$p-$히드록시벤조산, 나프탈렌디올 이성질체와 $\alpha,\omega-$비스(4$-$카르복시페녹시)알칸으로부터 유도된 열방성 코폴리에스테르

조 병 욱 · 성 기 윤 · 최 재 곤 · 장 진 해* · 진 정 일**

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Thermotropic Copolyesters Derived from p-Hydroxybenzoic Acid, Naphthalenediol Isomers and α,ω-Bis (4-carboxyphenoxy) Alkanes

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요 약 : 용융중합법을 이용하여, p-아세톡시벤조산, 디아세톡시나프탈렌 이성질체들과 α,ω-비스(4-카르복시페녹시)알간을 각각 2:1:1의 몰비율로 사용하여 마구잡이 폴리에스테르 공중합체를 합성하였고, 나프탈렌디올 이성질체구조 및 유연격자가 중합체들의 열적성질, 결정성 및 액정성에 미치는 효과들을 조사하였다. 이때 사용된 디아세톡시나프탈렌 이성질체 는 1,5-, 1,6-, 2,6- 및 2,7- 치환체들이고, 유연격자로는 테트라메틸렌, 펜타메틸렌 및 테카메 틸렌 등이다. 모든 중합체는 열방성 네마틱의 결정성이었다. 격자길이에 상관없이 2,6-나프탈 렌디올로부터 유도된 중합체의 경우가 가장 높은 용융점과 결정도를 나타냈으며, 메틸렌기를 기수개 갖는 중합체가 우수격자를 갖는것과 비교해 볼때, 모든 조성에서 비교적 낮은 결정성 을 갖는 경향을 나타냈다. 1,6-나프탈렌디올로부터 합성된 중합체에 있어서, 유연격자의 존재 는 결정성 증가에 효과적임을 알 수가 있었다.

Abstract : A series of random copolyesters were synthesized in melts from p-acetoxyben zoic acid, diacetoxynaphthalene isomers and α,ω-bis(4-carboxyphenoxy)alkanes in the molar ratio of 2:1:1 and characterized for the effects of structure of naphthalenediol isomer moieties and the spacers on the thermal, crystalline and liquid crystalline prop- erties of the resulting polymers. Diacetoxynap Diacetoxynaphthalene isomers used were 1,5-, 1,6-, 2,6- and 2,7-disubstituted ones and the spacer was either tetramethylene, or

Byung-Wook Jo, Ki-Youn Sung, Jae-Kon Choi, Jin-Hae Chang, and Jung-Il Jin

pentamethylene or decamethylene. The polymers were semicrystalline and thermotropic. They all formed nematic melts. The copolyesters derived from 2,6-naphthalenediol exhibited highest melting temperature and degree of crystallinity regardless of the length of the spacer. All of the compositions containing the odd-numbered pentamethylene spacer were lowest in crystallizing tendency when compared with those having the even-numbered tetra or decamethylene spacer. The presence of spacers was found to be helpful in crystallization of 1,6-naphthalenediol copolyesters.

INTRODUCTION

There are many factors that influence the properties of main chain, liquid crystalline polyesters. Some of our recent papers discuss the effect of the presence of unsymmetrical substituents on the phenylene rings,[1] linking order of ester bonds in the aromatic ester type mesogens,[2] length of polymethylene spacers interconnecting mesogens,[3] comonomer sequence and thermal history of polymers on the thermal, crystalline and thermotropic properties.[4,5] The role of the geometry of non-linear rigid structural unit also was a subject of a couple of our earlier studies.[6,7]

When various naphthalenediol isomers are copolymerized in melts with p-hydroxybenzoic acid and terephthalic acid, the resulting random copolyesters reveal a strong dependence of their crystallizing and mesomorphic properties on the structure of the naphthalene moieties included.[7] Moreover, it was found that the corresponding copolyesters that are in an ordered comonomer sequence exhibit drastically different solid state as well as thermotropic properties when compared with those of the random copolyesters.[4,8] Similar findings were reported also by Moore and Stupp[9] for the liquid crystalline polyesters containing polymethylene spacers.

In this paper we would like to describe synthesis and properties of a series of random copolyesters prepared in melts from p-acetoxy benzoic acid, α,ω-bis(4-carboxyphenoxy)alkanes and diacetoxynaphthalene isomers.

These copolyesters consist of aromatic ester type rigid units whose geometry vary according to the position of the two substituents in the naphthalene moieties. They also contain polymethylene spacers of varying length and number (odd or even) of methylene groups. It was hoped to delineate how the presence of polymethylene spacers modifies the geometrical effects brought about by the structure of the isomeric naphthalene moieties on the properties of the
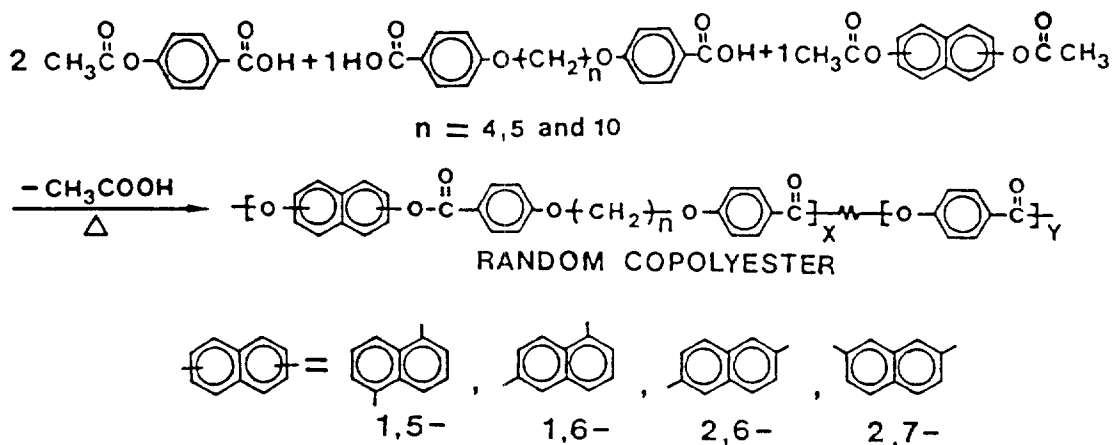
resulting polyesters.

For the sake of convenience, the symbol X, Y / Z is used to describe the composition derived from X,Y-diacetoxynaphthalene and α,ω-bis(4-carboxylphenoxy)alkane having Z methylene units. All of the polymers were prepared at the molar ratio of diacetoxynaphthalene : α,ω-bis(4-carboxyphenoxy)alkane : p-acetoxybenzoic acid = 1 : 1 : 2.

EXPERIMENTAL

Synthesis of Monomers

Diacetoxynaphthalenes,[7] α,ω-bis(4-carboxyphenoxy) alkanes[10] and p-acetoxybenzoic acid[11] were prepared following literature methods.

Preparation of Polymers

All of the polymers were prepared in melts.[7] Since the synthetic methods for the polyesters were almost the same, only a representative example for the preparation of 2,7 / 4 polymer is given : 2,7-diacetoxynaphthalene (1.22g : 0.50 $\times 10^{-2}$ mole), 1,4-bis(4-carboxyphenoxy) butane (1.65g : 0.50 $\times 10^{-2}$ mole) and p-acetoxybenzoic acid (1.80g : 0.10 $\times 10^{-1}$ mole) were placed in a polymerization tube. This mixture was heated with vigorous stirring in order for 30 min at 250°C, for 30 min at 270°C and then for 1 hour at 290°C under a steady stream of N$_2$ gas. Continuous generation of acetic acid was observed during this period. The temperature was raised to and maintained at 300°C for 30 min-

utes at a reduced pressure of 60 torr. Finally, the mixture was heated for 10 min at 310°C at the pressure of 1 torr.

The polymer formed was cooled to room temperature and recovered. The recovered polymers were ground using a mortal and pestle. The powders were thoroughly washed with distilled water and then with acetone. Table 1 summarizes polymerization conditions employed for the preparation of each polymer.

Characterization

Elemental analyses were performed by the Analytical Laboratory of the Korea Research Institute of Chemical Technology (see Table 2). Inherent viscosities of the polymers were measured at 40°C on solutions of 0.1g / dL in a mixed solvent of phenol / p-chlorophenol / 1, 1,2,2 - tetrachloroethane (W / W / W = 25 / 45 / 30).

The thermal properties were studied under a N$_2$ atmosphere on a DuPont DSC 910 at a heating rate of 10°C / min. the values of T$_g$ are the temperatures where initial slope changes on DSC thermograms were observed, while the DSC peak maximum positions were taken as T$_m$ and T$_l$. The optical texture and thermal behavior also were examined on a hot-stage (Mettler FP-2) attached to a polarizing microscope (Leitz, Ortholux). The degree of crystallinity was estimated approximately from the crystalline and the amorphous reflection areas in the wide angle X-ray diffractogram obtained

Table 1. Polymerization Conditions used for the Preparation of Copolyesters

Polymers X,Y / 4	Temperature / Min / Torr
1,5	260 / 30 / 760 → 280 / 60 / 760 → 290 / 60 / 760 → 300 / 30 / 760 → 310 / 60 / 160 → 315 / 60 / 1
1,6	260 / 30 / 760 → 280 / 60 / 760 → 300 / 120 / 760 → 310 / 60 / 760 → 310 / 40 / 160 → 315 / 30 / 1
2,6	260 / 30 / 760 → 280 / 60 / 760 → 300 / 120 / 760 → 300 / 60 / 160 → 310 / 50 / 1
2,7	260 / 30 / 760 → 280 / 60 / 760 → 300 / 90 / 760 → 300 / 60 / 160 → 310 / 60 / 1

Table 2. Results of Elemental Analyses of Poly esters

Polymers X, Y / n	Elemental Analyses,[a] wt, %		
		H	
1,5 / 4	72.65	4.40	23.12
	(72.61)	(4.36)	(23.03)
1,5 / 5	72.80	4.25	22.07
	(72.87)	(4.56)	(22.57)
1,5 / 10	74.22	5.50	20.67
	(74.11)	(5.45)	(20.57)
2,6 / 4	72.71	4.28	22.99
	(72.61)	(4.36)	(23.03)
2,6 / 5	72.90	4.74	22.60
	(72.87)	(4.56)	(22.57)
2,6 / 10	74.43	5.27	20.25
	(74.11)	(5.45)	(20.57)

[a]The values in parentheses are those calculated for the chemical formulas.

on a JEOL JDX-80 instrument using nickel-filtered Cu-K$_\alpha$ radiation.[12] Annealings were conducted for 3 to 6 hours in a vacuum oven preheated to a desired temperature. Afterwards, the annealed samples were slowly cooled to room temperature in the oven.

RESULTS AND DISCUSSION

General Properties

Table 2 shows that the results of elemental analyses of 1,5-and 2,6-polymers are in good agreement with calculated values, suggesting that the actual compositions of the copolyesters are very close to those of feeds. Although only selected data are shown in the table, same can be said also for the rest of the polymers. These polymers were not soluble in common solvents and, therefore, a mixed solvent consisting of phehol, p-chlorophenol and 1,1,2,2-tetrachloro ethane had to be used in the measurement of solution viscosities.

The solution viscosity numbers are reasonably high. In general, solution viscosity numbers of annealed samples are significantly higher than those of their as-polymerized precursors(Table 3~5), indicating that annealing causes increase in molecular weight due to solid state polymerization. Annealing temperature, T_a, was, in general, 20~30 degrees below the melting temperature, T_m.

Thermal Transition and Crystallization

The glass transition temperatures, T_g, of the polymers could be clearly determined from heating DSC thermograms(Fig. 1). T_g's of the polymers are relatively low ranging from about 65 to 85℃(Table 3~5). And, surprisingly enough, the T_g values are rather insensitive to the length and the number(odd or even) of methylene groups in the spacer. One would expect that the composition having a longer spacer undergoes glass transition at a lower temperature than that with a shorter spacer.

Our observation implies that the spacers are not really flexible as one may presume, probably due to the conformational constraints imposed to them by the rigid, aromatic ester type structures existing along the chain.[13~16] In fact, some of the alkylene segments take gauche conformation allowing the polymer chains in the crystalline and liquid crystalline states to bend and adopt an overall linear configuration.[13~16] The T_g values of annealed samples are practically the same as for or only slightly higher than those of the as-polymerized ones, suggesting that the original samples are of high enough molecular weight. It is well known that T_g of a polymer increases up to certain asymptotic value as its molecular weight increases.[17] The presence of the spacers, however, causes a substantial reduction in T_g compared with those(82-125℃) of the corresponding copolyesters derived from terephthalic acid in place of α,ω-bis(4-carboxyphenoxy) alkanes.[7] The presence of the polymethylene spacers along the chain certainly reduces the chain stiffness and probably also rotational barrier.

Regardless of the length of spacers, all of the polymers, especially after thermal treatment for 3 hrs at the annealing temperatures shown

Table 3. Properties of X, Y / 4-Series Polyesters

Polymer X,Y	T_a^a °C	η_{inh}	T_g °C	T_m °C	T_i °C	T_i Range	$\triangle H_m^b$ KJ / mole	$\triangle H_i^b$ KJ / mole	D.C.^{c} %
1,5	—	1.07	84	274	—	—	0.7	—	5
	170(3)	1.32	89	273	—	—	1.2	—	8
	170(6)	—	90	273	—	—	1.2	—	10
1,6	—	0.60	75	—	312	36	—	1.6	0
	150(3)	0.85	77	167	312	57	0.9	2.5	8
	150(6)	—	80	175	308	66	1.4	3.1	10
2,6	—	0.92	68	202	312	50	1.3	1.6	11
	180(3)	1.35	72	208	323	80	1.7	2.5	27
	180(6)	—	72	211	324	87	1.8	3.5	30
2,7	—	0.85	71	175	285	72	1.4	0.8	9
	150(3)	1.05	71	175	297	85	1.8	4.4	12
	150(6)	—	71	176	297	92	2.0	4.7	9

^{a} The values in the parantheses are annealing period in hrs.
^{b} The values were estimated from the endotherm areas on DSC thermograms.
^{b} The "mole" represents the values for the average repeating unit.
^{c} Degree of crystallinity.

Table 4. Properties of X, Y / 5-Series Polyesters

Polymer X,Y	T_a^a °C	η_{inh}	T_g °C	T_m °C	T_i °C	T_i Range	$\triangle H_m^b$ KJ / mole	$\triangle H_i^b$ KJ / mole	D.C.^{c} %
1,5	—	0.74	76	—	—	—	—	—	0
	160(3)	0.95	75	199	295	87	1.4	1.7	<3
1,6	—	0.63	82	—	—	—	—	—	0
	135(3)	0.86	85	154	294	94	0.5	6.2	6
2,6	—	1.08	69	199	284	90	0.9	2.9	8
	180(3)	1.22	70	200	298	103	1.2	1.3	18
2,7	—	0.62	72	161	295	97	1.2	2.9	<3
	145(3)	0.63	74	163	296	107	1.4	5.8	9

Table 5. Properties of X, Y / 10-Series Polyesters

Polymer X,Y	T_a^a °C	η_{inh}	T_g °C	T_m °C	T_i °C	T_i Range	$\triangle H_m^b$ KJ / mole	$\triangle H_i^b$ KJ / mole	D.C. %
1,5	—	0.76	68	154	—	—	0.6	—	<3
	145(3)	1.06	69	160	—	—	2.0	—	13
1,6	—	0.74	65	161	320	40	0.8	1.7	8
	120(3)	0.84	69	161	321	81	1.1	2.2	15
2,6	—	0.65	69	186	—	—	0.9	—	15
	160(3)	1.05	69	187	297	62	1.5	0.8	30
2,7	—	0.62	74	155	298	50	1.6	0.1	14
	140(3)	0.65	78	156	299	85	1.5	1.8	15

Byung-Wook Jo, Ki-Youn Sung, Jae-Kon Choi, Jin-Hae Chang, and Jung-Il Jin

in Tables 3~5, revealed melting transitions on DSC analysis(Fig. 1), indicating that they are semicrystalline. On the contrary, it was reported earlier by us[7] that the wholly aromatic copolyesters derived from 1,5-naphthalenediol, terephthalic acid and p-hydroxybenzoic acid in the same molar ratio of 1:1:2 was amorphous. For this particular case, it is clear that the presence of a flexible spacer promotes crystallization.

According to the data summarized in Tables 3~5, the crystalline melting temperature, T_m, is reduced with the length of spacer. And 1, 6-naphthalene copolyesters revealed highest degree of crystallinity when compared with other copolymers. 2,6-Naphthalene unit does not destroy the linear shape of the rigid, aromatic ester unit, which certainly favors more efficient molecular packing in the solid state. The reason for particularly high melting temperature for 1,5/4-copolymer is not clear.

Tables 3~5 summarize the changes in the properties of the copolyesters on annealing. Although chemical structures of the polymer chains must be quite irregular, all of the polymers are crystallizable to varying extents depending on the substitution position on the naphthalene rings. The influence exerted by the spacers on the crystallizing tendency is rather interesting: The polyesters having the pentamethylene spacer, i. e., with an odd number of methylene unit, revealed the lowest degree of crystallinity irrespective of the structure of naphthalene moieties. And those having the longest decamethylene spacer, in general, crystallize more readily compared with those of tetramethylene spacer. The odd spacer appears to make the molecular packing in the solid state more difficult than the even numbered ones. On the other hand, the longer spacer allows easier chain movement during annealing at the temperature higher than T_g, leading to more facile crystallization.

Figure 2. shows how DSC thermogram of the 2,6/4-polyester changes with the annealing time at 180℃. And the X-ray diffractograms shown in Fig. 3 are those for the same polymers. It is evident that T_m moves to higher temperature side and crystalline diffractions become more intense on annealing. In other words, annealing increases the thermal transition temperature and the degree of crystallinity. The increase in the degree of crystallinity on annealing is most remarkable for 2,6-polymers. It also was pointed out earlier that annealing causes molecular weight increase through the solid state polymerization.[5,7]

Mesophase Formation

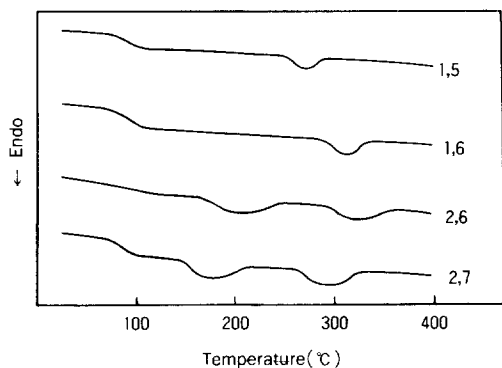All of the copolyesters, regardless of spacer

Fig. 1. DSC thermograms of the X, Y / 4-polymers obtained from the second scan. Heating rate was 10℃ / min.
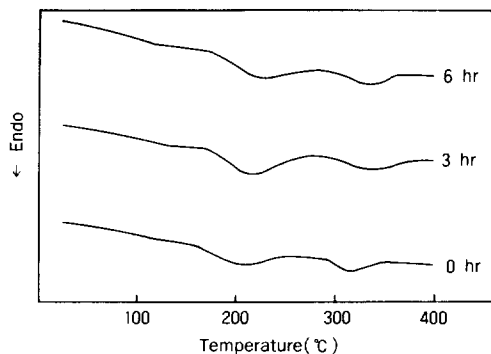

Fig. 2. DSC thermograms of the 2,6 / 4-polymer before and after annealing obtained from the second scan. The annealing temperature was 180 ℃. Heating rate was 10℃ / min.
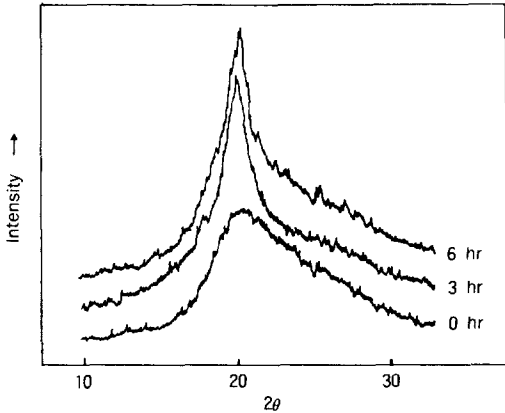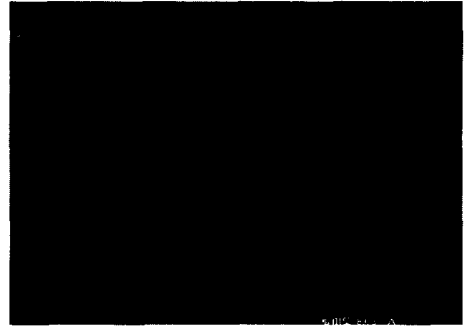
Fig. 3. Wide angel X-ray diffractograms of the 2,6 / 4-polymer before and after annealing. The annealing temperature was 180℃.

length and relative position of the two linking bonds on naphthalene rings, were found to form nematic melts, as judged by their optical textures observed through a polarizing microscope (Fig. 4). This is in contrast with our earlier report that the similar 1,5-polymer derived from terephthalic acid that does not contain any spacer, formed a smectic phase.[7] The present polymers contain linear rigid segments consisting of, on average, two p-oxybenzoyl unit and one terephthaloyl unit. Therefore, the linear rigid segments containing at least three consecutive, linearly connected aromatic ester type structure are long enough to make the molecules to form ordered structures in melts.

Isotropization temperature, T_i, could be determined by DSC analysis as shown in the DSC thermograms of Fig. 1. T_i's are close to about 300℃ regardless of the structure of naphthalene unit and the length of the spacers. T_i of the 1,5 / 4 polymer could not be determined unequivocally because clearing transition seemed to overlap with thermal decomposition. We noticed that the mesophase temperature range, i.e. $T_i - T_m$ value, varies greatly depending on the structure of rigid units and the length of the spacer. All of the polymers showed very broad biphasic temperature ranges. Coex-

a)
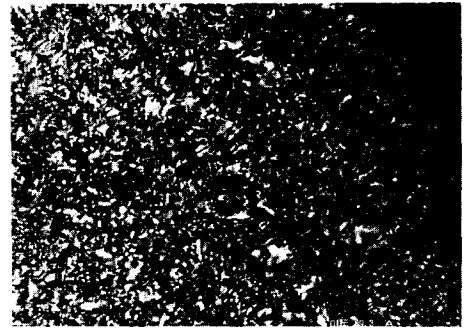
b)

Fig. 4. Photomicrographs for (a) 1,5 / 5- and (b) 2,7 / 4-polymers taken at 297℃ and 260℃, respectively. Magnification was 320X.

istence of mesophase and isotropic phase could be clearly observed during clearing transition.[18,19] The transition temperature ranges given in tables correspond to the temperature differences between the initial and final temperature of isotropization edothermic peaks on DSC thermograms.

Recently Martin and Stupp[20] reported that a random copolyester exhibited a biphasic region spanning 120℃ when observed through a optical microscope. The DSC curve of their copolymer did not reveal the presence of a discernible isotropization transition peak. They ascribed this observation to the occurrence of a very broad biphasic temperature range.

CONCLUSIONS

Following conclusions can be drawn from this work:

1. All of the copolyesters described in this paper are thermotropic and nematic indicating that linear, rigid units consisting of minimum three consecutive aromatic esters are long enough to induce mesophase formation.

2. The presence of the polymethylene spacers appears to promote crystallizing ability of the copolyesters:. This is particularly true for 1, 5-copolyesters. Conformational variations possible to polymethylene spacers appears to be the driving force for such increased crystallizing tendency.

3. Annealing increases molecular weight and degree of crystallinity.

4. The degree of crystallinity of 2,6-copolyesters are the highest. The linear geometry of 2,6-naphthalene unit results in more facile crystallization and effective molecular packing in the solid state.

5. All of the polymers exhibit very broad biphasic temperature regions where mesophase and isotropic phase coexist.

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