Effect of Polymerization Conditions on the Microstructure of a Liquid Crystalline Copolyester

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ABSTRACT: The melt polycondensation of mixtures of sebacic acid (S), 4,4′-diacetoxybiphenyl (B), and 4-acetoxybenzoic acid (H), carried out for the synthesis of semiflexible liquid–crystalline copolyesters referred to as SBH 1 : 1 : x, has been studied with the aim of clarifying the effect of the reaction conditions on the microstructure and the thermal properties of the products. It has been shown that the segregation of a liquid–crystalline phase within the polymerizing mixture, coupled with the thermodynamic tendency of the two phases to undergo compositional differentiation as polymerization proceeds, is responsible for the formation of blocky, rather than ideally random, copolyesters with poor processibility, when the mole ratio of H to the other two monomers is higher than $x \approx 1.90$. The results of this study have shown that this unwanted effect can be considerably limited by carrying out the polycondensation at a relatively high temperature from the very beginning, rather than by the standard technique involving progressive heating of the reaction mixture, thus allowing the production of SBH copolyesters with a higher degree of aromaticity. The results are discussed in terms of the relative rates of the condensation reactions, which are responsible for chain growth, and of the concurrent acidolysis and esterolysis reactions leading to copolyester sequence reorganization. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 141–150, 2000

Key words: liquid crystalline copolyesters; microstructure; transesterification; liquid crystallization induced reactions

INTRODUCTION

The preparation of a new family of semiflexible liquid–crystalline polymers (LCPs) by the melt copolycondensation of varying concentrations of 4-acetoxybenzoic acid (H) with equimolar amounts of 4,4′-diacetoxybiphenyl (B) and an aliphatic diacid with 3–10 methylene groups was disclosed in a patent issued some years ago to Eniricerche S.p.A. (now Enitecnologie S.p.A.).[1] As expected, the presence of main-chain flexible spacers, provided by the aliphatic diacid units, led to products with mechanical properties lower than those of most commercially available wholly aromatic LCPs.[2,3] On the other hand, the new copolyesters had melting points that could be varied in a fairly wide range by changing the molar concentration of the H units and the length of the methylene sequences of the diacid moieties and could therefore be used under a variety of process-

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ing conditions, including their *in situ* addition, as reinforcing agents, into commercial low-melting thermoplastics, such as polypropylene and polyethylene. Moreover, the flexibility of the macromolecules of these copolyesters, coupled with their axial symmetry, allowed the formation of fairly regular pseudo-hexagonal arrays of parallel aligned chains in the solid state. Upon appropriate processing conditions involving extensional flow, such as melt spinning, it was thus possible to produce oriented samples showing good crystallinity and appreciable mechanical properties up to the melting point.[4,5]

Among the many different compositions of the above semiflexible copolyesters, those carrying sebacic acid (S) as the diacid moiety were found to provide the best match of processability and physical and mechanical properties, and these were studied in more detail. It was found that, for these SBH copolyesters, the most appropriate compositions were in the range of molar ratio 1 : 1 : x of the S, B, and H monomers close to 1 : 1 : 2. In fact, using an H content of $x < 2$ resulted in a decrease of the degree of aromaticity, that is, the percent content of aromatic carbons over the total number of main chain atoms,[6] and of the thermal and mechanical characteristics. On the contrary, an attempt at improving the latter properties by increasing the H molar content above 2 led to the segregation of a crystalline phase rich in homopolymer H sequences, and this brought a deterioration of polymer processability and impact properties.[1–5] This result was rather surprising. In fact, according to simple model calculations[7] (cf. Appendix), an ideally random SBH copolyester with a 1 : 1 : x monomer units ratio should contain homopolymer H sequences with an average length, expressed as the number of consecutive H units, given by

$$L_H = (2 + x)/2$$

Thus, the homopolymer segments of a copolyester with, for example, the 1 : 1 : 3 composition, should comprise on average only 2.5 H units and should therefore be unable to cause the segregation of a crystalline phase. Notice that no segregation of oxybenzoate crystallites was ever observed for the copolyester of H and 2-hydroxy-6-naphthoic acid in the mol ratio 73 : 27 (Vectra-A® by Hoechst-Celanese, USA), though for this random copolyester the calculated average length of the H sequences is 3.7. The discrepancy between experimental results and theoretical expectation was interpreted as the result of a thermodynamic tendency of the polymerizing system to lead to the formation of H sequences longer than calculated for an ideally random copolyester.

In this work we studied the influence of polymerization conditions on the microstructure and the properties of SBH copolyesters with different compositions. The aim of the study was, on one side, a deeper understanding of the mechanism leading to the production of blocky copolymer sequences during the melt polycondensation of the S, B, and H monomer mixtures and, on the other, the determination of the optimum reaction conditions for the preparation of satisfactorily homogeneous SBH copolymers with the highest possible H units content.

EXPERIMENTAL

Sebacic acid, 4-hydroxybenzoic acid, and 4,4′-dihydroxybiphenyl were obtained from Aldrich (Milano, Italy). Reagent-grade sebacic acid was used for the copolyesterifications without further purification. 4-Acetoxybenzoic acid and 4,4′-diacetoxybiphenyl were prepared by refluxing the commercial hydroxyl compounds with an excess of acetic anhydride for 12 h. The pure products were obtained by precipitation in water and repeated crystallization from 95% ethanol. The melting points of 4-acetoxybenzoic acid and 4,4′-diacetoxybiphenyl were 196°C and 167°C, respectively.

The copolyesters were prepared by the melt polycondensation procedure described previously.[1–3] The appropriate mixture of the solid monomers was proportioned to obtain about 20 g of product, with a catalytic amount (about 0.01 g) of sodium acetate charged into a ~ 200 mL cylindrical, round-bottomed Pyrex reactor equipped with a stainless-steel anchor stirrer (40 rpm) and connected to a high vacuum line. After accurate purging with pure nitrogen, a salt bath preheated to the appropriate temperature was brought up around the flask, thus causing the rapid fusion of the monomers to a colorless isotropic liquid. Acetic acid was collected in a side trap cooled with liquid nitrogen, and the reaction was continued under stirring, while the temperature of the bath was controlled in order to follow the appropriate temperature profile. The polycondensation was completed by progressively reducing the pressure down to about 0.1 mm Hg. After nitrogen admission, the flask was opened under nitrogen flush, and the highly viscous product was extracted from the reactor with a stainless-steel spoon while hot and was then cooled and ground. The polymer powder was finally extracted with boiling acetone to remove the traces of low molar mass materials.

The ^{13}C-NMR spectra were recorded on a Brucker AMX 300 spectrometer in pentafluorophenol solution, at 45°C, without lock. Eight thousand transients were accumulated under proton irradiation, using an acquisition time of 2 s and a relaxation delay of 10 s.

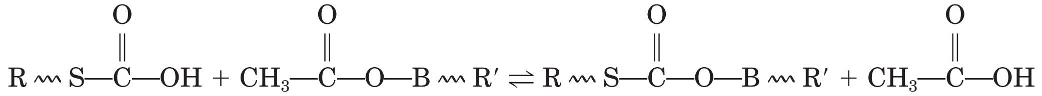
The powder X-ray diffraction spectra of the copolyesters were obtained on a D500 Siemens diffractometer, using the Ni-filtered CuKα radiation.

The thermal properties of the monomers and the polymers were determined by differential scanning calorimetry (DSC) with a Perkin Elmer DSC-7 apparatus, with heating/cooling rates of 20°C/min.

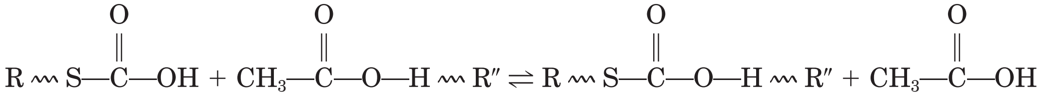
RESULTS AND DISCUSSION

Chemistry

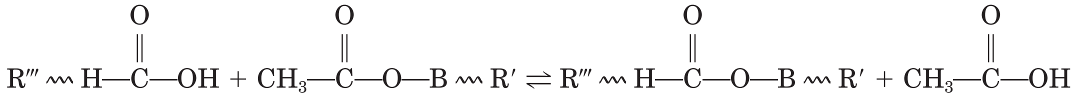
Most high-temperature melt polycondensation processes leading to liquid–crystalline copolyesters involve acidolysis reactions. Alcoholysis reactions cannot occur because the hydroxyl groups of the monomers are generally acetylated, while ester-exchange reactions can normally be neglected (except perhaps at the end of the polymerization) because they are characterized by considerably lower rate constants.[8] In particular, for the investigated system, based on mixtures of sebacic acid (S), 4,4′-diacetoxybiphenyl (B), and 4-acetoxybenzoic acid (H) as the raw materials, the ester bonds that are present in the reaction medium during the early stages of the process are mainly represented by the acetoxy end groups and, therefore, the acidolysis reactions to be considered are those indicated schematically by eqs. (1)–(4), where *R* through *R‴* may be either the functional groups of the S, B, and H monomers or short chain segments.



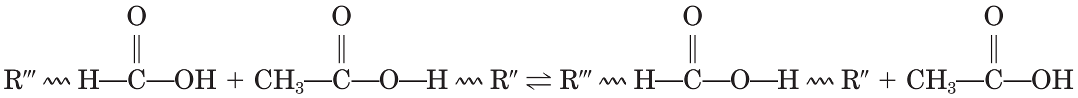
$$R \sim\!\sim S-\overset{O}{\overset{\|}{C}}-OH + CH_3-\overset{O}{\overset{\|}{C}}-O-B \sim\!\sim R' \rightleftharpoons R \sim\!\sim S-\overset{O}{\overset{\|}{C}}-O-B \sim\!\sim R' + CH_3-\overset{O}{\overset{\|}{C}}-OH \qquad (1)$$



$$R \sim\!\sim S-\overset{O}{\overset{\|}{C}}-OH + CH_3-\overset{O}{\overset{\|}{C}}-O-H \sim\!\sim R'' \rightleftharpoons R \sim\!\sim S-\overset{O}{\overset{\|}{C}}-O-H \sim\!\sim R'' + CH_3-\overset{O}{\overset{\|}{C}}-OH \qquad (2)$$



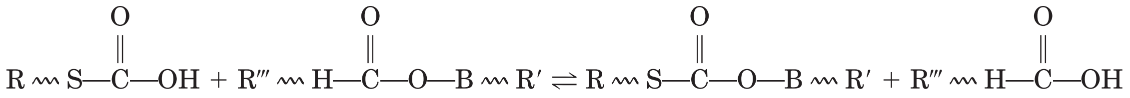
$$R''' \sim\!\sim H-\overset{O}{\overset{\|}{C}}-OH + CH_3-\overset{O}{\overset{\|}{C}}-O-B \sim\!\sim R' \rightleftharpoons R''' \sim\!\sim H-\overset{O}{\overset{\|}{C}}-O-B \sim\!\sim R' + CH_3-\overset{O}{\overset{\|}{C}}-OH \qquad (3)$$



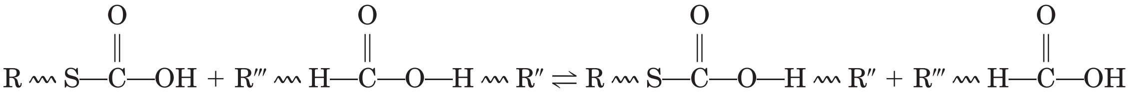
$$R''' \sim\!\sim H-\overset{O}{\overset{\|}{C}}-OH + CH_3-\overset{O}{\overset{\|}{C}}-O-H \sim\!\sim R'' \rightleftharpoons R''' \sim\!\sim H-\overset{O}{\overset{\|}{C}}-O-H \sim\!\sim R'' + CH_3-\overset{O}{\overset{\|}{C}}-OH \qquad (4)$$

These acidolysis reactions are practically irreversible and bring about a progressive increase of the average molar mass of the mixture's components because, under the melt polycondensation conditions, by-product acetic acid is rapidly distilled off. The formation of longer homopolymer sequences of H units, with respect to those expected for an ideally random copolyester, may occur during this stage of the process if the rate constant of reaction (4) is appreciably higher than those of the other reactions. It seems unlikely, however, that this mechanism may cause substantial departure from randomness.

As condensation proceeds, the concentration of the acetoxy end groups decreases, whereas that of the inner ester bonds concurrently grows. Thus, acidolysis reactions involving the latter's bonds become more and more likely. These reactions [eqs. (5) and (6)] are true equilibrium reactions in that the products have relatively high molar mass and cannot escape the mixture. The free carboxyl groups of the S and H end moieties make the reactions run in, respectively, the left to right and the right to left directions.



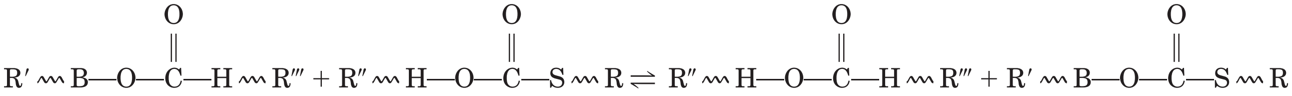
$$\mathrm{R}\sim\mathrm{S}{-}\overset{\displaystyle\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\mathrm{OH} + \mathrm{R'''}\sim\mathrm{H}{-}\overset{\displaystyle\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\mathrm{O}{-}\mathrm{B}\sim\mathrm{R'} \rightleftharpoons \mathrm{R}\sim\mathrm{S}{-}\overset{\displaystyle\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\mathrm{O}{-}\mathrm{B}\sim\mathrm{R'} + \mathrm{R'''}\sim\mathrm{H}{-}\overset{\displaystyle\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\mathrm{OH} \qquad (5)$$



$$\mathrm{R}\sim\mathrm{S}{-}\overset{\displaystyle\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\mathrm{OH} + \mathrm{R'''}\sim\mathrm{H}{-}\overset{\displaystyle\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\mathrm{O}{-}\mathrm{H}\sim\mathrm{R''} \rightleftharpoons \mathrm{R}\sim\mathrm{S}{-}\overset{\displaystyle\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\mathrm{O}{-}\mathrm{H}\sim\mathrm{R''} + \mathrm{R'''}\sim\mathrm{H}{-}\overset{\displaystyle\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\mathrm{OH} \qquad (6)$$

Contrary to reactions (1)–(4), the acidolysis reactions (5) and (6) do not change the average molar mass of the mixture. However, their important effect is a continuous change of the sequence distribution of the monomer units within the chains. If the system consists of a single phase in the thermodynamic sense, this sequence reorganization leads toward complete randomization. In fact, enthalpy changes are modest, and the process evolves in the direction of increasing entropy, leading to a copolyester with the most probable molar mass distribution, almost random sequence distribution, and compositional homogeneity. When this situation prevails, even if long H sequences had formed through reaction (4) during the early stage of the process, these would subsequently be shortened to the equilibrium value by, for example, reaction (6).

During the last stage of the polymerization process, when the molar mass of the polymer is high and the concentration of free carboxyl groups is very small, acidolysis reactions (1)–(6) become sluggish and make molar mass buildup and sequence reorganization proceed extremely slowly. Under these conditions, esterolysis reactions, such as that depicted by eq. (7), may become kinetically competitive.



$$\mathrm{R'}\sim\mathrm{B}{-}\mathrm{O}{-}\overset{\displaystyle\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\mathrm{H}\sim\mathrm{R'''} + \mathrm{R''}\sim\mathrm{H}{-}\mathrm{O}{-}\overset{\displaystyle\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\mathrm{S}\sim\mathrm{R} \rightleftharpoons \mathrm{R''}\sim\mathrm{H}{-}\mathrm{O}{-}\overset{\displaystyle\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\mathrm{H}\sim\mathrm{R'''} + \mathrm{R'}\sim\mathrm{B}{-}\mathrm{O}{-}\overset{\displaystyle\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\mathrm{S}\sim\mathrm{R} \qquad (7)$$

From a practical point of view, esterolysis reactions have the same effect of the acidolysis reactions (5) and (6), that is, an endless change of the copolymer sequence distribution that makes the microstructure of the copolyester approach that corresponding to thermodynamic equilibrium.

Reactions of the types (5)–(7) are also responsible for the sequence randomization taking place between dissimilar condensation polymers under reactive blending conditions.[9–13] Since dissimilar polymers are normally immiscible, the system is actually biphasic, at least at the early stages of blending, and the reactions can only take place in the interphase. However, as interchange reactions proceed, the two phases become more and more compatible until complete miscibility occurs.

From the above analysis it may be concluded that, although the rate of the condensation reactions decreases continuously with the increase of the polymer molar mass, that of the sequence reorganization reactions goes through a maximum, corresponding to an intermediate molar mass. At the end of the polymerization process, as well as in reactive blending processes, these reactions are relatively slow because of the small concentration of end groups, on the one side, and of the small rate constant of esterolysis, on the other.

Copolyesters Synthesis and Characterization

The above considerations suggest that the results of previous studies,[1–3] indicating that a blocky microstructure of the SBH copolyesters is obtained whenever the mole fraction of H in the monomer mixture exceeds about 50%, can only be explained on the basis of two equally important assumptions: (1) that as polymerization proceeds, the reaction mixture becomes biphasic and (2) that there is a thermodynamic tendency toward compositional differentiation of the two phases, rather than homogenization. This conclusion agrees with previous results found by some of

Table I Preparation Conditions and Characteristics of the Investigated Copolyesters

	Preparation Conditions			Molar Composition (S : B : H)		H Sequences Length (L_H)		
Sample	T. Profile (°C)	Raw Materials	Time (h)	Calculated	Found	Calculated	Found	Ratio ($L_{H\text{found}}$/$L_{H\text{calc.}}$)
SBH-1	220→280	S, B, H	5 + 1	1 : 1 : 2	1 : 1 : 1.40	1.70	2.07	1.22
SBH-2	240→280	S, B, H	5 + 1	1 : 1 : 2	1 : 1 : 1.58	1.79	1.91	1.07
SBH-3	270→280	S, B, H	5 + 1	1 : 1 : 2	1 : 1 : 1.75	1.87	1.89	1.01
SBH-4	290	PB8, S, B, H	1.5	1 : 1 : 2	1 : 1 : 1.85	1.92	2.41	1.26
SBH-5	220→280	S, B, H	5 + 1	1 : 1 : 3	1 : 1 : 2.42	2.21	2.54	1.15
SBH-6	270→280	S, B, H	5 + 1	1 : 1 : 3	1 : 1 : 2.50	2.25	2.30	1.02

us,[14–16] showing that the transesterification of PET with the same mixture of monomers employed in this work fails to produce a random copolyester, as would be expected in a homogeneous reaction medium, and leads to distinctly biphasic materials just because the segregation of a fairly ordered liquid–crystalline phase provides an enthalpy gain that pushes the process in the ordering direction.

In order to prove whether the same mechanism can be invoked to rationalize the behavior of the polycondensation considered in this work, a number of experiments have been carried out in which some of the reaction conditions were varied so as to influence the microstructure of the copolyesters. In particular, it was argued that changing the temperature profile of the polycondensation, as well as the type of the raw materials, could alter the relative rates of condensation and sequence reorganization reactions, thus allowing the identification of the conditions favoring the formation of quasi-random copolyesters. The conditions of some representative preparations are schematically indicated in Table I.

Preparation and Properties of SBH 1 : 1 : 2 Copolyesters

The sample indicated as SBH-1 was prepared following the conventional procedure,[1–3] that is, adding a mixture of the three monomers in the 1 : 1 : 2 mole ratio into the reactor, before dipping it into the salt bath and using a thermal profile consisting of an isothermal step (about 3.5 h at 220°C), during which the polycondensation takes place gradually to give a viscous, opaque mass, followed by a gradual (about 30 min) heating up to 280°C, by the application of vacuum, and by a final isothermal step of about 1 h. Copolyesters SBH-2 and SBH-3 were synthesized with a similar procedure but with a higher temperature (240 and 270°C, respectively) in the initial isothermal step. SBH-4 was prepared by the isothermal ($T = 290°C$) reaction of poly(4,4′-biphenylylene sebacate) (PB8), with a mixture of S, B, and H in the 1 : 1 : 4 mole ratio. The amounts of PB8 and of the monomer mixture were calculated to give an overall composition corresponding to SBH 1 : 1 : 2. PB8 was synthesized from equimolar amounts of S and B as described by Krigbaum and coworkers.[17]

The downfield region of the ^{13}C-NMR spectra of the SBH-1 and SBH-3 samples is shown in Figure 1 as an example, and the assignment of the peaks to the four types of carbonyl carbons corresponding to the S—B, S—H, H—B, and H—H diads is indicated in Table II. From the relative intensities of the four peaks, the actual composition of the copolyester could be obtained, as well as the average length of the H sequences, both for the ideally random copolymer and for the real product, as indicated in the appendix. The results of the calculations are collected in Table I.

It can be clearly observed that the actual content of H units of the copolyesters is systematically lower than that of the monomer feed. This result was tentatively explained[3] through the presence of short blocks of H units that fail to dissolve in pentafluorophenol and are not detected by the NMR analysis. Another possible origin of the discrepancy between product and feed composition lies in the stronger tendency of 4-acetoxybenzoic acid, in comparison to the other monomers, to escape the reaction mixture by sublimation. In fact, the effect was particularly evident in the present study because of the small amount (about 20 g) of polymer produced in each

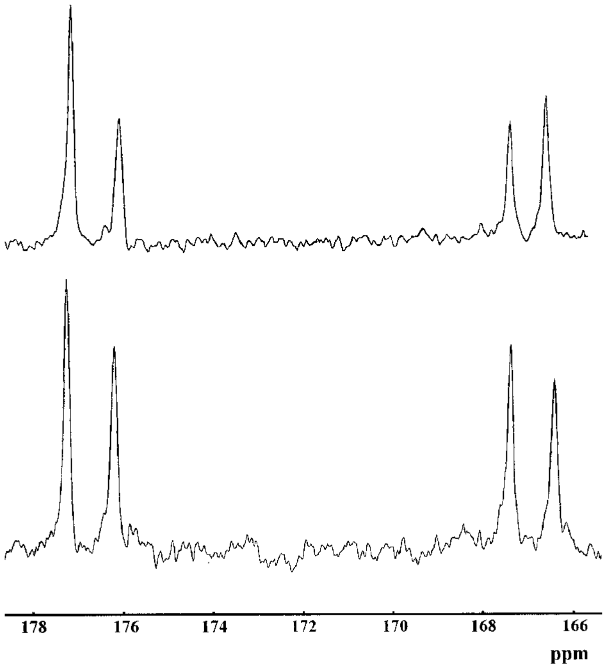


Figure 1 Downfield region of the ^{13}C-NMR spectra of pentafluorophenol solutions of: (a) SBH-1 and (b) SBH-3.

experiment, while it was shown[18] that the discrepancy becomes extremely small for scaled-up preparations. It is very interesting, however, that contrary to expectation, the loss of H by sublimation is lowered when higher reaction temperatures are employed from the very beginning of the polymerization: this means the rate of the condensation reactions [cf. eqs. (1)–(4)] increases more with an increase of temperature than does the rate of sublimation of H. As a matter of fact, a larger amount of sublimate was visually observed on the inner wall of the reactor cover at the end of the SBH-1 preparation.

As for the dependence of copolyester microstructure on the temperature profile used for the synthesis, it can be observed that SBH-1, with the lowest actual content of H units, displays the highest average length of H sequences (L_H = 2.07). Moreover, the relevant figure found for SBH-3 (L_H = 1.89) is very close to that calculated for a statistical copolyester (1.87). The degree of blockiness, qualitatively indicated as the ratio of the experimental value of L_H to that corresponding to ideal randomness (last column in Table I), decreases markedly along the series SBH-1, SBH-2, and SBH-3, thus showing that sequence reorganization is considerably hindered when the temperature of the first polymerization step is increased. This conclusion is in agreement with the observation by Erdemir and coworkers[19] that the best procedure for preparing HIQ copolyesters—by the melt polycondensation of H, isophthalic acid (I), and 1,4-diacetoxybenzene (Q)—involves the use of higher initial temperatures because the segregation of a high-melting solid phase within the reaction mixture can thereby be hindered.

The composition and the microstructure of the SBH sample (SBH-4) synthesized by transesterification of PB8 with a monomer mixture rich in H, shown in Table I, are in agreement with the above conclusions. In fact, the concentration of H units is relatively high ($x = 1.85$), as expected for a polymerization carried out isothermally at a high temperature (290°C); on the other hand, the degree of blockiness is also high ($L_H = 2.41$) because polycondensation of the 1 : 1 : 4 monomer mixture takes place concurrently with PB8 acidolysis, and the resulting polymer is probably characterized by a bimodal composition distribution, comprising PB8 blocks and sequences of a SBH 1 : 1 : 4 copolyester. Notice that the average length of *H* sequences calculated for a random SBH 1 : 1 : 4 polymer is $L_H = 3$.

The powder X-ray diffraction patterns of SBH-1, SBH-2, and SBH-3 are shown in Figure 2. The samples had been annealed for 15 h at 170°C in a nitrogen atmosphere, prior to X-ray analysis, in order to avoid the effect of possible differences in thermal history. The strong, sharp reflection at $2\theta \approx 20.6°$ is ascribed to the pseudo-hexagonal structure arising from the parallel alignment of longitudinally disordered macromolecules with cylindrical symmetry. In addition to the main peak, the X-ray diagram of SBH-1 shows two weak reflections, at $2\theta \approx 16°$ and $2\theta \approx 24°$, which approximately correspond to two strong reflections of the H homopolymer.[20,21] No such reflections are visible in the spectrum of SBH-3. Therefore, in agreement with the indications of the NMR analysis, it can be concluded that, despite

Table II Assignment of ^{13}C-NMR Carbonyl Resonance Peaks of SBH Copolyesters

Diad	Chemical Shift from TMS (ppm)
S—B	177.10
S—H	176.07
H—B	167.20
H—H	166.38

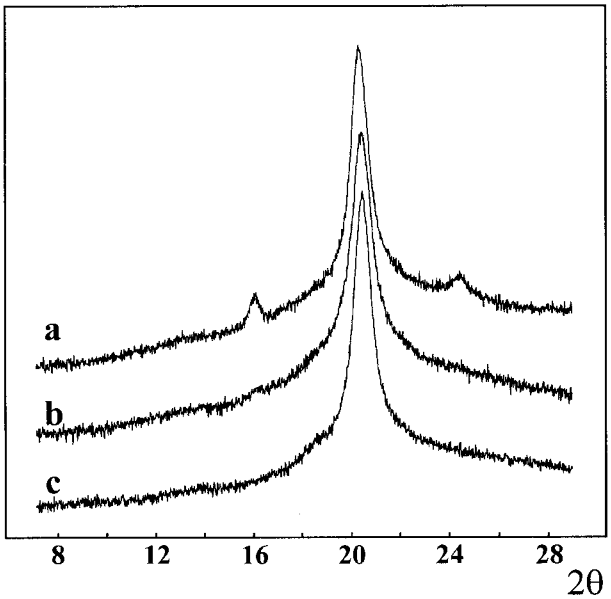


Figure 2 Powder X-ray diffraction patterns of: (a) SBH-1; (b) SBH-2; (c) SBH-3.

the lower content of H units, the microstructure of the SBH sample synthesized with the lower temperature profile (SBH-1) is appreciably far from that of a random copolyester having the most probable sequence distribution. On the contrary, both the NMR and the X-ray characterizations demonstrate that high-temperature synthesis leads to quasi-random materials, such as SBH-3.

The thermal behavior of SBH-1 and SBH-3 is illustrated by the DSC traces shown in Figure 3, and the calorimetric data of all the investigated copolyesters are reported in Table III. The DSC traces show very broad, asymmetric transition peaks. This confirms that the copolyesters are characterized by broad composition distribution. It is interesting that, with respect to SBH-3, SBH-1 shows slightly higher melting and crystallization temperatures. Previous results had shown that the melting point of SBH copolyesters synthesized with a standard procedure increases with the concentration of H.[3] The present data must therefore be interpreted as the result of differences in the microstructure of the two copolyesters, in agreement with the results of the NMR and X-ray characterizations.

Preparation and Properties of SBH 1 : 1 : 3 Copolyesters

The results described in the previous paragraph, showing that a polymerization procedure with the initial step carried out at high temperature (about 270°C) is capable of producing a quasi-random copolyester when applied to a 1 : 1 : 2 monomer mixture, prompted us to test the possibility of using the same technique to produce an SBH copolyester with a higher content of H units. Two polymerization experiments were therefore carried out using a mixture with the 1 : 1 : 3 mole ratio of the three monomers S, B and H: the standard procedure already used for the synthesis of SBH-1 was employed for the first prepara-

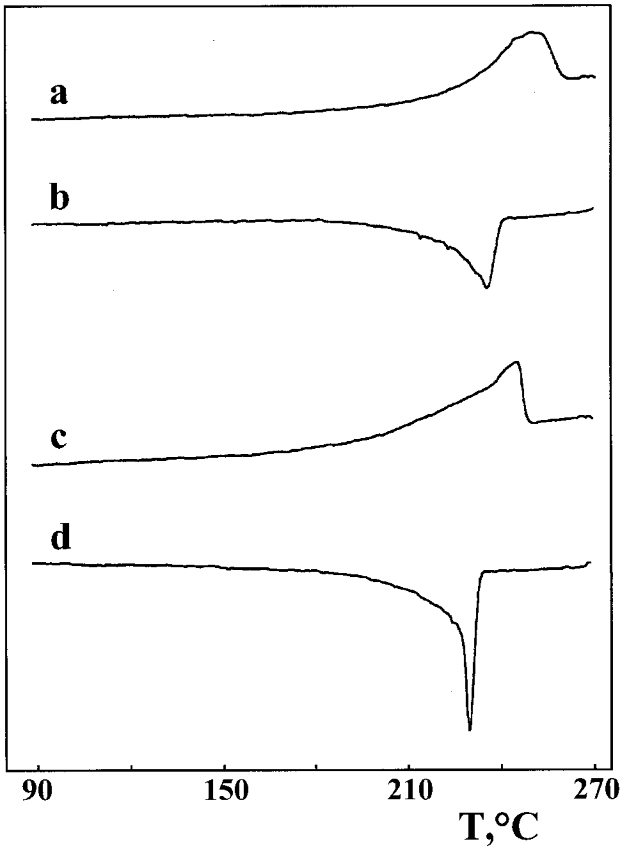


Figure 3 DSC traces of: (a) and (b) SBH-1; (c) and (d) SBH-3. (a) and (c) heating traces; (b) and (d) cooling traces; scanning rate 20°C/min.

Table III Calorimetric Data of SBH Copolyesters

Sample Code	T_c (°C)	ΔH_c (cal/g)	T_m (°C)	ΔH_m (cal/g)
SBH-1	234.7	1.99	248.4	2.01
SBH-2	230.2	2.05	245.8	2.07
SBH-3	229.7	2.11	243.9	2.18

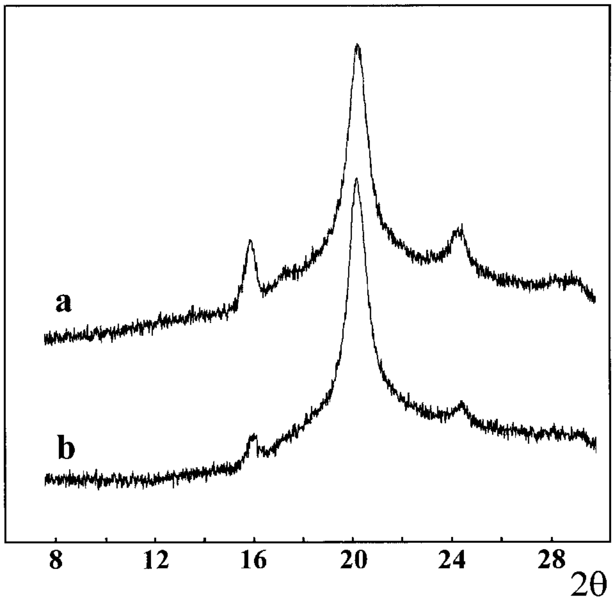


Figure 4 Powder X-ray diffraction patterns of: (a) SBH-5 and (b) SBH-6.

tion, while the second sample was prepared with the same procedure employed for SBH-3. The products SBH-5 and SBH-6 were characterized as described in the previous paragraph for the SBH 1 : 1 : 2 copolyesters.

As it is clear from the data in Table I, the average length of the H sequences of the last two copolyesters is obviously higher than that found for the 1 : 1 : 2 copolyesters synthesized with the corresponding procedure. Their actual number of H units is also appreciably lower than that of the feed. As far as the effect of the reaction conditions on the copolyesters microstructure is concerned, the ^{13}C-NMR characterization fully confirms the results discussed in the previous paragraph. In fact, although the sample prepared with the standard procedure (SBH-5) displays appreciable blockiness, that synthesized with the higher temperature profile (SBH-6) shows quasi-random microstructure. Further confirmation is provided by the X-ray diffraction patterns of SBH-5 and SBH-6, shown in Figure 4. The spectrum of SBH-6, with an actual content of H units $x = 2.50$ is very similar to that of SBH-1 (actual content of H units = 1.4, cf. Fig. 2) and of other 1 : 1 : 2 SBH samples (with the actual content of H moieties in the 1.50–1.90 range) synthesized previously with the standard procedure.[1–5]

CONCLUSION

A comparison of the behavior of semiflexible copolyesters, such as those (SBH $1 : 1 : x$) studied in this work, with that of wholly aromatic ones, such as Vectra-A®, shows that for the former the segregation of a liquid crystalline phase of higher aromaticity takes place during the polycondensation process, and compositional differentiation of the two resulting phases appears to be favored thermodynamically. Moreover, the SBH copolyesters give rise to the segregation of a crystalline phase already rich in H units for an actual average length of homopolymer H sequences equal to about 2.30 (cf. the case of SBH-6), while no such crystallization is found for Vectra-A®, with $L_H \approx 3.70$. These differences are evidently due to the presence of the long aliphatic units of sebacic acid, which makes the preparation of compositionally and morphologically homogeneous copolyesters more difficult.

In spite of this, the results of the present study demonstrate clearly that the use of a quasi-isothermal, high-temperature polycondensation procedure allows the synthesis of nearly random SBH copolyesters and strongly reduces the difference between actual and expected average length of the H homopolymer sequences that is commonly observed for samples prepared with the standard procedure involving gradual heating of the polymerizing mixture. As a consequence, it is now possible to increase the actual mole ratio of the H units of the $1 : 1 : x$ SBH copolyesters from $x = 1.50$–1.90 to $x = 2.3$–2.7, thereby improving their degree of aromaticity and, as expected, their mechanical characteristics without causing appreciable segregation of an H-rich crystalline phase that would impair processability and affect properties. The rheological behavior, the spinnability, and the mechanical properties of copolyester samples synthesized as described for SBH-6 are presently under investigation in our laboratories.

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APPENDIX

In a copolyester consisting of S (derived from sebacic acid), B (derived from biphenol), and H (derived from hydroxybenzoic acid) units, in the mole ratio 1 : 1 : x, the percent concentrations of the three monomer units is given by:

Unit	Formula	Mol (%)
S	$\text{—CO—(CH}_2)_8\text{—CO—}$	$100/(2+x)$
B	—O—Ph—Ph—O—	$100/(2+x)$
H	—O—Ph—CO—	$100x/(2+x)$

The percent concentrations, X_1, X_2, Y_1, and Y_2, of the different ester bonds that can be measured experimentally from the intensities of the ^{13}C-NMR absorption peaks corresponding to the four carbonyl carbons can be expressed as functions of x and X_1:

S—B X_1

S—H $X_2 = 200/(2 + x) - X_1$

H—B $Y_1 = X_2 = 200/(2 + x) - X_1$

H—H $Y_2 = X_1 - 100(2 - x)/(2 + x)$

As X_2 and Y_2 cannot be negative, it must be:

$$100(2 - x)/(2 + x) \le X_1 \le 200/(2 + x) \qquad \text{(I)}$$

in addition to:

$$0 \le X_1 \le 100 \qquad \text{(II)}$$

The copolyester sequence distribution is intermediate between the two extreme situations corresponding to the maximum and the minimum value of X_1: when $X_1 = 200/(2 + x)$, we have $X_2 = Y_1 = 0$, and the copolyester is actually a physical blend of the two homopolymers $[\text{SB}]_n$ and $[\text{H}]_n$; when $X_1 = 0$ or $X_1 = 100(2 - x)/(2 + x)$, X_1 or Y_2, or both, are equal to zero, and the copolyester microstructure corresponds to maximum alternation.

In the general case, let us call L_{SB} and L_H the average lengths (number of monomer units) of the homopolymer blocks [SB] and [H], respectively. They can be written as functions of x and X_1 as follows:

$$L_{SB} = 200/[200 - (2 + x)X_1] \qquad \text{(III)}$$

and

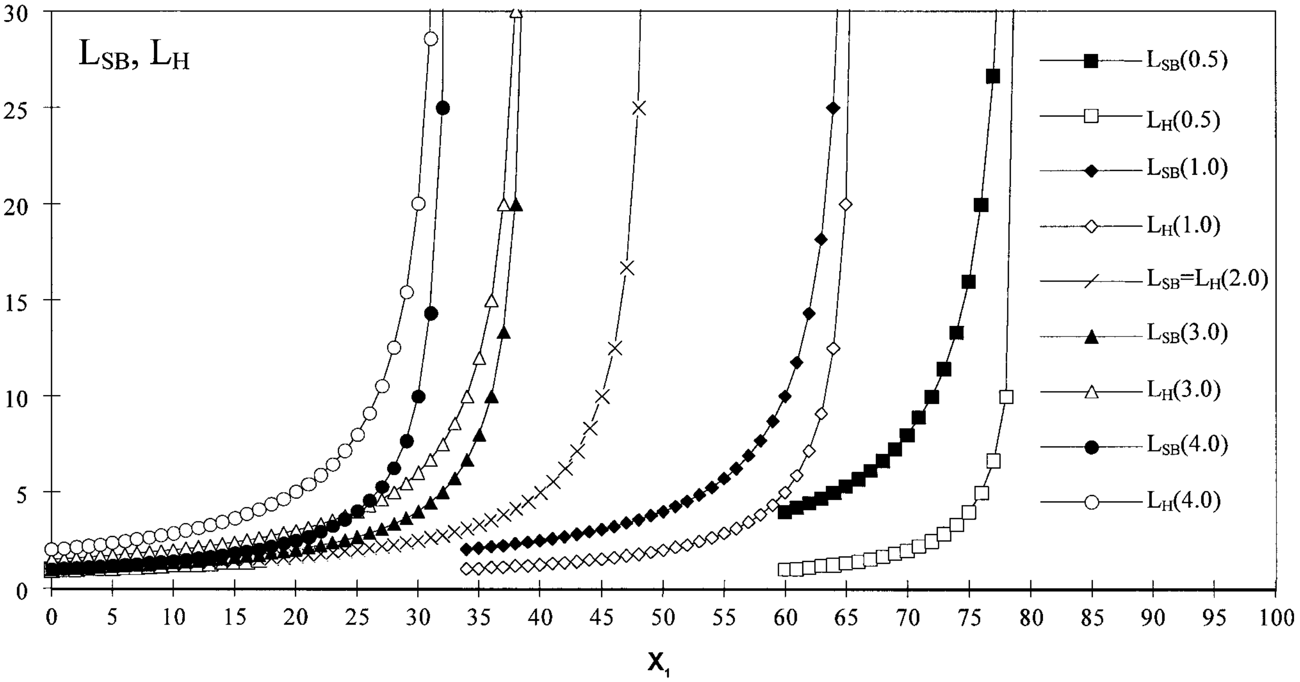

Figure A.1 Average length (number of monomer units) of the homopolymer blocks of a 1 : 1 : x SBH copolyester as a function of the percent concentration of S—B bonds (X_1) for different values of x (indicated in legend).

$$L_H = 100x/[200 - (2 + x)X_1] \qquad \text{(IV)}$$

The dependence of L_{SB} and L_H on X_1, for different values of x, is shown graphically in Figure A.1.

In the case of "ideal randomness," the reactivity of, for example, the carboxyl groups of sebacic acid toward the hydroxyl groups of B and H will be equal. Thus, the ratio of the formed bonds will be equal to the ratio of the concentrations of the two types of hydroxyl groups:

$$X_1/X_2 = [2 \times 100/(2 + x)]/[100x/(2 + x)]$$

From the expression of X_2 we obtain:

$$X_1 = 400/(2 + x)^2 \qquad \text{(V)}$$

and

$$L_H = (2 + x)/2 \qquad \text{(VI)}$$

A comparison of the experimental value of L_H [eq. (IV)] with that calculated for a random copolyester [eq. (VI)] provides a measure of the degree of blockiness of the product.

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