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Structure in Mesogenic Diol-Containing Polyesters

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Abstract: Copolyesters synthesized from two mesogenic monomers have been investigated. The monomers are 4,4'-bis(6-hydroxyhexoxy)biphenyl (BHHBP) and the *p*-diester made from terephthaloyl dichloride and *p*-hydroxybenzoic acid. The incorporation of a very rigid, second mesogen increases the ability of BHHBP to form tilted mesophases. An untilted smectic A phase is formed initially, but the final, stable phase is a highly ordered, tilted smectic phase. Similar behavior is observed when BHHBP is combined with a mixture of the diacids of the crown ether dibenzo-18-crown-6. A copolymer of this type also forms a smectic A phase. For both types of copolymers, there is good agreement between the measured and calculated values for the layer distances.

Key words: main-chain polymers, X-ray diffraction, smectic phases, bisphenol, polyesters.

INTRODUCTION

Knowledge of the influence of certain parts of mesogens or of whole mesogens on the liquid crystalline behavior of molecules contributes to our understanding of the stability and structure of mesophases. Because interest has been mainly focused on an investigation of the different structures or types of mesophases in polymeric liquid crystals, the influence of the different comonomers on the stability and structure of the mesophase is still unknown. In studies of mesomorphic, thermotropic polyurethanes and polyesters, we have examined the effects of a mesogenic monomer on the phase behavior of a number of polymers with differing comonomers. The common monomer, 4,4'-bis(6-hydroxyhexoxy)biphenyl (BHHBP), is a mesogen with a very stable, highly ordered smectic phase:^{1,2}

Scheme 1

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Model compounds for polyesters and polycarbonates containing BHHBP show similar phase behavior.³ Because of the functionality of BHHBP, it can be combined with a variety of different comonomers (aliphatics and aromatic diacids and diisocyanates). This chemical flexibility has made our investigations somewhat different from the well-known studies of phase behavior in homologous substances.

In the present study we have tried to correlate the formation of different mesophases with the chemical nature of the monomers. The characterization of the mesophases and the measurements of the molecular and supermolecular distances were carried out with wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS). The results of these studies were corroborated by differential scanning calorimetry (DSC), which also provided information about the type of mesophase present.

EXPERIMENTAL

The copolymers used in this study are listed in Table 1. Their syntheses are described elsewhere.^{4–7} X-ray diffraction data were obtained with a fine-focusing X-ray tube equipped with a graphite monochromator and a pinhole collimator, or a collimator with two pairs of crossed slits. The detection device used was a Xentronics

TABLE 1. Copolymers with BHHBP

Sample number	Comonomer ^a	Polymer type ^b
1	Adipic acid	PE
2	2,4-TDI	PU
3	<i>N</i> -Methyl-2,4-TDI	PU
4	TA	PE
5	IA	PE
6	34% IA, 66% TA	PE
7	47% 2,4-TDI, 53% 2,6-TDI	PU
8	Blend A ^c	PU
9	Blend B ^d	PU
10	<i>p</i> -Triad ^e	PE
11	DB-18-C-6 diacid	PE

^a TDI, toluene diisocyanate; TA, terephthalic acid; IA, isophthalic acid; DB-18-C-6, crown ether dibenzo-18-crown-6.

^b PE, polyester; PU, polyurethane.

^c Blend A: 61.1% PU 2,4-TDI/BHHBP; 38.9% PU 2,6-TDI/BHHBP.

^d Blend B: 40.7% PU 2,4-TDI/BHHBP; 59.3% PU 2,6-TDI/BHHBP.

^e See text.

area detector from Nicolet-Siemens (Madison, WI), coupled with a PC system for collecting, storing and analyzing X-ray images. The copolymer samples were drawn and annealed fibers. Oriented low molecular weight liquid crystalline samples were obtained by using the wall effects or magnetic field effects in sealed Lindemann glass capillaries. Differential scanning calorimetry was performed with a Perkin-Elmer DSC-7 (Norwalk, CT).

Molecular modeling and energy-minimum calculations were carried out with an AST Premium 286 PC (Irvine, CA) and a Molecular Graphics Program Package (Department of Chemistry, University of Washington, Seattle, WA).

RESULTS AND DISCUSSION

As already mentioned, the mesogenic monomer BHHBP forms a highly ordered and stable smectic liquid crystalline phase. From the X-ray patterns obtained, we calculated by two methods the tilt angle of an oriented sample. In the first method, we measured the tilt angle directly, using the existing software on the PC system with a rotating cursor to measure the azimuthal angle of the layer reflections. The second method was indirect; it entailed calculating the length of the monomer molecule with the molecular graphics software and then comparing these data with the measured *d*-spacing and calculating the tilt angle from the difference. By both measurements, the tilt angle (ϕ) was found to be 28°. Because only one mesophase was observed with DSC,^{1,2} it was concluded that this mesogenic diol has a strong tendency to form a highly ordered, tilted smectic phase.

Fig. 1. Phase behavior of the diesters of BHHBP. Reprinted, with permission, from Ref. 7. The type of smectic phase is unknown.

Further evidence of the presence of the smectic phase in BHHBP has been provided by Smyth *et al.*,¹ who observed ring-flip motion of the biphenyl mesogens and detected a high transition heat into the isotropic state. In addition, low molecular weight model derivatives synthesized by Sato *et al.*,³ with BHHBP as the central group, showed a strong tendency to form stable smectic mesophases³ (see Fig. 1). The stability of these compounds is comparable to the stability of the pure BHHBP (crystalline 98 smectic 179 isotropic). Sato, however, did not indicate the phase type and the method for detecting the presence of a smectic phase. Nevertheless, the absence of a nematic phase in these compounds and the presence of a broad smectic phase indicate a strong influence of BHHBP on the nature and properties of the mesophases. In the *n* = 6, 7 and 8 derivatives of BHHBP, the biphenyl moiety is in the center of approximately 18 segments of a flexible chain, so it is 'solvated' in a flexible environment. From these facts, we infer, in contrast to the conclusion of Smyth *et al.*,¹ that hydrogen bonds at the ends of the BHHBP molecule play an important role in determining the order of the mesophase in BHHBP.

In contrast to the homologous BHHBP series, low molecular weight compounds containing a biphenyl group (synthesized from bisphenol diisocyanate) connected with two urethane linkages in the center of the molecule do not form liquid crystals.⁸ In these crystalline compounds the hydrogen bonds play an important role, the transitions into the isotropic state occurring at high temperatures (192–220°C). The melting points increased because of these strong interactions above the transition temperature into the mesophase.

Similar behavior was observed in copolymers of BHHBP. Polyesters and polycarbonates formed from BHHBP and aliphatic comonomers showed, in general, one or more smectic phases. In no case was a nematic phase observed. Unexpectedly, we found that the copolyesters with a conformational 'kink' in the comonomer, such as the malonic esters prepared by Reck &

Ringsdorf,⁶ not only showed a broad smectic range but also formed a stable smectic phase of higher order and an additional tilted smectic phase. A comparison of the BHHBP-containing copolymers with the copolymers formed from the 4,4'-bis(2-hydroxyethyl)biphenyl (BHEBP) showed that both copolymer classes exhibited approximately the same behavior.⁹ *Thus the moiety influencing the phase structure and phase stability of the mesophase must be the ether-linked bisphenol group.* Polyesters synthesized from BHHBP and adipoyl chloride (sample 1, Table 1) also showed two orders in the layer reflections in the mesophase, a result indicating the presence of a smectic mesophase. The type of mesophase has not yet been determined, but DSC traces showed a low transition heat into the mesophase and a high transition heat into the isotropic state, a result indicating a highly ordered smectic phase. In addition, wide-angle X-ray reflections are not diffuse (see Fig. 2), a finding indicating a phase of higher order. The temperature range of the mesophase is not as high as expected.

Copolymers with aromatic comonomers such as diacids or diisocyanates have a more complex behavior than copolymers containing aliphatic comonomers. Polyurethanes containing 2,4-toluene diisocyanate (2,4-TDI) (sample 2) as comonomer have been studied^{4,5,10} and exhibited a tendency to form either a highly ordered smectic phase or a disordered crystalline phase^{5,10} (see Fig. 3). The development of the disordered crystalline phase from a smectic A phase was observed upon annealing the samples (drawn fibers). The phase shift was indicated by the 'splitting' of the wide-angle reflections in the diffraction patterns shown in panels a and b in Fig. 3. Although there was no observable tilt in the layer reflections, the *d*-spacing was still slightly smaller than that calculated for an extended chain monomer molecule. This finding indicates either that gauche conformations are present in the polyethylene spacer chains, that a backfolding of the main chain at the TDI site is occurring, or that the phases are tilted. These conclusions were supported by the findings that for the disordered crystalline phase the *d*-spacing was smaller than that

Fig. 2. Intensity plot of the X-ray diffraction pattern of the polyester BHHBP + adipic acid (sample 1); mesophase, 130°C.

Fig. 3. (a) X-ray diffraction pattern of the polyurethane BHHBP + 2,4-TDI (sample 2); smectic A phase, drawn fiber, 25°C. (b) X-ray diffraction pattern of the polyurethane BHHBP + 2,4-TDI (sample 2); disordered crystalline phase, developed after annealing the drawn fiber, 25°C.

calculated for an extended chain, and that no tilt in the layer reflections was observed.

In copolymers containing *N*-methylated polyurethane (sample 3), a smectic C phase began to develop out of a nematic phase. The phase change was indicated by the splitting of the layer reflections. This 'phase developing' behavior with annealing could only occur because of the low melting points of these copolymers and the consequent high viscosity of the mesomorphic melt. The slow development of an ordered phase out of a nematic might have been occurring, but whether a final, stable phase can be attained is still undetermined. The formation of a

stable liquid crystalline phase is more likely to occur in this case; the absence of hydrogen bonds in these molecules, unlike the regular hydrogen bonding in most polyurethanes, obviously decreases the tendency of the *N*-methylated compound to form crystalline phases. However, it seems that these polymers tend to form into ordered phases, i.e. liquid crystals, and that they also tend to form phases of higher order than the nematic.

This conclusion is also supported by results obtained from the study of polyesters that were made from terephthalic or isophthalic acids, or from mixtures of both and BHHBP (samples 4–6). That the copolyester containing terephthalic acid formed a liquid crystal is not very surprising; this copolymer has a strong tendency to crystallize. On the other hand, the copolyester containing isophthalic acid as comonomer formed a highly ordered smectic A phase. The X-ray diffraction patterns showed intense layer reflections of the first and second order (see Fig. 4). It should be noted that the measured layer distances are more likely to be those of an extended chain, because the calculated layer distances for a backfolded main chain are much shorter (see Table 2).

Obviously, a kink in the copolymer structure favors the formation of a liquid crystalline phase because it decreases the melting point and hence decreases the tendency of the copolymer to crystallize. Nevertheless, in this case we have a good example of a smectic A phase. Thus we conclude that the kink in the chain due to the presence of the isophthalic acid group destroys the ability of the chain to form tilted phases. The structure of the copolyester synthesized from BHHBP (50%), terephthalic acid (33%) and isophthalic acid (17%) (sample 6) is close to that deemed optimal for obtaining the liquid crystalline properties of BHHBP in a copolymer (Fig. 5). The X-ray diffraction patterns of this copolymer show a

Fig. 4. X-ray diffraction pattern of the polyester BHHBP + terephthalic acid (sample 4); drawn fiber, smectic A phase, 25 °C.

tilted, highly ordered smectic phase (see Fig. 6), which has a tilt angle of about 12–13 degrees (ϕ). Qualitatively, the number of kinks in this copolymer is optimal for suppressing a rapid crystallization and retaining the ability of BHHBP to form tilted, high-order smectic phases.

The behavior of copolyurethanes of 2,4-TDI, 2,6-TDI and BHHBP, and of blends A and B (which are blends of the homopolyurethanes 2,4-TDI and BHHBP and 2,6-TDI and BHHBP, respectively) (samples 7–9), is also very interesting. These copolymers formed more stable, but less ordered, smectic A phases.

The postulated layer structure can arise from one of two conformations: the TDI unit may be backfolded or

TABLE 2. *d*-Spacing of the copolymers containing aromatic comonomers

Sample ^a	Phase type ^b	<i>d</i> -Spacing (Å)	
		Calculated	Experimental
1 BHHBP + adipic acid	S ₇	33–34	30.0, 15.1
2 BHHBP + 2,4-TDI (HMW), annealed	S _A (?)	28–30 ^c	29.0, 14.2
	S ₇	32–33 ^d	25.2, 12.4
3 BHHBP + 2,4-TDI, <i>N</i> -methylated, annealed	N → S _C	28–30	28.5, 14.1
4 BHHBP + TA	S _A	32, 15	13.5
5 BHHBP + IA	S _A	28, 32, 16	31.5, 15.3
6 BHHBP + 17% IA + 33% TA	S ₇	—	13.8 ($\phi = 13^\circ$)
7 BHHBP + 47% 2,4-TDI + 53% 2,6-TDI	S _A	28–30	28.4, 14.2
8 Blend A	S _A	28–30	28.4, 14.2
9 Blend B	S _A	28–30	28.4, 14.2
10 BHHBP + <i>p</i> -triad	S _A	42	20.5
11 BHHBP + DB-18-C-6 diacid	S _A	38.5–41	37.5

^a HMW, high molecular weight. See Table 1 for the meanings of the other abbreviations.

^b S₇, smectic phase of undetermined type; S_A, smectic A phase; S_C, smectic C phase; N, nematic phase.

^c Backfolded chain.

^d Straight chain.

Fig. 5. X-ray diffraction pattern of the polyester BHHBP + isophthalic acid (sample 5); drawn fiber, smectic A phase, 25°C.

the main chain may be extended (see Fig. 7). Both conformations have approximately the same molecular distances and both are representative of a conformational energy minimum. Therefore we believe that one or both structures were present in the copolymer structure. The experimentally measured molecular distances were slightly shorter than the calculated distances, but the two sets were still in good agreement. However, the mixture of both species (2,4- and 2,6-TDI) in the copolymer chain obviously suppressed not only the tendency to order but also the tendency to crystallize.

Finally, we studied two copolymers containing two different mesogenic monomers. First, we investigated the copolyester containing BHHBP and '*p*-triad', which is made from terephthaloyl chloride and *p*-hydroxybenzoic acid¹¹ (sample 11) (Fig. 8). The incorporation of a very

Fig. 7. Backfolded and straight (extended) conformations of the polymers.

(a)

(b)

Fig. 8. (a) X-ray diffraction pattern of the polyester BHHBP + triad (*p*-hydroxybenzoic acid + terephthalic acid) (sample 10); drawn fiber, smectic A phase, 25°C. (b) Undetermined smectic phase, 25°C.

Fig. 6. X-ray diffraction pattern of the polyester BHHBP + 17% isophthalic acid + 33% terephthalic acid (sample 6); drawn fiber, undetermined smectic phase, 25°C.

Fig. 9. X-ray diffraction pattern of the polyester BHHBP + DB-18-C-6 diacid (sample 11); drawn fiber, smectic A phase, 25°C.

rigid second mesogen increased the ability of the BHHBP to form high-order mesophases. As a result, an untilted smectic A phase was formed initially, whereas the final stable phase was a more highly ordered smectic phase. The same is found for the copolyester combining BHHBP and a mixture of the diacids of the crown ether DB-18-C-6 (sample 11) (Fig. 9).¹² This copolymer shows a smectic A phase (see Table 2).

For both copolymers, there is good agreement between the measured and the calculated layer distances. The copolymerization with a second rigid monomer leads to formation of an untilted smectic A phase in the first step. However, the final stable phase, like that of the aliphatic comonomers, is a highly ordered tilted smectic phase as a result of the influence of the BHHBP.

CONCLUSIONS

The present investigation has shown that the properties of a liquid crystalline diol have a profound influence on the

properties of all the compounds synthesized with this diol, including copolymers. The tendency of BHHBP to generate highly ordered liquid crystalline phases is difficult to overcome. In no case was a stable nematic phase present; rather, all copolymers and low molecular weight compounds tended to form highly ordered smectic phases and/or disordered crystalline phases. Copolymers formed from a nonlinear monomer like isophthalic acid or TDI tend to form untilted rather than tilted phases.

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