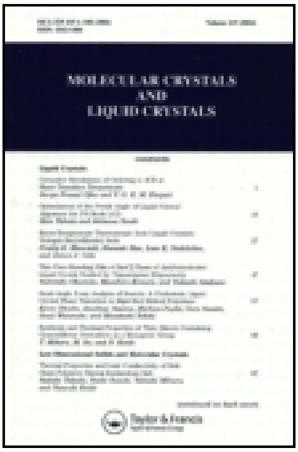

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Microchemical Structures and Properties of Main Chain Thermotropic Polyesters

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MICROCHEMICAL STRUCTURES AND PROPERTIES OF MAIN CHAIN THERMOTROPIC POLYESTERS

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Abstract This paper reviews how some of the structural variables influence the mesomorphic properties of main chain polyesters. Among the many possible variables 1) linking order of the ester group, 2) comonomer sequence, 3) regioregularity of substituents, and 4) location of the substituents are the four important structural factors to be discussed about. A close examination of the dependence of the thermal and liquid crystalline properties of the main chain thermotropic polyesters on their microchemical structures provides us with an insight how to control their macroscopic properties.

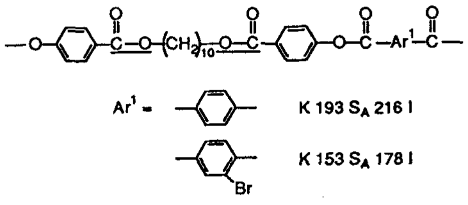
INTRODUCTION

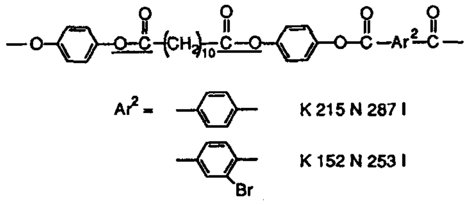
The microchemical structure of a polymer not only controls the properties of a single molecule, but also plays a decisive role in controlling the properties of the molecular assembly. One approach to establish a structure-property relationship of thermotropic polyesters is to change their structures systematically and try to learn how those structural changes influence their properties. The structural variables examined by us and others are 1) the structure and length of mesogenic units, 2) the nature, number and position of the substituent(s) on the mesogenic units, 3) the structure and length of the flexible spacers, 4) existence of the chiral centers along the spacer or in the substituents attached on the mesogenic units, 6) molecular weight, 7) thermal history, and 8) copolymerizations. One[1] of our earlier reports critically analyzes the effects of those structural factors in controlling the properties of the thermotropic, main chain polymers. There have been numerous additional research papers[2-10] published since our review appeared. But, in general, their observations or conlusions made on new and novel compositions do not contradict our earlier analyses.

In this report, we would like to offer an in-depth analysis of some of our recent findings on the structure-property relationships of thermotropic, aromatic polyesters. Especially, we will focus on the effects of 1) linking order of the ester groups i.e., $-\overset{O}{\overset{\|}{C}}-O-$ vs. $-O-\overset{O}{\overset{\|}{C}}-$, 2) comonomer sequence, i.e., random vs. regular sequence, 3) regioregularity or positional isomerism of the substituents on the aromatic rings, i.e., random vs. regioregular positioning, and 4) location of the substituent(s) i.e., at the central vs. terminal position of the mesogenic units.

Linking Order of the Ester Groups

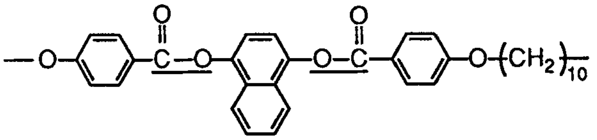
It is generally accepted that stronger lateral interaction between liquid crystalline molecules favor the formation of the smectic phase[11]. The major intermolecular force for a lateral intermolecular attraction is the high permanent dipole moment in lateral direction. The permanent dipole moment of a molecule is, of course, the total vector sum of all of the bond moments. Therefore, the reversal of the linking order of the ester group in a molecule would not result in a change in the magnitude and direction of the molecular permanent dipole moment, unless molecular geometry changes accordingly. In other words, one would expect that reversal of the ester group's linking order in a polymer does not influence the nature of the mesophase that it forms. The following examples, however, demonstrates that it is not so[12]. The first two polymers form the smectic A phase, whereas the second two the nematic phase :



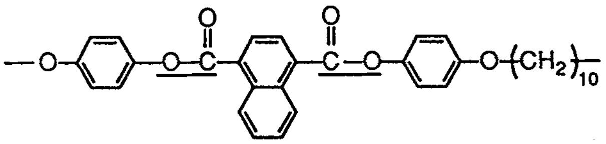


The only difference lies in the orientation of the ester groups which link the mesogenic groups(M) to the spacers(S). In the formers, the ester groups are in the order of $\mathrm{M{-}\overset{O}{\overset{\|}{C}}{-}O{-}S}$, whereas in the latters they are in the order of $\mathrm{M{-}O{-}\overset{O}{\overset{\|}{C}}{-}S}$. One of the conjectures that we can think of, in order to explain this rather intriguing phenomenon, is the fact that the length of the mesogenic groups of the first polymers are slightly longer than that of the second ones, because in the formers the two carbonyl groups in the ester groups linking the mesogenic units to the spacers are in direct conjugation with the phenylene rings to which they are attached. This will result in the extension of the rigid core, which is known to favor the formation of the smectic phases. The reason for the consistently higher isotropization temperatures for the second polymers, however, remains to be answered.

Comparison of mesophase-forming ability of the following two polymers is even more dramatic[13]; the top one is nematic while the bottom one is not liquid crystalline.

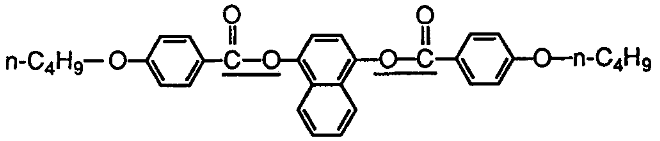


K 225 N > 315 I

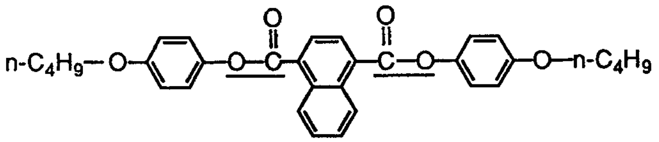


K 195 I ; no LC

The exact same phenomenon is observed also for the model compounds:



K 161 N 191 I



K 131 I ; no LC

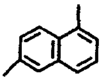
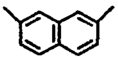
In this case, the orientation of the inner ester groups in the mesogenic units is reversed. Although we do not have any direct information of the minimum energy conformations of the mesogenic units, it is very possible that the naphthalene rings in the non-mesomorphic ones have to twist out of the coplanarity due to the repulsive interactions between the carbonyl oxygens and the protons at 5 and 8 positions, depending on the orientation of the carbonyl groups[14].

Comonomer Sequence

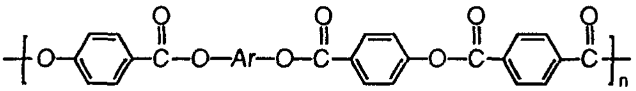
It is very well established that comonomer sequence influences physical and mechanical properties of the vinyl copolymers. But the studies about the effects of comonomer sequence on the properties of condensation copolymers, especially of the thermotropic copolyesters, are rather limited. Krigbaum et al.[15] and more recently Martin and Stupp[16] demonstrated that the thermal transition behavior of the main chain thermotropic polyesters containing the polymethylene spacers strongly rely on the comonomer sequence order. Bilibin et al.[17] reported synthesis of a series of aromatic copolyesters having ordered comonomer sequence. But they did not compare their properties with those of random comonomer sequence.

We[18] could prepare a series of aromatic copolyesters containg p-hydroxybenzoic acid moiety via multistep synthetic routes, and Table 1 compares the properties of two representative compositions with those of their

TABLE I. Comparison of the Properties of Sequentially Ordered Copolyesters[a] with Those of Random Copolyesters

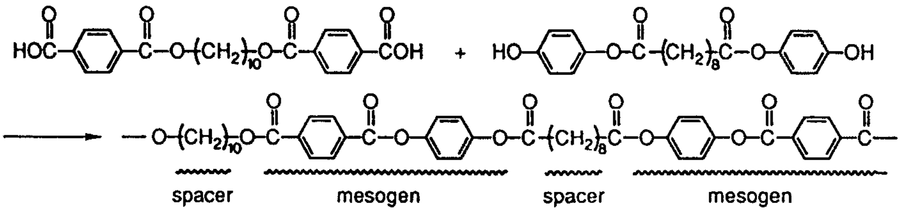
Polymer	Ar	Tg,℃	T_m,℃	LC	D.C. %
OS-1/6		n.o.	280	no	∼5
RS-1/6		124	amorphous	nematic	0
OS-2/7		116	290	nematic	24
RS-2/7		106	191	nematic	10

a



random counterparts[19]. First of all, we note that the random copolyester(RS-1/6) derived from 1,6-naphthalenediol is amorphous, but thermotropic, whereas the ordered sequence copolyester(OS-1/6) is slightly crystalline, but non-liquid crystalline. Since the 1,6-naphthalenediol moiety is not symmetrical, even OS-1/6 should contain structural irregularities resulting in poor chain packing, which, in turn, is expected to give rise to a low degree of crystallinity. In contrast, the irregular RS-1/6 is amorphous due to additional irregular structures along the chains brought about by the random sequence of the comonomers. The mesophase-forming capability of RS-1/6 can be explained by the presence of dimeric or longer, repeated p-hydroxybenzoic acid moieties along the chain. In OS-1/6, all of the p-hydroxybenzoic acid units, however, exist in a monomeric unit and every 1,6-naphthalenediol moiety destroys the linear structure of polymer chain. Therefore, OS-1/6 does not have long enough linear segments to give it a mesophase-forming ability.

The data for the 2/7 polymers derived from 2,7-naphthalenediol tell us that the melting point and degree of crystallinity of the ordered sequence polymer(OS-2/7) are impressively higher than those of the random copolymer. The melting point difference, i.e., 290℃ vs 191℃, is really remarkable. The regular comonomer sequence undoubtedly favors much better chain packing due to structural regularity along the chains. The similar dependence of the melting points was observed even for an aromatic-aliphatic alternating copolymer and a random copolyester having the same overall chemical composition as shown below[20]:



Ordered : K 251 N 279 I

Random : K 166 N195 I

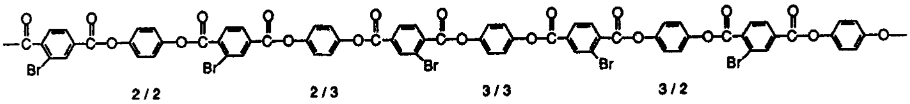
The ordered sequence, aromatic-aliphatic alternating copolymer can be prepared via solution polycondensation of the two monomers using a condensing agent at a relatively low temperature[18,20], whereas the corresponding random sequence copolyester is prepared by high temperature melt condensation of the monomers[19].

The higher isotropization temperature of the ordered sequence copolyester is explained by the presence of separated spacers. On the other hand, in the corresponding random copolyester, it is very possible to have a relatively long oligomeric aliphatic ester segments along the chains, which will destabilize the mesophase. As the length of the spacers becomes too long, the mesogenic units along the chain lose the mesophase-forming capacity[21].

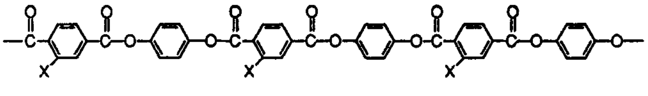
It should be added at this point that the ester groups are labile and can be involved in several types of chemical reactions at an elevated temperature, which causes randomization of comonomers sequences of the regular polymers when heated to high temperatures[22-25]. This randomization appears to proceed very slowly below melting temperature for fully aromatic copolyesters[18], but occurs in a moderate rate at temperatures higher than melting temperature. There is a very interesting recent[26] report by Stupp and Wu that the ester groups in the thermotropic polyesters are much resistant to such transesterification reactions especially in the mesophase, probably due to stabilizing effect by the mesophase morphology. This effect is pronounced when the terminal groups of a thermotropic polyester are blocked.

Regioregularity of Substituents

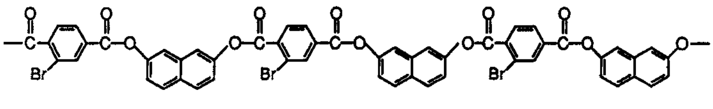
The use of the unsymmetrically ring-substituted aromatic compounds is a very efficient way to depress the melting temperature of aromatic polyesters[1]. Such a melting point depression by the substituents is caused not only by the increase of the interchain distance and hindrance of effective chain packing, but also by their positional irregularity along the chain. If one polymerizes 2-bromoterephthalic acid and hydroquinone, orientation of the bromine substituents in the neighboring two terephthalic acid moieties can be at 2/2, 2/3, 3/3 or 3/2 due to the possible positional isomerism. In other words, the chemical structure of the polymer along the chain is, in a strict sense, not homogenous and, therefore, can be taken as a copolyester. This positional isomerism brings about an extra degree of structural irregularity, which is expected to cause a melting point depression as well as the diminished degree of crystallinity. In general, the larger the size of the substituent, the greater the effect is.



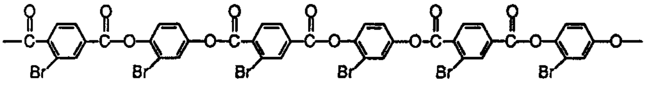
While studying the substituents' effects on the thermal and liquid crystalline behavior, we became interested in the synthesis and properties of regioregularly substituted aromatic polyesters and in comparing their properties with those of the randomly substituted ones[27].



R - Br (X = Br) and R -NO_2 (X = NO_2)



R - BrN



R - Br / Br

The general properties of these polymers are compared with those of randomly substituted ones in Table 2. Although there are significant differences in their molecular weights as reflected by their solution viscosity values, we can make some generalization : 1) the glass transition temperatures of the regioregularly substituted polymers are higher than those of irregularly substituted ones, when either the size of the substituent is large as in R-NO_2 or the repeating unit contains two substituents, one each on the two aromatic rings as in R-Br/Br. 2) The regioregularly substituted polymers have significantly higher T_m values than their irregularly substituted counterparts. 3) When the repeating unit contains only one, relatively small substituent as in R-Br, R-BrN and the corresponding random copolymers, the degree of crystallinity(DC) is high. At the same time, the DC values of the regioregularly

TABLE II. Comparison of the Properties of Regioregularly Substituted Polyesters with Those of Irregularly Substituted Ones

Polymer	η_{inh}	T_g, °C	T_m, °C	D.C., %
R-Br	0.72	78	365	38
random	0.43	77	286	26
R-NO_2	ins.	92	345	11
random	1.01	77	220	10
R-BrN	1.09	135	312	34
random	0.52	139	223	19
R-Br/Br	2.60	110	284	~3
random	2.15	88	211	~2

substituted polymers appear to be higher than those of the irregular polymers. In addition, details of the X-ray diffractograms(Figure 1) of the regularly and irregularly substituted polymers are much different, suggesting that they have different crystal structures. Since the regioregularly substituted polymers described here are the only compositions reported up until now, much further studies on the effects of regioregularity of the substituents are deemed necessary.

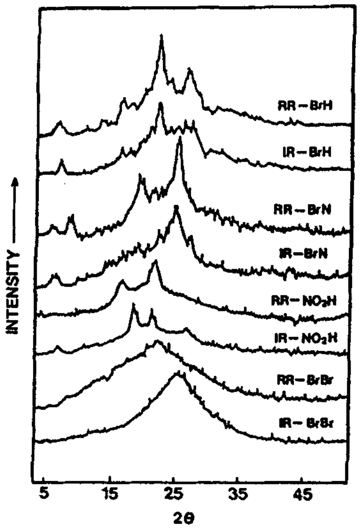
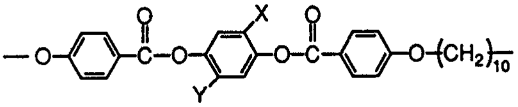


Figure 1 Wide angle X-ray diffractograms of polymers.

Location and Number of the Substituents

As described in the previous section, inclusion of a unsymmetrically substituted ring in the mesogenic unit depresses the melting point(T_m) of the resulting polymers. An example is shown below[14] :



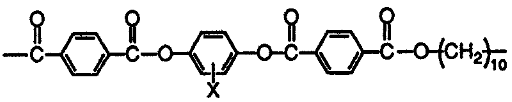
X = Y = H ; K 236 N 294 I

X = H , Y = Cl ; K 157 N 279 I

X = Y = Cl ; K 200 N 255 I

At the same time, the isotropization temperature(T_i) also drops down by the presence of the unsymmetrical substituent. When another substituent is placed on the same ring to render the mesogenic unit symmetrical, the T_m increases significantly. In the above examples, the T_m of the symmetrically disubstituted polymer is 200℃, while the value for the monosubstitued one is 157℃; the difference amounts to 43℃. But the T_m value(200℃) of the disubstituted polymer is still far lower than that(236℃) of the unsubstituted one. The T_i value, however, steadily decreases with increasing the number of the substituents. Certainly, the presence of the substituent increases the molecular breadth, which, in turn, is expected to destabilize the mesophase lowering T_i. And this decrease in T_i is further augmented by the presence of the two substituents.

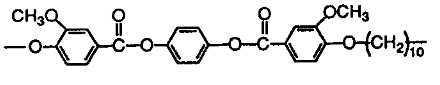
The thermal behavior of the following two polymers is even more dramatically different[28,29]; the unsubstituted polymer melts into nematic phase, whereas the methoxy substituted one does not form any liquid crystalline phase on heating. The substituted polymer, however, forms a nematic phase on cooling the isotropic melt indicating that the polymer is monotropic.



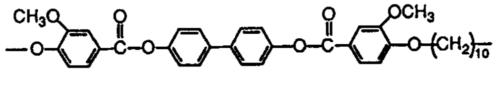
X = H ; K 231 N 267 I

X = OCH_3 ; K 158 I (I 148 K 116 on cooling)

To the contrary, the following polyester is not liquid crystalline[30]. One should recall that the corresponding unsubstituted polymer(the first polymer mentioned in this section) is enantiotropically nematic. This polymer carries two methoxy groups, one each on the two terminal phenylene rings in the mesogenic unit. According to a molecular model the axial ratio of the rigid unit of this polymer is only 2.1, significantly smaller than the value(2.85) for the unsubstituted polymer. The value for the rigid unit of the monotropic polymer mentioned above lies inbetween and is 2.6.



non - LC (K 139 I)



K 229 N 265 I

Replacement of the central hydroquinone moiety with 4,4′-biphenol structure revives the mesophase-forming capability. This structural changes increases the L/D value of the rigid unit from 2.1 to 3.2.

Although the structure of spacers must also play an important role in controlling the mesophase-forming ability of a polymer, it is clear from the above analysis that, as long as one campares the LC forming ability of a series of the polymers having the very similar, analogous structures, the simple estimation of the axial ratio of the mesogenic units can provide us with an easy way to predict the liquid crystallinity of a polymer. At the same time, it should be noted that the introduction of the methoxy groups at the terminal parts of the mesogenic units results in a substantial increase in the breadth of the rigid unit when compared with the mosogenic unit having the methoxy group located in the middle phenylene ring of the mesogenic unit.

Acknowledgement : The support of this work by the Korea Science and Engineering Foundation and Korea Research Foundation is gratefully acknowledged. Contributions by J.-H. Chang, C.-S. Kang, I.-H. Lee, H.-S. Choi, S.-C. Ryu and B.-W. Jo are also acknowleged.

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