Macromolecules 1989, 22, 4402–4408

Synthesis and Properties of Copolyesters Having an Ordered Monomer Sequence. A Series of Poly(oxynaphthyleneoxycarbonyl-1,4-phenyleneoxyterephthaloyl-4-oxy-1,4-phenylenecarbonyl)s

Jung-Il Jin*,† and Jin-Hae Chang†,‡

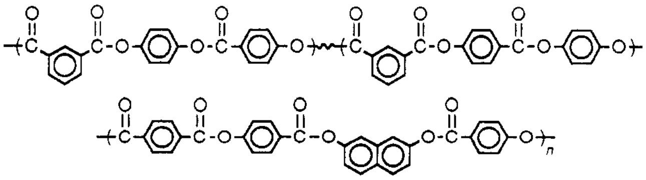
Chemistry Department, College of Sciences, Korea University, Seoul 136-701, Korea, and Polymer Science and Engineering Department, Kum-Oh Institute of Technology, Gumi City 730-070, Korea. *Received January 23, 1989; Revised Manuscript Received April 6, 1989*

ABSTRACT: A series of sequentially ordered copolyesters were prepared from terephthalic acid and isomeric naphthalenediyl bis(4-hydroxybenzoate)s. All of the copolyesters are composed of terephthalic acid (TERE), naphthalenediol (NAPH), and *p*-hydroxybenzoic acid (POB) units in a 1:1:2 mole ratio. The polymer chains are made up of the exact sequence order of –POB–NAPH–POB–TERE– segments. The diols used are 1,5-, 1,6-, 2,6-, and 2,7-naphthalenediols. Glass transition temperatures, melting points, and crystallizability of these copolymers were found to be much higher than those of the corresponding random copolymers having the same overall compositions. Among the four copolyesters, only the copolyester prepared from unsymmetrically disubstituted 1,6-naphthalenediyl bis(4-hydroxybenzoate) has a very low degree of crystallinity, less than 5%. It was also found that annealing increases the molecular weight, melting temperature, and the degree of crystallinity. The copolyesters derived from 1,5-, 2,6-, and 2,7-naphthalenediyl bis(4-hydroxybenzoate) were thermotropic, whereas the one prepared from the 1,6 isomer was not.

Introduction

Properties of copolyesters are expected to depend not only on their overall chemical composition but also on the comonomer sequence distribution.[1–4] Synthetic methods that can be utilized for the synthesis of copolyesters of predesigned comonomer distribution, however, are very limited. Therefore, development of synthetic methods for the preparation of copolyester with ordered monomer sequences is highly desirable in order to establish their structure–property relationships. In light of the present interest in the properties of liquid-crystalline aromatic polyesters, development of synthetic methods for thermotropic aromatic copolyesters having predesigned, ordered monomer sequences should be even more scientifically rewarding.

We have recently succeeded in preparing thermotropic aromatic copolyesters having an alternating sequence of two structural units. The first copolymer consists of isophthaloyl and 4-(oxyphenyl) 4′-oxybenzoate units[3] in a 1:1 mole ratio, and the second one is composed of terephthalic acid (TERE), 2,7-naphthalenediol (NAPH), and *p*-hydroxybenzoic acid (POB) in a 1:1:2 mole ratio.[4] The polymer chain is made up of the sequence order of –POB–NAPH–POB–TERE– segments:



The first copolyester is not an exactly alternating copolyester, because the diol used in the synthesis, 4-hydroxyphenyl 4′-hydroxybenzoate, is not a symmetrical diol and the two hydroxy groups are not equivalent. The polymer chain can therefore form two nonequivalent linkages with the terephthaloyl unit, but the *p*-oxybenzoyl unit should appear at every third monomer position in the chain. The second copolymer was prepared at low temperature from 2,7-naphthalenediyl bis(4-hydroxybenzoate), a symmetrical diol, and terephthalic acid and possesses precisely ordered sequences. The copolyester with the ordered monomer sequence has thermal transitions and crystallizing properties very different from those of the corresponding random copolyester with the same overall composition. In the random copolyesters prepared via melt transesterification reaction of the three monomers, the *p*-oxybenzoyl unit is expected to be located randomly along the chain. Moreover, because the comonomer *p*-acetoxybenzoic acid can undergo homocondensation, a broad distribution in its sequence length is expected with the result that its average sequence length is greater than that of the ordered sequence copolymer.[5,6]

There have been earlier efforts to establish the property differences between random copolyesters and those of an ordered comonomer sequence.[1,5–8] However, the synthetic methods employed in some of those studies do not warrant claims that precise monomer sequences were obtained. In general, ester-type, diad aromatic diols were reacted with diacids in melts, and the reaction temperatures were very high (~300 °C). Under such reaction conditions one can expect transesterification of ester linkages to occur, thereby destroying, at least partly, the preset sequence of the diad used. Although such a sequence disordering must have occurred during polymerization, it was still reported that the polymers prepared via polycondensation of a premade dimeric or trimeric diol with terephthalic acid reveal substantial differences in physical properties when compared with those random copolymers prepared directly from a mixture of the monomeric compounds.[1,7] A recent paper by Moore and Stupp[2] describes the synthesis of a liquid-crystalline polyester with a flexible spacer that is of an ordered sequence. They employed a low-temperature solution polycondensation of an ester-type bisphenol mesogen of a predesigned sequence and the dichloride of an aliphatic dicarboxylic acid.

In this paper we describe the synthesis of a series of sequentially ordered and regioregular copolyesters from terephthalic acid and isomeric naphthalenediyl bis(4-hydroxybenzoate). We will compare their basic properties such as glass transition temperatures, melting points, and crystallizability with those of the corresponding random

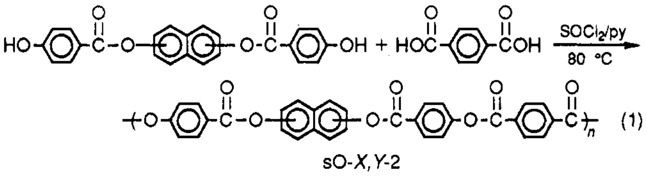
---

[†] Korea University.

[‡] Kum-Oh Institute of Technology.

0024-9297/89/2222-4402$01.50/0

copolyesters[9] having the same overall compositions and prepared from monomer mixtures of terephthalic acid, isomeric diacetoxynaphthalenes, and *p*-acetoxybenzoic acid. The latter copolymers were recently reported by us.[9] Preliminary results on the 2,7-naphthalenediol copolymer were reported in one of our previous papers.[4] For simplicity the copolyesters will be described as sO-*X*,*Y*-2 (eq 1). The s stands for solution polymerization and O for the ordered sequence. *X* and *Y* are the substitutent positions on naphthalene rings, and the number 2 signifies that the copolymer contains 2 equiv of the *p*-oxybenzoyl structure per repeating unit.



(1)

sO-*X*,*Y*-2

Experimental Section

Synthesis of Monomers. Isomeric naphthalenediyl bis(4-hydroxybenzoate)s were synthesized via a multiple-step route. A representative synthetic method can be found in our previous paper.[4] The structures of the compounds were confirmed by elemental analyses (Analytical Department, Korea Research Institute of Chemical Technology, Daejon, Korea) and by their IR and NMR spectra. The purity of the compounds was checked by TLC and liquid chromatography. The melting points of the compounds are as follow: 1,5-naphthalenediyl bis(4-hydroxybenzoate), 335 °C; 1,6-naphthalenediyl bis(4-hydroxybenzoate), 234 °C; 2,6-naphthalenediyl bis(4-hydroxybenzoate), 333 °C; 2,7-naphthalenediyl bis(4-hydroxybenzoate), 234 °C.

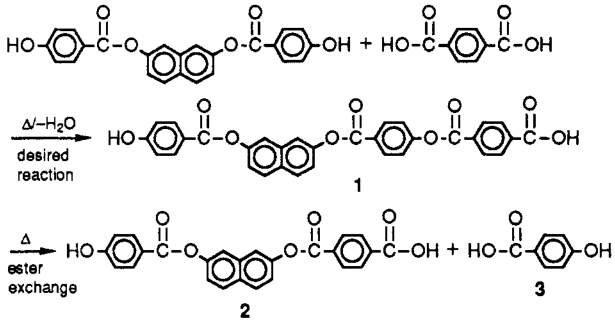
Synthesis of Polymers. All of the polymers were prepared by direct polycondensation of equivalent weights of the appropriate naphthalenediyl bis(4-hydroxybenzoate) and terephthalic acid in the presence of thionyl chloride and pyridine. The detailed procedure was earlier described by us[4] and Higashi et al.[10] The polymers formed were thoroughly washed with methanol, dilute HCl, and then with water prior to drying at 60 °C in a vacuum oven.

Characterization of Polymers. The polymers' solution viscosity values were measured at 25 °C using a Cannon–Ubbelhode-type viscometer. Measurements were made on 0.1 g/dL solutions in a pentafluorophenol/*p*-chlorophenol/chloroform = 30/30/40 (v/v) mixture. ^{13}C NMR spectra of the polymers were obtained on a Bruker AM-300 using a mixture of CF_3COOD and $CDCl_3$ [1/1(v/v)]. Thermal properties were studied under an N_2 atmosphere on a Du Pont 910 DSC and a Perkin-Elmer TGS-2 at a heating rate of 10 °C/min. All of the DSC curves and data presented in this paper are from the first scans. When necessary, a faster or slower heating rate was employed. Indium was used as a reference for temperature and enthalpy change. Wide-angle X-ray diffractograms were obtained on a JEOL JDX-8D instrument using Ni-filtered Cu Kα radiation. The scan speed was 4 deg/min. The approximate degree of crystallinity was estimated from the crystalline and the amorphous reflection areas in the diffractogram.[11] The optical texture[12] and thermal behavior of the melts were also examined on a hot-stage (Mettler FP-2) attached to a polarizing microscope (Leitz, Ortholux).

Annealing Study. All of the polymers were subjected to thermal annealing. Accompanying changes in properties were examined on a DSC instrument and on an X-ray diffractometer. The solution viscosities were again measured as described above.

Results and Discussion

Synthesis of Copolyesters. There are many different synthetic methods for the preparation of copolyesters. Among these, low-temperature solution polymerization, the Schotten–Baumann reaction at room temperature, and ester interchange polycondensation at an elevated temperature are the most frequently utilized methods. The last method, however, suffers from inescapable shortcomings when preparing copolyesters of an ordered or a predesigned sequence. In addition to a desired polymer-forming reaction, there can be sequence randomization reactions between the monomers. For example, in the early stages of polymerization of 2,7-naphthalenediyl bis(4-hydroxybenzoate) and terephthalic acid, the following two major reactions are possible:

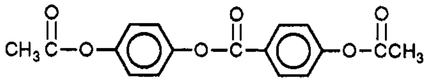


(2)

(3)

The initial products, **1**–**3**, can either undergo further polymerization or engage in ester-exchange reactions either between themselves or with growing chain ends and remaining unreacted monomers. It is therefore expected that occurrence of such side reactions certainly will result in sequence randomization because of the ability of *p*-hydroxybenzoic acid to homopolymerize.

Recently, Moore and Stupp[6] polymerized the following diacetoxy monomer with pimelic acid under transesterification condition and found that the number-average sequence length of oxybenzoate units was 1.3–1.4.



This indicates that the central ester bond participated in side reactions. If no such reactions occurred, the average sequence length of oxybenzoate units would be unity. In fact the numbers 1.3–1.4 are very close to that of a completely random sequence, 1.5, and suggest that transesterification of the central ester bond was not a minor reaction.

However, low-temperature direct polycondensation of a diol with a dicarboxylic acid promoted by thionyl chloride and pyridine reported earlier by Higashi et al.[10] precludes any possibility for similar sequence randomization during polymerization. We employed this simple method for the preparation of all of the present copolyesters using naphthalenediyl bis(4-hydroxybenzoate) and terephthalic acid (eq 1). We indeed could confirm by NMR analysis that all of the sO-*X*,*Y*-2 copolyesters are of the predesigned sequence, i.e., in the order of *p*-oxybenzoyl (POB)–naphthyl (NAPH)–*p*-oxy-1,4-phenylenecarbonylterephthaloyl (TERE) along the chain. For example, in the ^{13}C NMR spectra of sO-2,7-2 shown in Figure 1, we could observe only one ^{13}C NMR peak at 169.4 ppm for the carbonyl carbon of the *p*-oxybenzoate unit located between the naphthalene and terephthaloyl units. The ^{13}C NMR peak for the carbonyl carbon in the terephthaloyl unit appears at 168.1 ppm as a single peak. If undesired transesterification of ester bonds in naphthalenediyl bis(4-hydroxybenzoate) occurred, we should observe additional ^{13}C peaks for the carbonyl carbon of the dimeric or longer *p*-oxybenzoate blocks as well as more than one carbonyl peak for terephthaloyl units. The corresponding random copolyester prepared in the melt from *p*-acetoxybenzoic acid, 2,7-diacetoxynaphthalene, and terephthalic acid exhibited at least four distinctive multiplet carbonyl resonance peaks at 170.1, 169.7, 169.1, and 168.7

Table I
Properties of As-Polymerized and Annealed (3 h), Ordered Sequence Polymers

	as-polymerized							annealed (3 h)					
polymer	yield, wt %	η_{inh}[a]	T_g, °C	T_m, °C	ΔH_t, kJ/mol	DC,[b] %	LC[c]	T_a,[d] °C	η_{inh}	T_g, °C	T_m, °C	ΔH_t, kJ/mol	DC, %
sO-1,5-2	73	1.10	110	341	4.8	14	S	230	ins	112	365	6.2	30
sO-1,6-2	53	0.56	no[e]	280	4.0	~5	NO	210	0.86	no[e]	301	10.9	~5
sO-2,6-2	62	0.81	150	348	4.3	22	N	250	ins	150	350	10.9	25
sO-2,7-2	57	1.20	116	290	11.1	24	N	235	ins	116	291	14.2	38

[a] Inherent viscosities of the copolyesters were measured at 25 °C at a concentration of 0.1 g/100 mL in a pentafluorophenol/*p*-chlorophenol/chloroform = 30/30/40 (v/v/v) mixture. [b] Degree of crystallinity. [c] Liquid-crystal phase; N stands for a nematic phase, S for a smectic phase, and NO for a non-liquid-crystalline phase. [d] Annealing temperature. [e] Not observed.

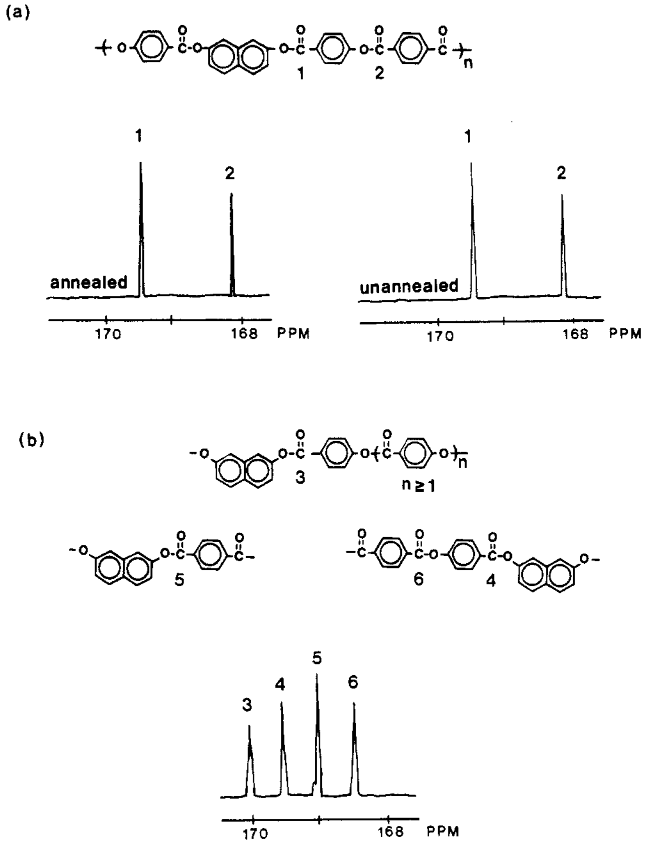


Figure 1. ^{13}C NMR spectra of (a) sO-2,7-2 before and after annealing and (b) random-2,7-2 polymer ($CF_3COOD/CDCl_3$).

ppm (peaks 3–6 in Figure 1), which were tentatively assigned to ester carbonyl carbons in segments with two or longer consecutive *p*-oxybenzoyl units, NAPH–POB, NAPH–TERE, and POB–TERE linkages, respectively.

In conclusion, all of the copolyesters we have prepared are composed of the ordered sequence, -POB–NAPH–POB–TERE-. Therefore, polymerization conditions we employed in the present study do not produce undesired transesterification of the starting naphthalenediyl bis(4-hydroxybenzoate) that would otherwise lead to sequence randomization. One disadvantage noted in the direct polycondensation method was that polymers precipitated out of the reaction mixture as they formed. Precipitation of polymer must be the reason why the solution viscosities (Table I) of the present copolyesters were slightly lower than those of the corresponding random copolyesters prepared in melts.[9] The results of elemental analyses (Table II) are in good agreement with calculated values for composition.

Table II
Results of Elemental Analyses of the Polymers

polymer	C, wt % (72.45)[a]	H, wt % (3.40)[a]	polymer	C, wt % (72.45)[a]	H, wt % (3.40)[a]
sO-1,5-2	72.47	3.37	sO-2,6-2	72.73	3.28
sO-1,6-2	72.43	3.54	sO-2,7-2	72.54	3.39

[a] Values in parentheses represent calculated values assuming that actual compositions are the same as those in the feed.

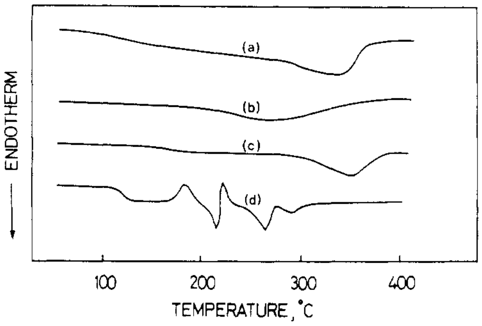


Figure 2. DSC thermograms of (a) sO-1,5-2, (b) sO-1,6-2, (c) sO-2,6-2, and (d) sO-2,7-2.

General Properties. None of the polymers is soluble in such solvents as chloroform, 1,1,2,2-tetrachloroethane (TCE), *p*-chlorophenol, and TCE/phenol mixtures. They are soluble in mixed solvents of CF_3COOH/chloroform and pentafluorophenol/*p*-chlorophenol/chloroform. Therefore, a mixed solvent of pentafluorophenol/*p*-chlorophenol/chloroform was used in the measurement of solution viscosities. Since solubilities were rather low even in the mixed solvent, a concentration of 0.1 g/dL was employed for the solution viscosity measurement. The solution viscosity numbers (Table I) range from 0.56–1.20. Considering the fact that the polymers precipitated out of the reaction medium as the polycondensation proceeded, these numbers can be regarded as being reasonably high. The solution viscosity value (Table I) of sO-1,6-2 was increased significantly, after annealing, from 0.56 to 0.86. Other samples became insoluble on annealing, probably due to their increased molecular weights and enhanced degree of crystallinity; this point will be discussed later.

The T_g's of the polymers, with the exception of sO-1,6-2, could be precisely determined from heating curves of their DSC analyses; see parts a–d of Figure 2. The T_g value of sO-2,6-2, 150 °C, was the highest, and the T_g's of the rest of the polymers were in the range of 110–116 °C. These values are much higher than those of corresponding random copolyesters, which ranged from 82 to 125 °C.[9] This can be ascribed to lower free volumes for the ordered sequence copolyester than those for the random sequence counterparts. The most drastic change in T_g values was observed for the copolyesters derived from 2,6-naphthalenediol. As mentioned, the T_g value of sO-2,6-2 is 150 °C. The T_g value of the corresponding random copolyester is only 82 °C,[9] which clearly demonstrates how strongly the T_g of a copolyester depends on the comonomer sequence order. The reason we did not observe a T_g transition on DSC analyses of sO-1,6-2 is not yet clear.

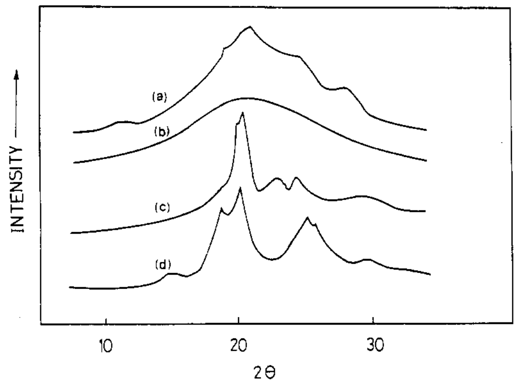


Figure 3. Wide-angle X-ray diffractograms of (a) sO-1,5-2, (b) sO-1,6-2, (c) sO-2,6-2, and (d) sO-2,7-2.

Regardless of the structure of naphthalene units, all of the as-polymerized samples showed clear melting endotherms on DSC analysis (parts a–d of Figure 2). The T_m values range from 280 to 348 °C, with those of sO-1,5-2 and sO-2,6-2 being higher than 340 °C and those of sO-1,6-2 and sO-2,7-2 being lower than 300 °C (Table I). These values are higher by as much as about 80–100 °C than those of corresponding random copolyesters.[9] Moreover, the random copolyester derived from 1,5-naphthalenediol does not show a melting endotherm on DSC analysis,[9] whereas the corresponding ordered sequence copolyester, sO-1,5-2, exhibits a definite melting endotherm. In other words, although the random copolyester is amorphous, the polymer with the ordered sequence is crystalline. Certainly, regular sequences of comonomers along the chain favors regular molecular packing in the solid state.

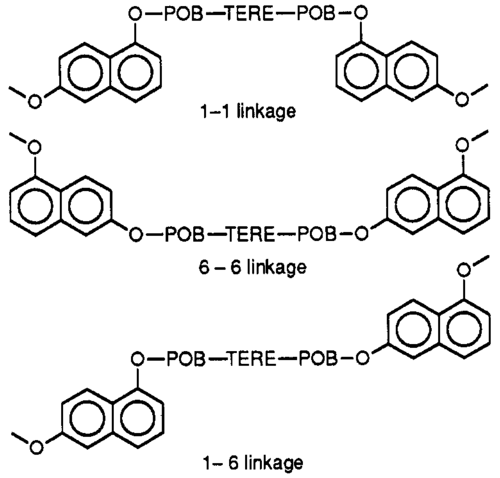
Thermal behavior of sO-2,7-2 examined by DSC analysis is peculiar when compared with the other polymers (Figure 2). The DSC thermogram of sO-2,7-2 exhibits an exotherm beginning at about 180 °C followed by the first endotherm whose minimum point temperature is 226 °C. Right after the first endotherm, an exotherm appears and is followed by a second endotherm whose minimum point temperature is 272 °C. After that, the final endotherm appears at 290 °C. The low-temperature endotherms seem to be associated with premelting but not with any crystal–crystal transitions. This point will be further discussed later. Crystallization exotherms like the ones observed for sO-2,7-2 during heating were not visible for the remaining compositions, which implies a tendency to particularly facile crystallization on the part of sO-2,7-2. The geometrical symmetry of the 2,7-naphthalenediol moiety appears to be a part of the reason.

Table III
Properties of sO-2,7-2 Polymer after Stepwise Annealing

T_a,[a] °C (t_a,[b] h)	η_{inh}[c]	T_g, °C	T_{m1}, °C	T_{m2}, °C	T_{m3}, °C	T_{m4}, °C	ΔH,[d] kJ/mol	DC,[e] %
	0.61	116	226	272	282	290	4.3	24
205 (1)	0.79	116	226	273	282	290	6.9	31
245 (1)	0.94	116		274	282	291	10.8	39
272 (1)	ins	118	219	278		298	8.0	33
280 (1)	ins	116	222	278		300	8.0	33

[a] Annealing temperature. [b] Annealing time. [c] Inherent viscosities of the copolyesters were measured at 25 °C by using 0.1 g/100 mL solution in a pentafluorophenol/p-chlorophenol/chloroform = 30/30/40 (v/v/v) mixture. [d] Total enthalpy changes for crystal transitions. [e] Degree of crystallinity.

Thermal Treatment and Crystallization. As mentioned above, all of the as-polymerized samples showed melting endotherms by DSC, implying that they are semicrystalline. Their crystalline nature can be further supported by X-ray diffraction studies; see Figure 3. According to the diffractograms shown in Figure 3, sO-2,6-2 and sO-2,7-2 show rather sharp crystalline diffraction peaks, whereas sO-1,6-2 shows very weak crystalline diffractions. The approximate degrees of crystallinity obtained from the diffractograms of as-polymerized samples are given in Table I. The copolyester consisting of the linearly disubstituted naphthalene unit, sO-2,6-2, and the copolyester with the symmetrically disubstituted naphthalene unit, sO-2,7-2, have a degree of crystallinity higher than 20%, while sO-1,6-2, which contains an unsymmetrically disubstituted naphthalene unit, has a very low degree of crystallinity, less than 5%. Such a large difference in crystallizability of these copolyesters can be ascribed to the differences in structural regularity of the chains. In contrast to the rest, only sO-1,6-2 was synthesized from unsymmetrically disubstituted 1,6-naphthalenediyl bis(4-hydroxybenzoate). Therefore, if we consider the structure of the segment of the pentad sequence, -NAPH-POB-TERE-POB-NAPH-, there are three possible linking methods or conformational isomers of the two naphthalene units along the chain:



The three possible linking modes of the 1,6-naphthalene unit along the chain must generate irregular structures that would make it difficult for sO-1,6-2 to achieve effective chain packing in the solid state.

The corresponding random copolyesters previously reported by us,[9] in general, had significantly lower degrees of crystallinity than the present copolyesters with ordered sequences. Their diffraction patterns were much different from those of the present series. In particular, as-polymerized samples of the random copolymers derived from 1,5- and 1,6-naphthalenediols exhibited only amorphous diffraction patterns in X-ray analysis. In contrast, the degree of crystallinity of sO-1,5-2 and sO-1,6-2 are 14 and 5%, respectively.

All of the polymers were subjected to thermal treatment for 3 h at the annealing temperatures, T_a, shown in Table III. The temperatures where the last melting endotherms observed on DSC thermograms of the as-polymerized samples started to appear were arbitrarily taken as T_a's. Figure 4 compares the X-ray diffractograms of sO-1,5-2 and sO-2,7-2 before and after annealing and the Table I summarizes changes in the degree of crystallinity on annealing. The DSC thermograms of annealed samples are included in Figure 5.

In general, with the exception of sO-1,6-2, the copolyesters undergo further crystallization on annealing. The increase in the degree of crystallinity with annealing is particularly great for sO-1,5-2 (from 14 to 30%) and sO-2,7-2 (from 24 to 38%). As already discussed earlier, the possible structural irregularity of sO-1,6-2 must be re-

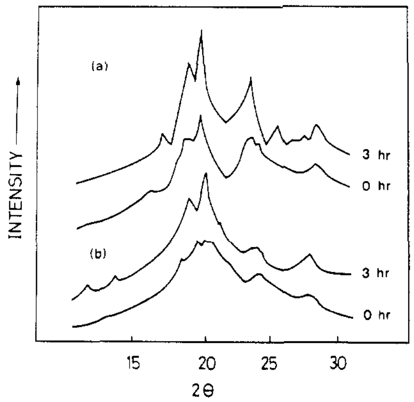


Figure 4. X-ray diffractograms of (a) sO-2,7-2 and (b) sO-1,5-2 before and after annealing.

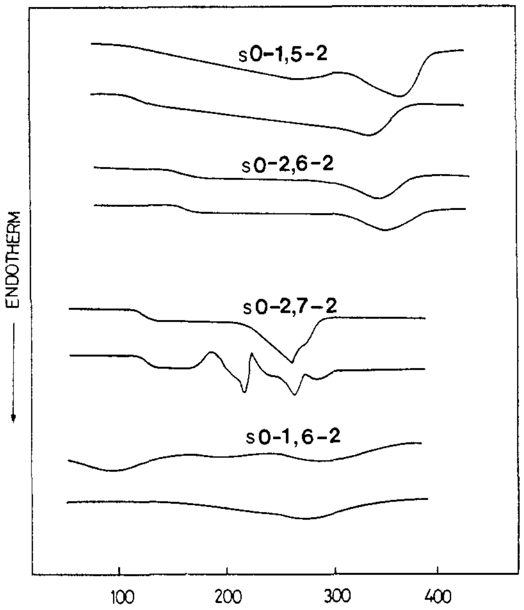


Figure 5. DSC thermograms of the polymers before and after annealing.

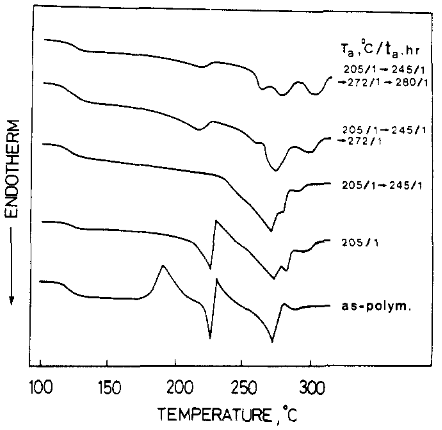


Figure 6. Change in DSC thermograms of sO-2,7-2 obtained after stepwise annealing.

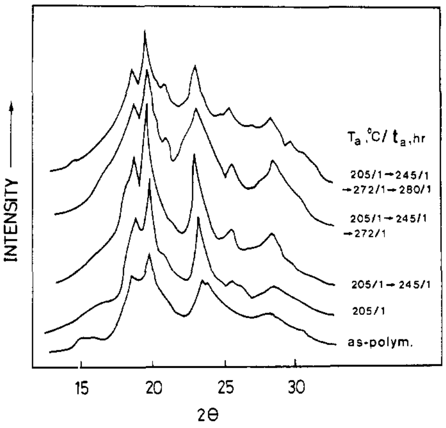


Figure 7. X-ray diffractograms of sO-2,7-2 obtained after stepwise annealing.

sponsible for the poor crystallizability of the sample even on annealing. Another important point to be noted is that final melting points are elevated (sO-1,5-2) after annealing. As expected, thermal treatment also can be accompanied by disappearance of the low-temperature endothermic transition (DSC thermogram of sO-2,7-2 shown in Figure 5).

Comparison of the two X-ray diffractograms shown in parts a and b of Figure 4 immediately leads to the conclusion that the samples' crystalline structure do not change on annealing, although detailed analysis of X-ray diffraction requires further studies.[13,14] If a polymer were polymorphous and the low-temperature endotherm came from the melting of one of the polymorphs, the X-ray diffractogram of the annealed sample should lack some of the diffraction peaks contained in the diffractogram of the original as-polymerized sample. Such an absence of peaks would show combined crystalline diffractions originated from both the lower and higher temperature polymorphs. As mentioned above, the DSC thermogram of the annealed sample of sO-2,7-2 (Figure 5) is missing the low-temperature endotherm at 226 °C that was originally present (Figure 2) for the as-polymerized sample. Its X-ray diffractogram, however, remains practically unchanged on annealing. We can conclude that the low-temperature endotherm corresponds to premelting but not to the crystal–crystal transition. Premelting can be due to reorganization such as the melting of crystalline regions of high defects or of very small crystallite size. This phenomenon has been observed for many other polymers.[15,16] It also is possible that the presence of a low molecular fraction caused premelting.

We subjected sO-2,7-2 to a further thermal treatment study by increasing the annealing temperature stepwise. The DSC thermogram and the X-ray diffractograms of the sample after each thermal treatment are shown in Figures 6 and 7. As T_a is increased, the shape of DSC thermograms changes drastically, especially in regard to two aspects: overall shapes of the thermograms differ from each other and, as T_a becomes higher, the high-temperature endothermic peak becomes dominant. When T_a was 280 °C, there appeared a final, large endothermic peak centered around 300 °C. The X-ray diffractograms, however, remain practically unchanged, suggesting again that annealing did not cause any change in crystal structure. Table III summarizes information obtained from the DSC and X-ray analyses. The solution viscosity value steadily increases with annealing temperature and time, with the polymer finally becoming insoluble. The degree of crystallinity reaches 39% on annealing for 1 h at 205 °C followed by an additional 1 h of annealing at 245 °C. Afterward it appears to decrease somewhat to about 33%. This unexpected decrease must have been caused by thermal degradation of the polymer after experiencing prolonged thermal history at elevated temperatures.

Summarizing the effects of thermal treatment on the polyesters, annealing increases (1) the molecular weight, (2) T_m, and (3) the degree of crystallinity. We observed earlier the similar effects of heat treatment on the corre-

Table IV
Results of Thermogravimetric Analyses of the Polymers[a]

polymer	T_D^i, °C	T_D^{max}, °C	T_D^{50}, °C	wt^R, %
sO-1,5-2	475	495	580	46
sO-1,6-2	435	480	570	48
sO-2,6-2	480	520	560	39
sO-2,7-2	435	475	555	46

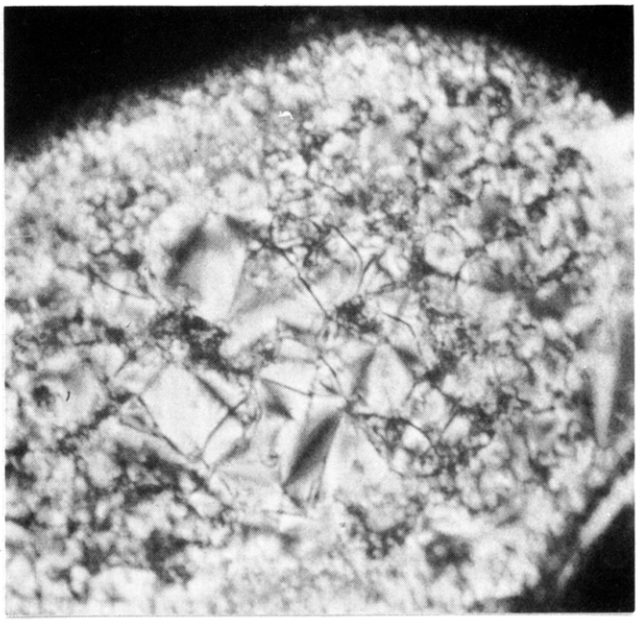
[a] T_D^i and T_D^{50} are the temperatures at which initial and 50% weight loss, respectively, were observed. T_D^{max} is the temperature at which the maximum rate of weight loss was observed. wt^R stands for the weight percent of residue remaining after the sample was heated to 600 °C.

sponding random copolyesters.[9] The increase in molecular weight and degree of crystallinity on annealing is in part responsible for the increase in T_m. Reduction in crystal defects by annealing should also be another factor elevating T_m. Since fine details of the X-ray diffractograms of copolyesters do not change even after prolonged heat treatment at T_a's, it can be said that under the annealing conditions employed they did not undergo any sequence randomization. It is well-known that X-ray diffraction patterns of a copolyester should be very sensitive to its sequence.[13,14] We also observed that their ^{13}C NMR spectra remain unchanged as shown in Figure 1.

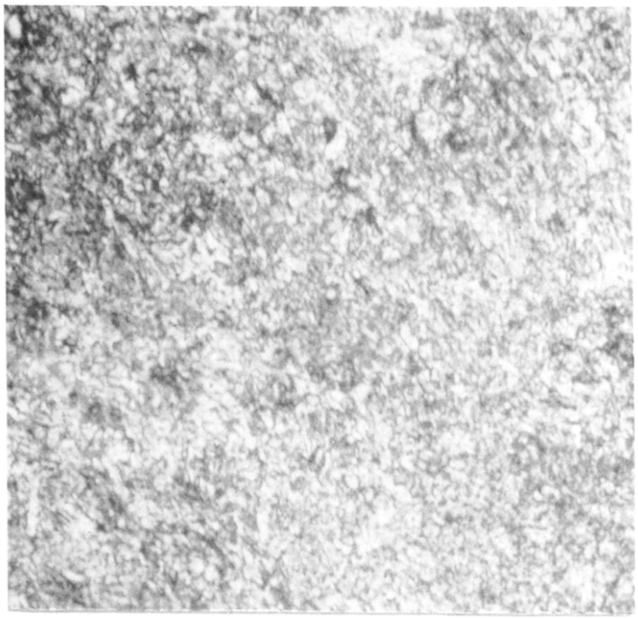
Nature of Mesophase. Among the four copolyesters, only sO-1,6-2 was not liquid crystalline while the others formed mesophases in the melt. Previously, we reported that the corresponding random copolyester derived from 1,6-naphthalenediol was nematic. Such a difference can be explained by the presence of dimeric or longer, repeated *p*-oxybenzoyl units along the chain in the random copolyester. On the other hand, in sO-1,6-2 all of the *p*-oxybenzoyl units exist in a monomeric unit connected to a terephthaloyl structure on one side and to a 2,6-naphthalene unit on the other side. Since every 1,6-naphthalenediol moiety destroys the linear structure of the polymer chain, sO-1,6-2 is not capable of having enough linear segments to give it a mesophase-forming capability. One of our earlier studies[17] demonstrated that the presence of long (three or more consecutive linear monomer structures) rigid rodlike segments in aromatic copolyesters leads to mesophase formation.

The rest of the copolyesters possess a more or less linear molecular shape, and they are expected to be liquid crystalline, as we indeed observed. However, surprisingly enough, sO-1,5-2 formed a smectic phase in the melt, whereas sO-2,6-2 and sO-2,7-2 were nematic. Figure 8 shows a fan-type smectic texture for sO-1,5-2 and a schlieren nematic texture for sO-2,7-2 observed through a polarizing microscope. We[9] earlier reported that the corresponding random copolyester prepared from 1,5-naphthalenediol was smectic. The steplike substitution mode of the 1,5-naphthalenediol moiety seems to be able to make the polymer chains form smectic layers through lateral interchain fittings. Wide-angle X-ray diffraction patterns of the quenched melts of the liquid-crystalline polymers showed broad peaks centered aroung 2θ of about 20° corresponding to spacing of about 4 Å, which represents an average interchain distance.

Thermal Stability. The thermal stability of the polymers as studied under N_2 atmosphere by DSC and TGA methods is comparable to that of the corresponding random copolyesters that were reported earlier by us.[9] Initial weight loss was observed at 435–480 °C depending on the polymer structure. The temperature at which the maximum rates of weight loss were observed ranged from 475 to 520 °C, and the temperature where 50 wt % loss was observed was 555–580 °C. Weight of residues at 600 °C was 39–48% depending on the structure of the polymers. The results are summarized in Table IV. These observations suggest that all of the copolyesters are fairly thermally stable.



(a)



(b)

Figure 8. Photomicrographs taken for the quenched (a) sO-1,5-2 and (b) sO-2,7-2 taken at 278 °C (magnification 150×).

Acknowledgment. We gratefully acknowledge the support of this work by the Asan Foundation and the Korea Science and Engineering Foundation. ^{13}C NMR spectra were obtained by Prof. H.-K. Shim at the Korea Institute of Technology, for which we are thankful. We also are thankful to Prof. C. K. Ober for previewing this manuscript.

Registry No. sO-2,7-2 (copolymer), 119897-10-8; sO-2,7-2 (SRU), 119897-13-1; sO-1,5-2 (copolymer), 122847-43-2; sO-1,5-2 (SRU), 122847-51-2; sO-2,6-2 (copolymer), 122847-45-4; sO-2,6-2 (SRU), 122847-52-3; sO-1,6-2 (copolymer), 122847-47-6; sO-1,6-2 (SRU), 123001-64-9.

References and Notes

(1) Krigbaum, W. R.; Kotek, R.; Ishikawa, T.; Hakemi, M.; Preston, J. *Eur. Polym. J.* **1984**, *20*, 225.

(2) Moore, J. S.; Stupp, S. I. *Macromolecules* **1988**, *21*, 1217.

(3) Jin, J.-I.; Lee, S.-H.; Park, H.-J. *Polym. Bull.* **1988**, *20*, 19.

(4) Jin, J.-I.; Chang, J.-H.; Jo, B.-W. *Polym. Bull.* **1988**, *20*, 525.

(5) Lenz, R. W.; Jin, J.-I.; Feichtinger, K. A. *Polymer* **1983**, *24*, 327.

(6) Moore, J. S.; Stupp, S. I. *Macromolecules* **1987**, *20*, 273.

(7) Jin, J.-I.; Park, H.-J. Unpublished results. Park, H.-J. Ph.D. Thesis, Korea University, Seoul, Korea, Feb 1987.

(8) Tsay, J.; Volksen, W.; Dawson, B. L.; Economy, J. *In Liquid Crystals and Ordered Fluids*; Griffin, A. C., Johnson, J. F., Eds.; Plenum Press: New York, 1984; Vol. 4, pp 363–373.

(9) Jin, J.-I.; Chang, J.-H.; Shim, H.-K. *Macromolecules* **1989**, *22*, 93.

(10) Higashi, F.; Kubota, K.; Sekizuka, M.; Higashi, M. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 2681; **1983**, *21*, 3241; **1984**, *22*, 2181; **1986**, *24*, 97.

(11) Rabek, J. F. *Experimental Methods in Polymer Chemistry*; John Wiley and Sons: New York, 1980, p 507.

(12) Demus, D.; Richter, L. *Textures of Liquid Crystals*; Verlag Chemie: Weinheim, FRG, 1978.

(13) Gutierrez, G. A.; Blackwell, J. *Macromolecules* **1984**, *17*, 2744.

(14) Blackwell, J.; Cheng, H. M.; Biswas, A. *Macromolecules* **1988**, *21*, 39.

(15) Jaffe, M.; Wunderlich, B. *Kolloid Z. Z. Polym.* **1967**, *203*, 216.

(16) Hamada, F.; Wunderlich, B.; Sumida, T.; Hayashi, S.; Nakajima, A. *J. Phys. Chem.* **1968**, *72*, 178.

(17) Lenz, R. W.; Jin, J.-I. *Macromolecules* **1981**, *14*, 1405.

Liquid Crystal Polymers Containing Macroheterocyclic Ligands. 2.[†] Side Chain Liquid Crystal Polysiloxanes and Polymethacrylates Containing 4-(ω-Alkan-1-yloxy)-4′-(4′-carboxybenzo-15-crown-5)biphenyl Side Groups

Virgil Percec* and Randall Rodenhouse

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106-2699. *Received January 25, 1989; Revised Manuscript Received May 5, 1989*

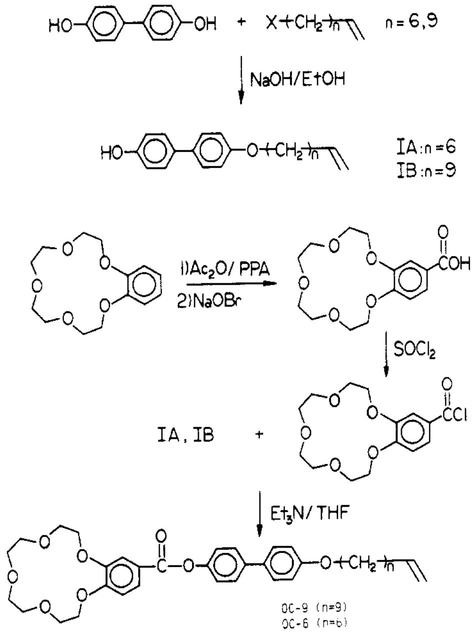
ABSTRACT: The synthesis and characterization of two poly(methylsiloxane)s containing 4-(ω-alkan-1-yloxy)-4′-(4′-carboxybenzo-15-crown-5)biphenyl side groups [where alkan = undecan (PSC-11) and octan (PSC-8)] and of poly[4-((11-methacryloylundecan-1-yl)oxy)-4′-(4′-carboxybenzo-15-crown-5)biphenyl] (PMC-11) are described. Both PSC-8 and PMC-11 display a nematic and a smectic enantiotropic mesophase, while PSC-11 displays a nematic and two smectic enantiotropic mesophases. Their parent monomers exhibit only monotropic mesophases. These polymers represent the first examples of side chain liquid crystal polymers containing macroheterocyclic ligands within their mesogenic side groups.

Introduction

The insertion of macroheterocyclic ligands capable of forming host–guest complexes within the structure of liquid crystalline compounds may lead to systems that combine the molecular features of the macroheterocyclic unit with the supramolecular arrangement of the units into a mesomorphic phase.[1] Liquid crystal macroheterocyclic ligands may add a new dimension to the field of host–guest chemistry that so far was performed either in an isotropic solution or in a three-dimensional crystalline phase.[1–3] They would represent the simplest examples of phase-dependent operating systems and could provide a new approach to systems that combine a highly selective recognition coupled with external thermal or electromagnetic regulation.[1,4]

So far, there are only two examples of low molar mass liquid crystals containing macroheterocyclic ligands. The first refers to disclike amide derivatives of macroheterocyclic polyamides that exhibit columnar mesophases.[1,5] The second refers to a series of rigid rodlike low molecular mass liquid crystals containing a benzocrown ether moiety. This second series of compounds exhibit calamitic mesophases.[6] To date, there is no example of side chain liquid crystal polymer containing crownlike ethers or any other kind of macroheterocyclic receptor.[7,8]

Scheme I
Synthesis of OC-6 and OC-11



The first example of main chain liquid crystalline polymer containing dibenzo-18-crown-6 based structural units was recently reported from our laboratory.[9]

[†] Part 1: Percec, V.; Rodenhouse, R. *Macromolecules* **1989**, *22*, 2043.