental value was determined. The value was calculated from the weight fractions of soluble and insoluble fraction and bromine content found in the insoluble fraction.

<sup>c</sup> Decomposed before melting.

CHCl<sub>3</sub> extracted portions of the three copolymers had four points in common : 1) They are of lower  $\eta_{inh}$  compared with as-polymerized samples and unextractable portions, 2) Their bromine contents are consistently higher than those of insoluble fractions, 3) They exhibit two glass transitions at lower temperature than the  $T_g$ s of their respective insoluble fractions, 4) Their  $T_m$ s are lower than those of residue fractions, These facts imply that CHCl<sub>3</sub> extracted fractions are richer in the 2-bromoterephthalic acid moiety and are of lower molecular weights than the unextractable fractions. Therefore, it can safely be said that CHCl<sub>3</sub> extraction resulted in molecular weight as well as compositional fractionations.

IR spectra of as-polymerized, extractable and unextractable samples of 49/51 composition are illustrated in Figure 3. The naphthalene double bond stretching modes at 1640 cm<sup>-1</sup> and the peaks at 1190 cm<sup>-1</sup> show that the insoluble fraction contains

higher amount of 1,5-naphthylene moiety than



**Fig. 3.** IR spectra of 49PET / 51BTA-DAN copolyester.

either the starting material or the soluble fraction. The stronger aliphatic C-H stretching absorption for the soluble fraction also indicates that soluble portion is richer in ethylene glycol unit than insoluble fraction. The exact same phenomenon also was observed for the other two compositions listed in Table 3.

The results obtained from IR spectra and elemental analysis of as-polymerized, soluble and insoluble fractions reveal that the soluble fractions are richer in ethylene glycol and 2-bromoterephthalic acid moieties, and that the insoluble fractions are richer in naphthalene diol and terephthalic acid moieties.

Moreover, we found that the soluble portions of 49/51 and 59/41 compositions showed no, or very little liquid crystallinity when observed through the polarizing microscope, while the insoluble fractions clearly showed nematic textures in melts. All the observations made on the starting polymers, soluble and insoluble fractions strongly indicate that the copolyesters described in this work consist of several fractions of differing compositions. In fact, the data discussed suggest that even the separated fractions are heterogeneous in composition. Although the systems used are different, this is in line with a recent report by Quach et al.<sup>4</sup> that there exists a compositional variation in liquid crystalline copolyesters derived from *p*-acetoxybenzoic acid and poly(ethylene terephthalate). Also very recently Nicely et al.<sup>8</sup>, through NMR spectroscopy, concluded that the deviations from randomness of the sequence distribution become significant at high levels of *p*-oxybenzoate in the same copolymers. Unfortunately, we do not yet have similar NMR analysis for the present copolymers.

## CONCLUSION

The following conclusions can be drawn from

the present investigation :

- 1) PET copolymers containing more than 50 mole % of 2-bromoterephthalic acid and 1,5-naphthalene moieties appeared to be nematic, thermotropic.
- 2) As-polymerized samples revealed two  $T_g$ s, implying that they are mixtures of aliphatic rich and aromatic rich fractions.
- 3) Inclusion of relatively low level of 2-bromoterephthalic and 1,5-naphthalenediol moieties destroyed PET crystallinity.
- 4) Properties of the chloroform extracted and unextractable fractions support the deduction that these copolymers consist of fractions of differing compositions.

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