Communications to the Editor

Effect of Branching and Molecular "Kinks" on the Properties of Main Chain Thermotropic Liquid Crystalline Polymers Containing Flexible Spacers

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Main chain thermotropic liquid crystalline polymers (MCLCP's), both wholly rigid rod systems and those that incorporate flexible spacers, have been a subject of intensive investigation for over two decades now.[1−3] The effect of various structural variations such as lateral substitutions, molecular kinks, comonomer incorporation, etc. have been investigated, especially in the wholly aromatic systems, primarily as an approach to decrease the melting temperatures and facilitate processing.[1−3] In cases where the mesogenic units are incorporated into the polymer backbone along with flexible spacer segments, the structural variations have essentially focused on incorporation of different types of mesogens, such as biphenyl,[4−6] stilbene,[7,8] azobenzene,[9,10] phenyl benzoate,[11] etc., and also on the variation of the nature and length of the flexible spacers. Most of the approaches for the preparation of such LCP's with flexible spacers have utilized an A−A + B−B type condensation route. An A−B type self-condensation route, on the other hand, permits the generation of novel types of main chain liquid crystalline polymers with better control over some unique molecular structural features, such as configurational isomers,[12] and well-defined placement of lateral substituents[11] along the polymer backbone.

One other interesting structural feature that can be introduced using the A−B type approach is the controlled degree of branching, which can be achieved by copolymerization of the A−B type mesogenic monomer with controlled amounts of an AB_2 type monomer. In this report, we describe the synthesis of a series of such branched liquid crystalline polyesters by copolymerization of a biphenyl containing A−B type monomer, ethyl 4-[4-(*ω*-hydroxydiethyleneoxy)phenyl]benzoate (BEO2), and an AB_2 monomer, ethyl 3,5-bis(*ω*-hydroxydiethyleneoxy)benzoate (EBHDB), based on 3,5-dihydroxybenzoic acid. In addition to introducing branching, this AB_2 comonomer also introduces molecular "kinks" by virtue of the 1,3,5-connectivity on the aromatic ring. Therefore, copolymers with a kink-introducing monomer, ethyl 3-(*ω*-hydroxydiethyleneoxy)benzoate (EHDB), based on 3-hydroxybenzoic acid were also prepared for comparison.

Experimental Section. ^{1}H NMR (200 MHz) spectra were recorded on a Bruker ACF-200 instrument using the TMS/solvent signal as an internal reference. Differential scanning calorimetric studies were done using a Rheometric Scientific DSC Plus instrument at a heating rate of 20 °C/min under nitrogen. All the samples were heated to 250 °C and then quenched to room temperature before recording the first scans. Reproducibility was checked by running second heating/cooling scans. Polarizing light microscopic studies were done on Leitz Ortho Lux 12POL-BK microscope attached to a Mettler FP82 HT hot stage. Viscosity measurements were made using an Ubbelohde viscometer in a constant temperature bath. All the monomers were synthesized using reported procedures starting from commercially available starting materials like 4-phenylphenol (for BEO*n*),[13] 3-hydroxybenzoic acid (for EHDB), and 3,5-dihydroxybenzoic acid (for EBHDB).[14]

Results and Discussion. Three A−B type biphenyl monomers (BEO*n*), where "*n*" represents the number of ethyleneoxy units, were prepared from the 4-(4-hydroxyphenyl)benzoic acid[13] and the appropriate monochlorooligo(ethylene glycol)s. The monomers (BEO*n*) were polymerized under standard transesterification conditions using ca. 1 mol % of tetraisopropyl orthotitanate as catalyst. The polymerization was initially carried out under a nitrogen atmosphere at 200 °C for 2 h and then under dynamic vacuum (0.05 mbar) for an additional 15 h. The structures of the various polyesters are shown in Figure 1. Polymers PBEO2 and PBEO3 were soluble in solvents like *p*-chlorophenol, trifluoroacetic acid, tetrachloroethane, and/or their combinations, but PBEO1 was insoluble. The inherent viscosity of PBEO2 (0.2% solution in *p*-chlorophenol at 50 °C) was found to be 0.53 dL/g and that of PBEO3 (0.2% solution in chloroform at 30 °C) was 0.51 dL/g, indicating that they are of moderately high molecular weights. The ^{1}H NMR spectra of the soluble polymers were in accordance with the expected structure.

The DSC thermograms of the polymers PBEO2 and PBEO3 showed multiple endothermic transitions, while that of PBEO1 showed only a single endotherm. The various transition temperatures of the polymers are given in Table 1. Both PBEO2 and PBEO3 exhibited fluid birefringent patterns, when viewed under a polarizing microscope at the expected mesophase temperatures, but the textures were not clearly identifiable. Of the three linear polyesters, PBEO2 with a diethyleneoxy spacer exhibits the largest mesophase range of 82 deg. Thus, in order to examine the effect of molecular kinks and branching, the monomer BEO2 was used for the copolymerization studies.

Copolymerization of BEO2 with varying mole fractions of EHDB and EBHDB, under standard transesterification conditions, yielded two series of copolyesters, PBEO2-M-*X* and PBEO2-B-*X*, respectively (where *X* is the mole percent of the comonomer in the feed) (Figure 1). Unlike the linear polyester PBEO2, the copolyesters were insoluble in most common solvents but swell in solvents such as *p*-chlorophenol. Hence, these polymers were extracted with *p*-chlorophenol, washed with acetone, and dried. Due to the insolubility of the copolyesters, their compositions could not be determined and therefore are taken to be equal to the feed compositions of the monomers. In wholly aromatic polyesters, Kricheldorf et al. utilized an AB_2 type

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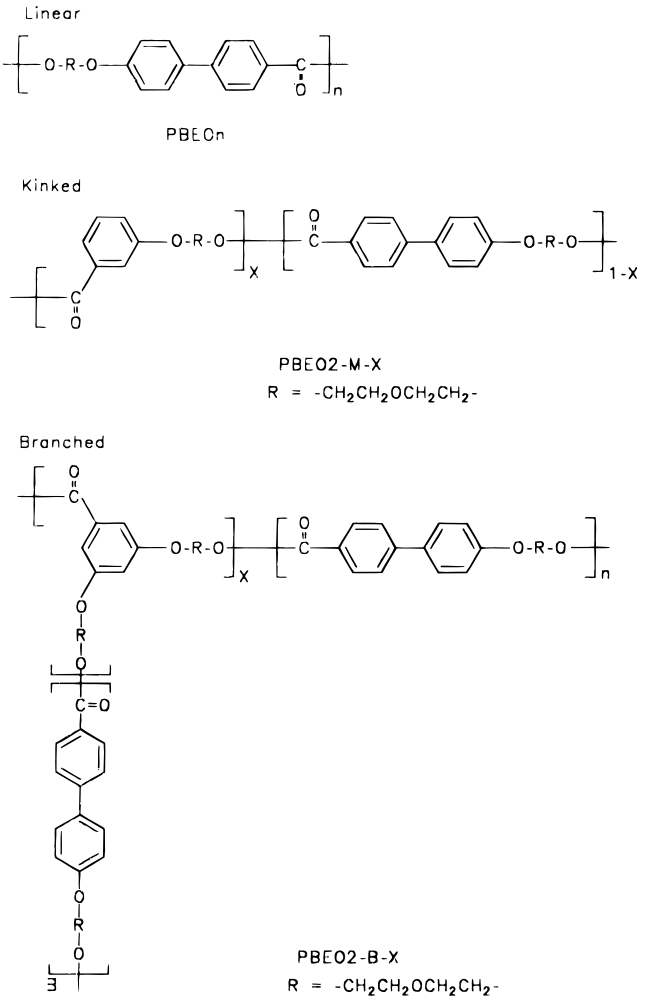

Figure 1. Structures of the linear, kinked, and branched polyesters.

Table 1

polymer	yield (%)	T_m (°C)[a]	T_i (°C)[a]	ΔT
PBEO1	85		272 (4.34)	
PBEO2	86	139 (1.68)	221 (2.43)	82
PBEO3	81	117 (1.77)	153 (1.99)	36
PBEO2-M-4.8	86	130 (0.92)	188 (1.90)	58
PBEO2-M-9.4	90	129 (0.75)	173 (1.20)	44
PBEO2-M-15	91	134 (0.71)	161 (0.50)	27
PBEO2-M-20	85	135 (0.55)	156 (0.32)	21
PBEO2-M-30	87		131 (0.91)	
PBEO2-B-5.6	89	139 (0.89)	180 (1.69)	41
PBEO2-B-7.7	88	121	137	16
PBEO2-B-11	92		132 (0.38)	

[a] Transition temperatures as observed while cooling. The values in the parentheses are the enthalpy change in cal/g.

monomer to introduce branching; however, their properties were not investigated in detail.[15]

The DSC thermograms of the homopolymer PBEO2 and copolymers PBEO2-M-*X* and PBEO2-B-*X* are shown in Figure 2. It is clear that the mesophase range (i.e. the temperature window over which the mesophase is exhibited) decreases with the increase in the mole percent of the comonomer (EHDB) (Table 1). At 30 mol %, the sample PBEO2-M-30 exhibited only a single transition and no mesophase formation is observed. The cooling curves show some supercooling but indicate essentially the same behavior with composition. The behavior in the case of the branched copolyesters, PBEO2-B-*X*, is also similar, but for the fact that the mesophase disappears at a much lower branching

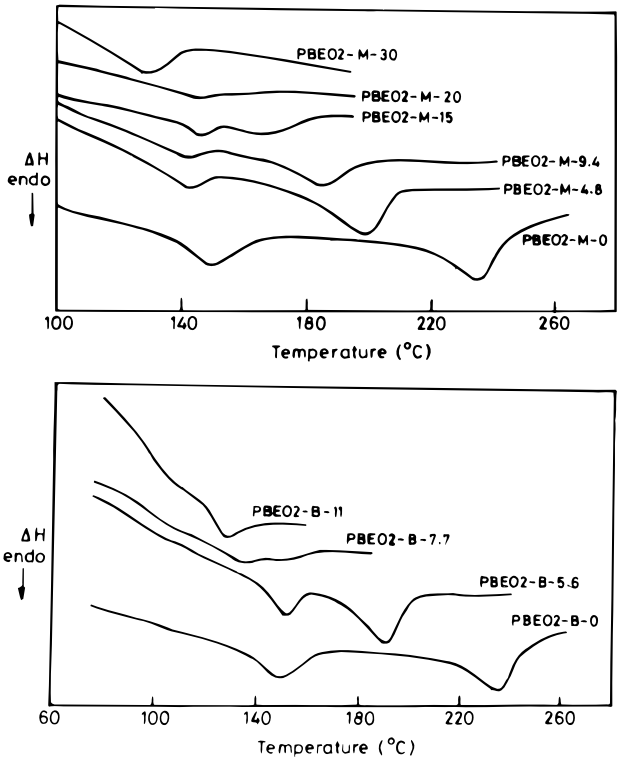

Figure 2. DSC curves (heating) of PBEO2-M-*X*, (top) and PBEO2-B-*X* (bottom).

monomer composition of ca. 11 mol %. It must also be added here that the cooling curve of PBEO2-B-11 does not exhibit any exotherm, indicating that the kinetics of crystallization is slow. This is further substantiated by the fact that it had to be annealed for 14 h at 113 °C before one can observe the endotherm due to melting during subsequent heating scans. Thus, 11% branching defects, in addition to destroying the mesophase, also slows down the rate of crystallization considerably. All the copolymer samples exhibited fluid birefringence in the expected temperature region, when viewed under a polarizing microscope. The textures were, however, not clearly indicative of any specific mesophase type. Furthermore, some of the copolymers exhibited a very high melt viscosity in the mesophase, making it difficult to obtain very thin films and therefore to obtain good textures of these mesophases.

A plot of the mesophase range ΔT (i.e., $T_i - T_m$) versus mole percent of the comonomer for the two series of copolymers is shown in Figure 3. It is clear from this plot that the mesophase range, ΔT, decreases linearly with both the mole percent of kinks and with the mole percent of branching. It may be noted that the decrease in ΔT is essentially due to the decrease in T_i with increasing amounts of defects (kinks or branching); T_m remains almost constant except at very high defect concentrations (Table 1). The slopes of the two least squares fit straight lines suggest that branching is far more detrimental to mesophase formation than is the presence of molecular kinks. The intercepts on the *X*-axis suggests that 10% branching and 25% of kinks would be adequate to destroy the ability of the copolymers to form a mesophase. The DSC thermograms of the copolymers with 11% of branching comonomer, PBEO2-B-11, and 30% of meta comonomer, PBEO2-M-30 (Figure 2), show only a single transition and no mesophase, hence validating this plot. If one assumes a simple additivity of the two effects, namely kinks and branching, then it may be possible to predict the effect

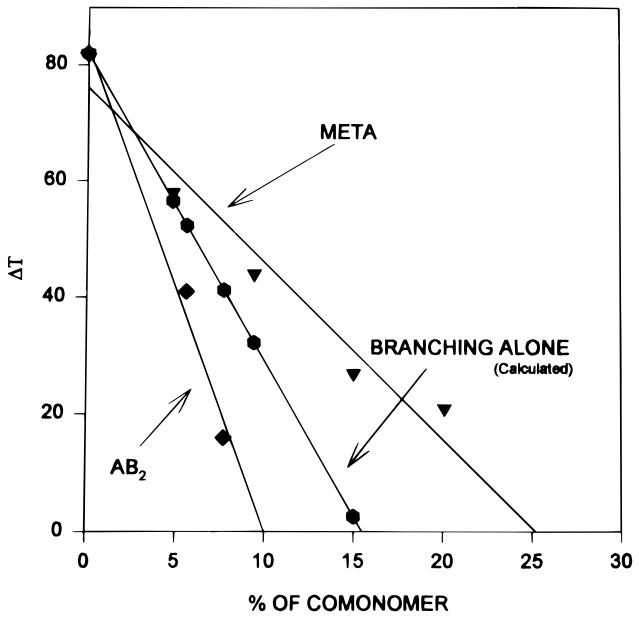

Figure 3. Variation of the mesophase range (ΔT) with the mole percent of branching and kinks.

of branching alone by a simple subtraction of the slope of the kinks line from that of the branching line. Such a calculated line (Figure 3) suggests that, if an alternate branching agent that does not introduce kinks were used, the mesophase would be destroyed at a higher comonomer composition of ca. 15 mol %. It must, however, be added that while qualitatively clear trends with regard to effects of branching and kinks are discernable, quantitative conclusions cannot be made in the absence of exact molecular weight data and the exact copolymer composition. Furthermore, it must also be noted that in the present system the branching comonomer is nonmesogenic and therefore acts as a diluent leading to an overall reduction in the mesogen concentration per unit volume. The effect of dilution alone, therefore, must also be factored in for completeness, which may be easily achieved by copolymerization with the *p*-isomer of EHDB. Studies to understand the exact nature of the mesophase using polarized light microscopy and X-ray diffraction, and also the effect of mesogen dilution, are currently underway.

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Supporting Information Available: Experimental details (4 pages). Ordering information is given on any current masthead page.

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