Synthesis and characterization of a homologous series of aromatic-aliphatic polyesters with non-coplanar 2,2'-dimethylbiphenylene units

Heidi Österholm*, Wolfgang Fiebig† and Hans-Werner Schmidt
Materials Department, College of Engineering, University of California, Santa Barbara, CA 93106, USA
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We report on the synthesis and characterization of a series of semiflexible polyesters containing a non-coplanar biphenylene unit and a flexible alkylene spacer of variable length. The number of methylene groups in the spacer was varied from three to eight. The polyesters were synthesized by interfacial polycondensation. The polymer properties were characterized by thermal analysis, optical microscopy and wide-angle X-ray diffraction. Melting transitions and glass transition temperatures show a strong odd–even effect with respect to the number of methylene groups in the flexible spacer. The crystallinity is reduced by the incorporation of the 2,2'-dimethylbiphenylene unit. In the polyesters with an odd number of methylene groups the crystallization is suppressed and indications of a crystalline phase were only observable after extensive annealing.

(Keywords: aromatic-aliphatic polyesters; odd–even effect; synthesis)

Introduction

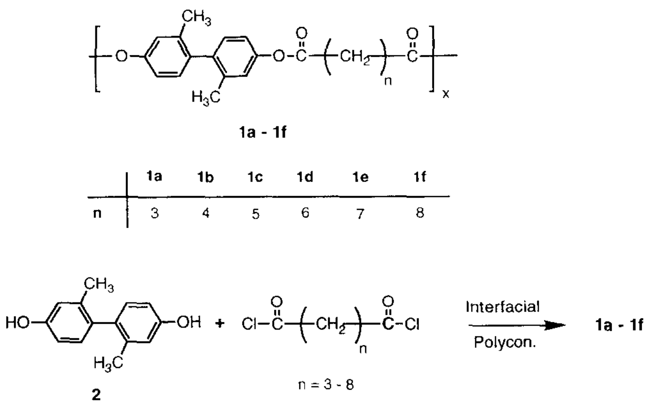
Semiflexible polyesters have been studied in different laboratories[1-14] during the last 10–15 years. Linear aliphatic segments are incorporated for the purpose of lowering transition temperatures and to improve the solubility and thereby increasing the overall polymer processability. In most cases, these materials are reported to exhibit mesomorphic behaviour due to the presence of a rigid aromatic group, which results in a long persistence length. A study on 4,4'-dihydroxybiphenyl and aliphatic dibasic acids containing 5–12 methylenes revealed an odd–even effect, the mesophase being nematic for odd-numbered spacers and smectic for even-numbered spacers[1]. This series is homologous to ours, the only difference being the presence of methyl substituents in the biphenyl unit of our samples.

The purpose of this study was to investigate how non-coplanar rigid units, in combination with linear aliphatic segments, affect the thermal and morphological properties of the polymers. We found that the non-coplanarity suppresses the formation of liquid crystalline properties and that the aliphatic segments dominate the thermal properties with their distinct odd–even effect due to the number of methylene groups in the flexible spacer. We also found that crystallization occurs at lower rates with increasing spacer length and at extremely low rates for polymers containing odd-numbered spacers.

Experimental

Materials. The 2,2'-dimethylbiphenyl-4,4'-diol was synthesized and purified according to a procedure previously described[15,16]. All aliphatic diacid chlorides were prepared from the dicarboxylic acids with thionyl chloride and carefully distilled twice prior to polycondensation. All other chemicals and solvents were used as received.

Polymer synthesis. The polymerization was performed via an interfacial polycondensation reaction in water (60 ml) and 1,2-dichloroethane (90 ml) using benzoyl triethyl ammonium chloride (0.4556 g) as a phase transfer catalyst. 2,2'-Dimethyl-4,4'-biphenyl hydroxide (10 mmol) in 0.5 N NaOH (40 ml) was added under slow stirring, followed by the addition of dicarboxylic chloride (10 mmol) in dry 1,2-dichloroethane (60 ml) under vigorous mixing. After reacting for 10 min the polymer was precipitated in methanol, collected by filtration and dissolved in tetrahydrofuran (THF). The solution was added to ice-cold petroleum ether whereby precipitation of the polymer occurred. The chemical structure (*Scheme 1*) was confirmed by ^{1}H n.m.r. and i.r.[15].



	1a	1b	1c	1d	1e	1f
n	3	4	5	6	7	8

Scheme 1 Chemical structures of aromatic-aliphatic polyesters **1a**–**1f** with non-coplanar 2,2'-dimethylbiphenylene units

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* Permanent address: Technology Center, Neste Oy, PO Box 310, FIN-06101 Porvoo, Finland. To whom correspondence should be addressed

† Permanent address: Fachbereich Physikalische Chemie-Polymere, Philipps University Marburg, Hans Meerwein Straße, W-3550 Marburg, Germany

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Table 1 Inherent viscosity, molecular weight and polydispersity of the aromatic-aliphatic polyesters **1a**–**1f**

Polymer	n	$\eta_{inh}{}^{a}$ ($dl\,g^{-1}$)	$M_w{}^{b}$ ($g\,mol^{-1}$)	D^{c}
1a	3	0.31	2400	2.0
1b	4	0.20	6200	2.1
1c	5	0.21	3500	2.1
1d	6	0.25	9600	2.1
1e	7	0.39	4300	2.2
1f	8	0.35	8600	2.1

[a] Inherent viscosity in chloroform at 25°C (concentration $0.5\,g\,dl^{-1}$)
[b] G.p.c. with THF as eluent at 25°C, calibration with polystyrene standards
[c] Polydispersity, $D = M_w/M_n$

Characterization. Inherent viscosities (η_{inh}) were measured in chloroform at 25°C ($0.5\,g\,dl^{-1}$) using an automatic Cannon–Ubbelohde type viscosimeter. Average molecular weights were determined by g.p.c. using a Waters GPC equipped with u.v. and refractive index detectors. Calibration was done using polystyrene standards and THF as eluent. Thermal stabilities of the polyesters were determined under a nitrogen atmosphere using a Mettler TGA 50 analyser with heating rates of $10°C\,min^{-1}$. D.s.c. was carried out under dry nitrogen atmosphere using a Mettler DSC 30. The heating and cooling rates were $20°C\,min^{-1}$. The transition temperatures, e.g. melting and crystallization temperatures, were determined from the peak maxima and minima, respectively, while the glass transition temperature (T_g) was determined from the inflection point. Visual observations of thermal transitions were made using an optical microscope (Nikon Microphot-FX) equipped with crossed polarizers and a Mettler FP 52 hot stage. Wide-angle X-ray scattering (WAXS) patterns of non-oriented samples were obtained using a Scintag XDS 2000 powder diffractometer in the reflection mode. The radiation used was Ni-filtered Cu Kα (45 kV, 30 mA). The patterns were collected at room temperature in 0.1° 2Θ steps and 3 s counting time between $2\Theta = 2°$ and 35°, respectively.

Results and discussion

Polymer synthesis. The polyesters **1a**–**1e** were synthesized by interfacial polycondensation of 2,2′-dimethylbiphenyl-4,4′-diol and aliphatic diacid chlorides. Weight-average molecular weights (M_w) were found to vary between 2400 and 9600. The polymers containing even-numbered spacers showed M_w values of 6200, 9600 and 8600 for $n=4$, 6 and 8, respectively, while the polymers containing odd-numbered spacers showed M_w values of 2400, 3500 and 4300 for $n=3$, 5 and 7, respectively. The polymerization conditions were identical for all polymers, indicating that the comonomers containing even-numbered spacers exhibited a higher rate of polymerization with 2,2′-dimethylbiphenyl-4,4′-diol than did the comonomers containing odd-numbered spacers. The polydispersity varied from 2.0 to 2.2. The inherent viscosity varied from 0.20 to 0.39 (*Table 1*). This is in contrast to g.p.c. data since, in general, higher average molecular weight, or the presence of a fraction of high molecular weight polymers, increases the viscosity. It is obvious, therefore, that the interactions between the polymer chains differ in an odd–even manner.

As previously reported[2], the thermal transitions are observed to be independent of the degree of polymerization for values of $M_n \geqslant 6000$–$10\,000$. The thermal transitions do not appear at drastically lower temperatures for oligomers than for polymers with $M_n \geqslant 10\,000$, the difference in melting points being $< 10°C$ and in the isotropization temperatures $< 17°C$. We assume that the variations in degree of polymerization play an insignificant role in the thermal observations of our study.

Thermal properties. The copolymers containing an even number of methylene units in the flexible spacer were obtained as white powders while those with an odd number of spacers were obtained as transparent and sticky materials. Presumably, the odd-number spacer length gives rise to a polymer whose T_g is below room temperature. The transition temperatures are found to be dependent on molecular weight.

The alternating sequence of comonomers results in a structurally regular polymer, in contrast to a statistical distribution, where rigid and flexible segments can be selectively incorporated in anisotropic and/or isotropic phases giving rise to polyflexibility. Polyflexibility has been considered as one cause for biphasic behaviour of liquid crystalline statistical copolymers[2]. The copolyesters of this study are alternating and biphasic behaviour is observed for the even-numbered spacer polymers. The biphasic behaviour can be detected from the double melting peaks in d.s.c. combined with hot stage microscopy. The d.s.c. pattern for polymer **1b**, $n=4$, shown in *Figure 1*, has an endotherm at 115°C and another at 142°C. Using hot stage microscopy showed that after 5–10 min at 115°C the birefringent sample became partially isotropic with birefringent domains. Cooling slightly below 115°C gave a completely birefringent and solid polymer. At the second endotherm at 142°C, the sample became isotropic.

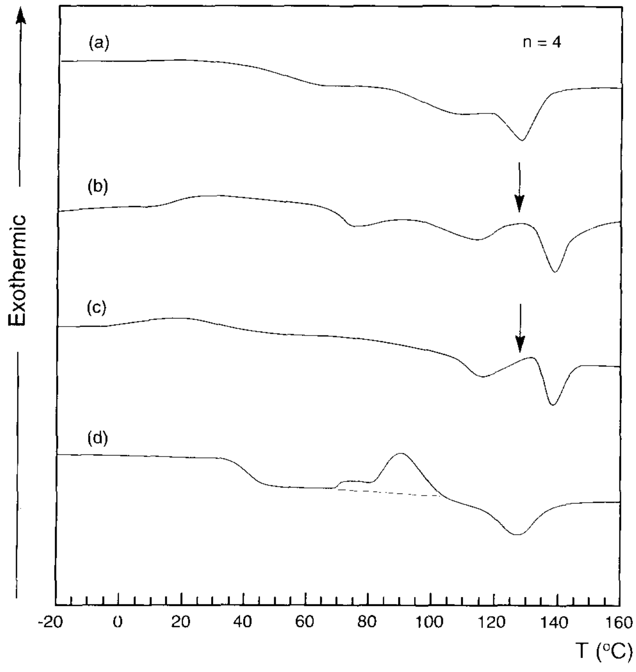

Figure 1 D.s.c. curves of polyester **1b**: (a) as synthesized; (b) annealed 6 h at 130°C; (c) annealed 20 h at 130°C; (d) quenched from 170 to −30°C. The arrows indicate annealing temperature

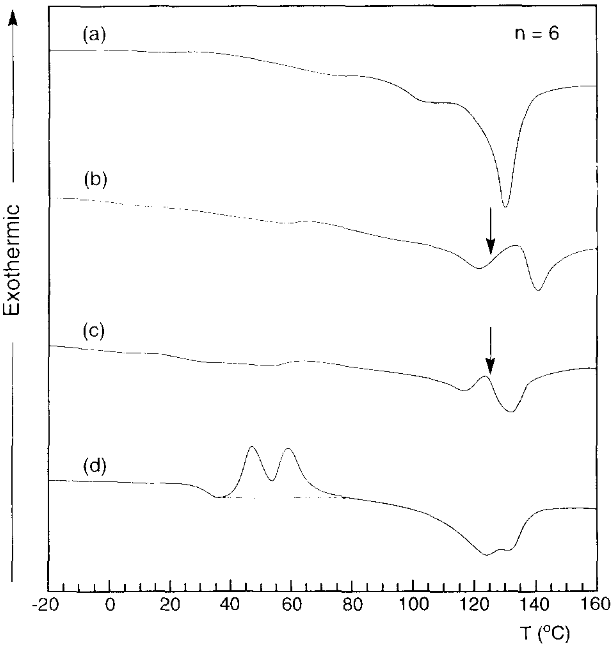

Figure 2 D.s.c. curves of polyester **1d**: (a) as synthesized; (b) annealed 6 h at 130°C; (c) annealed 20 h at 130°C; (d) quenched from 170 to −30°C. The arrows indicate annealing temperature

Table 2 Thermal transitions of the aromatic-aliphatic polyesters **1a**–**1f**, as observed by d.s.c. and hot stage microscopy

Polymer	n	T_g[a] (°C)	T_{m1}[b] (°C)	T_{m2} (°C)
1a	3	23	–	88[c]
1b	4	40	115	142[d]
1c	5	18	–	73[c]
1d	6	30	120	138[d]
1e	7	9	–	57[c]
1f	8	12	75	90[d]

[a] T_g is determined from the heating curve of the quenched polymer
[b] T_{m1} is the temperature of the lowest melting crystal structure, from d.s.c. data
[c] T_m is the temperature observed by hot stage microscopy and from the very weak d.s.c. endotherm, only observed after extensive annealing
[d] T_{m2} is the temperature of the highest melting crystal structure

The sample was annealed for 6 and 20 h at 130°C and subsequently quenched to −30°C in the differential scanning calorimeter. The heating curve showed cold crystallization prior to the endotherm at 115°C, indicating that the lower melting material does not cocrystallize with the higher melting phase during annealing above its melting point. Crystallization can be suppressed extensively when the sample has been quenched from the completely isotropic phase as observed from the subsequent heating curve that exhibits a strong T_g at 40°C. When the polymer is heated above its T_g cold crystallization was observed as a double exotherm, followed by a double melting endotherm. The cooling curve contained only one crystallization exotherm with a considerable degree of supercooling, 30°C at heating and cooling rates of 20°C min^{-1}. Molecular mobility is high in liquid crystalline phases and thus significant supercooling should not be observed. The thermal behaviour of this polymer, two cold crystallization exotherms followed by two melting peaks on heating, indicates the presence of two coexisting crystalline phases. Upon cooling one super-cooled crystallization peak is present, which in combination with the above-mentioned thermal and optical observations indicate that this polymer does not act as a liquid crystalline polymer[3].

The thermal properties of polymer **1d**, $n = 6$, are similar to **1b**, the melting endotherms being 120°C and 138°C, as shown in *Figure 2* and *Table 2*. Polymer **1f**, $n = 8$, exhibited two melting endotherms, 75°C and 90°C, and the T_g was observed at 12°C. Curve d in *Figure 3*, heating of a sample quenched from the isotropic phase, is different from those in *Figures 1* and *2* by the absence of cold crystallization and melting peaks, i.e. the crystallization was so slow that cold crystallization did not occur during heating at 20°C min^{-1}. The length of the eight methylenes exceeds the length of the mesogen when the molecular dimensions were estimated using bond lengths and angles from International Tables[17]. The four- and six-membered methylene spacers are shorter than the mesogen. It is obvious from the low transition temperatures of polymer **1f** that the alkylene comonomer dominated the thermal properties. There are no indications of liquid crystalline properties in polymers with four-, six- or eight-membered methylene spacers.

The polymers with an odd number of methylenes in the spacer exhibited uniform thermal properties, the glass transition being the only transition that was evident in the d.s.c. patterns (*Figure 4*). Samples that had been annealed at room temperature for extended periods appeared birefringent in the optical microscope. The temperature for the disappearance of birefringence upon heating was taken as the melting point. These melting points corresponded to extremely weak endotherms that could be observed by d.s.c. on the first heating of extensively annealed samples, at 88, 83 and 57°C for $n = 3$, 5 and 7, respectively. The T_gs were observed at 23, 18 and 9°C, which allowed annealing to occur at room temperature.

The odd–even effects in thermal transition temperatures, illustrated in *Figure 5*, are in good agreement with

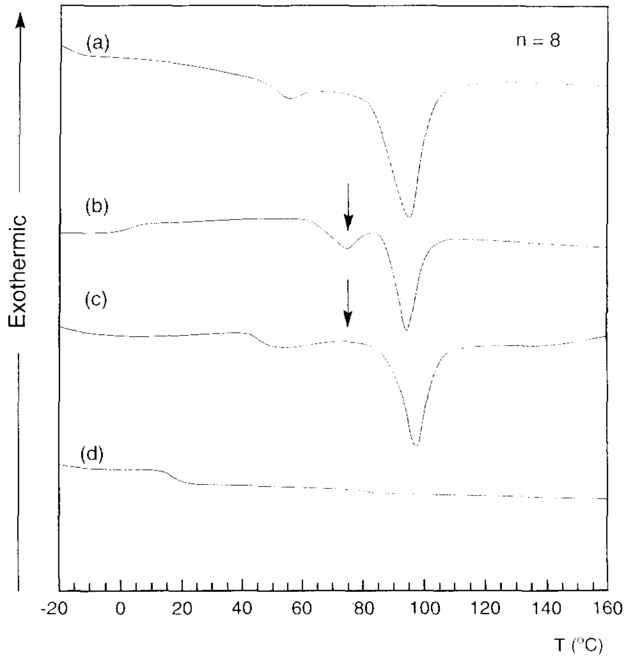

Figure 3 D.s.c. curves of polyester **1f**: (a) as synthesized; (b) annealed 6 h at 75°C; (c) annealed 20 h at 75°C; (d) quenched from 75 to −30°C. The arrows indicate annealing temperature

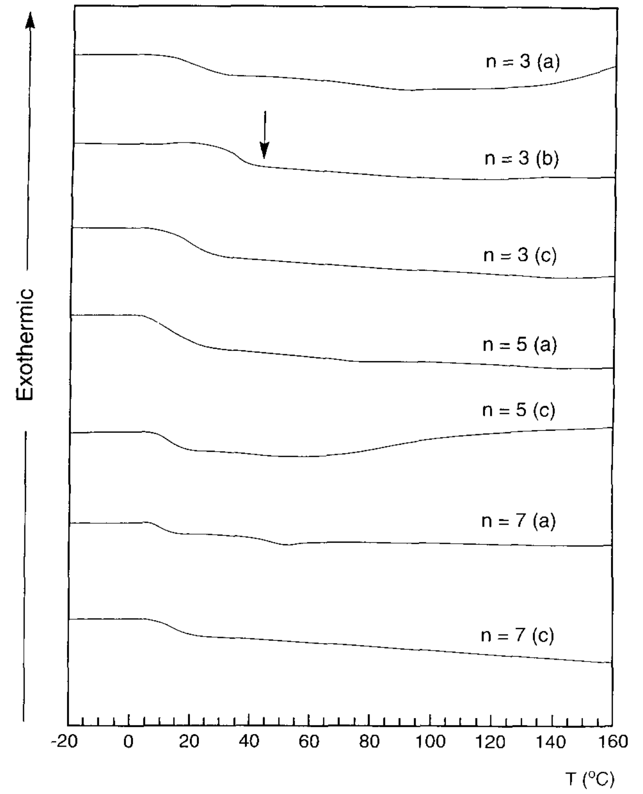

Figure 4 D.s.c. curves of polymers **1a**, **1c** and **1d** with spacer length 3, 5 and 7: (a) as synthesized; (b) annealed 20 h at 60°C; (c) quenched from 120 to −30°C. The arrow indicates annealing temperature

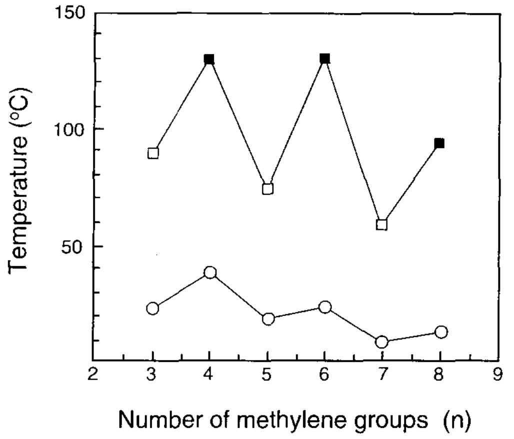

Figure 5 Transition temperature as a function of spacer length: (○) glass transition temperature at deflection point; (■) melting point of highest melting crystal phase, determined by d.s.c.; (□) melting points' observed by hot stage optical microscopy and by extremely weak endotherms observed by d.s.c.

previously reported data on semiflexible polymers with the flexible spacer in the main chain[4,5]. The conformation of odd- and even-membered spacers are reported to be different; the odd-membered spacers result in a more bulky conformation with the rigid units in a non-parallel position to each other, while the even-membered spacers give a zig-zag conformation where the rigid units are allowed to align parallel to each other, thus allowing closer packing and a higher degree of order[6].

Table 3 Peak positions and relative intensities from WAXS patterns obtained in reflection. The annealing of the samples was done at room temperature for **1a**, **1c** and **1e**, and at 130°C for **1b** and **1d**, and at 75°C for **1f**

Polymer	n	Observed d-spacings (Å) and their relative intensities[a]
1a	3	4.5 amorphous
1b	4	9.4(W) 5.7(W) 4.67(S) 3.19(W)
1c	5	4.5 amorphous
1d	6	11.8(W) 5.9(W) 4.86(S) 4.19(M) 3.66(W)
1e	7	4.5 amorphous
1f	8	13(W) 9.8(W) 5.6(M) 4.96(S) 4.73(M) 4.28(S) 3.67(W) 3.48(M)

[a] Peak intensity: S, strong; M, medium; W, weak

X-ray analysis. WAXS patterns obtained at room temperature of polymers with $n=4$, 6 and 8 show that polymers quenched from the isotropic phase were mostly amorphous for polymers **1b** and **1d**, while **1f**, $n=8$, was crystalline. This is in good agreement with the thermal data, since the T_gs of **1b** and **1d** were above room temperature and that of **1f** was below, thus allowing crystallization to occur in **1f** after quenching and prior to WAXS analysis at room temperature. The annealed samples showed a considerable degree of crystallinity. From WAXS patterns of powders it is impossible to draw any conclusions about the crystal structure of these polymers. The observed d-spacings are summarized in *Table 3*. From the comparison of the observed d-spacings with the estimated length of the extended repeating units[17], one can say that there are no reflections that coincide with the full length or half of the full length. The mechanical properties of the polymer films were poor due to low degree of polymerization. Due to poor mechanical coherence oriented samples could not be obtained for structural determination. The number of reflections, four to eight between 2° and 35° 2Θ, in the WAXS patterns for all the even-membered spacer polymers indicate a three-dimensionally ordered crystal structure. The WAXS patterns for **1a**, **1c** and **1e** show amorphous haloes with maximum intensity at 4.5 Å. This is the average distance between polymer chains. The WAXS data are in good agreement with the data obtained by microscopy and d.s.c. This study demonstrates that none of these polymers is liquid crystalline, although the d.s.c. patterns contain multiple endotherms on heating due to biphasic crystal behaviour. The lack of mesomorphic behaviour is due to the combination of non-coplanarity of the rigid unit and the aliphatic spacers. The odd–even behaviour in thermal properties and structure are pronounced to such an extent that long-range order in the polymers with odd-numbered aliphatic spacers is suppressed. It is obvious that the combination of non-coplanar rigid units and flexible spacers, of smaller cross-sectional area, are suppressing mesomorphic properties.

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