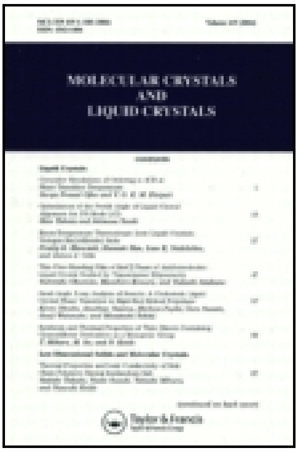

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Synthesis, Properties and Processability of a New Class of Semirigid Liquid Crystalline Copolyesteramides

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SYNTHESIS, PROPERTIES AND PROCESSABILITY OF A NEW CLASS OF SEMIRIGID LIQUID CRYSTALLINE COPOLYESTERAMIDES

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Abstract A new family of semirigid main chain liquid crystalline polymers (LCPs), referred to as SBAN, characterized by fairly good processability and mechanical properties, and improved thermal resistance, have been synthesized by the melt polycondensation of sebacic acid (S), 4,4'-dihydroxybiphenyl (B), 4-aminobenzoic acid (A), and 2-hydroxy-6-naphthoic acid (N), in a wide range of compositions. The molar concentration of the A and N units, in these LCPs must be kept lower than ca. 40 and 60%, respectively, in order to avoid the formation of homopolymeric blocks, which impair spinnability. The presence of A units grants the formation of hydrogen bonds between neighboring macromolecules, and this leads to higher tensile moduli and improved thermal resistance, with respect to analogous semirigid LC polyesters.

INTRODUCTION

In recent years, an increasing attention has been paid, by both academy and industry, to liquid crystalline polymers (LCPs).[1-5] In particular, much interest has been devoted to the synthesis and the characterization of main-chain LCPs comprising intrinsically rigid polyester or polyesteramide macromolecules. Although the backbone rigidity of these materials implies very high mechanical properties, it also leads to high melting points and high processing temperatures, and this may mean a drawback if the LCPs have to be blended with flexible thermoplastic polymers, which are usually processed at moderate temperatures. In addition, wholly aromatic LCPs display poor compatibility with respect to the latter host resins.

Semirigid LCPs, containing an appropriate concentration of one or more flexible moyeties in the backbone, may show reduced melting temperatures and, still, fairly high mechanical properties.[5-10] Moreover, a better compatibility with conventional thermoplastics, attributed to the flexible spacers, has been demonstrated for these materials.[4,5,11-15] Among semirigid LCPs, those synthesized from aliphatic diacids, such as sebacic acid (S), 4,4'-dihydroxybiphenyl (B) and 4-hydroxybenzoic acid (H), referred to as SBH polymers, and those containing 2-hydroxy-6-naphthoic acid (N) moyeties, in addition to the abovecited ones, referred to as SBHN polymers, have been recently studied in some detail.[6-10] The latter copolyesters show melting points ranging in a wide interval, depending on composition, and mechanical properties which can also be modulated by properly choosing the degree of aromaticity, i.e., the ratio of aromatic to aliphatic units. In particular, the LCPs of the SBHN type show better spinnability and higher mechanical properties, with respect to SBH LCPs having similar melting point, due to their higher aromaticity. However, the LCPs containing N units show lower crystallizability and, therefore, poorer mechanical properties at high temperatures.[10]

Although the performance of these semirigid LCPs can be optimized in view of a number of different applications, their intrinsically low glass transition temperatures may be a drawback in some instances. In order to improve the thermal and thermomechanical properties of these SBHN polymers, a new family of semirigid LCPs has been synthesized, which comprise moyeties introducing the amide bond in the chain. In particular, 4-aminobenzoic acid (A) was choosen as the source of these moyeties and was used in place of H. We theorized that hydrogen bonds could improve the molecular interactions thus enhancing the temperature resistance of these LCPs, without impairing their compatibility toward flexible polymers.

In this work, the synthesis and the characterization of this new class of LCPs, referred to as SBAN polymers, are presented.

EXPERIMENTAL

The chemical structure of SBAN polymers is shown below:

S B A N

The composition of these copolyesters may be defined by the molar ratio x:y:z of the recurring units S/B, A, and N, respectively. Thus, notations such as SBAN 1:0.5:2, which indicates the copolyesteramide containing 0.5 A, and 2 N units, for 1 S/B unit, will be used hereinafter. The compositions of the copolyesteramides discussed in this paper are indicated in Table I, together with their degree of aromaticity, calculated as the ratio of the numer of aromatic carbons (8x + 4y + 6z) to the total number of backbone atoms (20x + 6y + 8z).

TABLE I Composition of the investigated copoliesteramides.

Polymer	S (% mol)	B (% mol)	A (% mol)	N (% mol)	Aromaticity (%)
SBAN 1:0:3	20.0	20.0	0	60.0	59.1
SBAN 1:0.5:2	22.2	22.2	11.1	44.4	56.4
SBAN 1:0.5:1	28.6	28.6	14.3	28.6	51.6
SBAN 1:1:3	16.7	16.7	16.7	50.0	60.0
SBAN 1:1:2.5	18.2	18.2	18.2	45.4	58.7
SBAN 1:1:2	20.0	20.0	20.0	40.0	57.1
SBAN 1:1:1	25.0	25.0	25.0	25.0	52.9
SBAN 1:2:4	12.5	12.5	25.0	50.0	62.5
SBAN 1:2:3	14.3	14.3	28.6	42.8	60.7
SBAN 1:2:2	16.7	16.7	33.3	33.3	58.3
SBAN 1:2.5:1	18.2	18.2	45.4	18.2	55.8

Materials

All monomers were purchased from different japanese firms, except 4-aminobenzoic acid which was a Fluka product. They were used without further purification.

The copolyesteramides were synthesized by melt polycondensation. The process was accomplished in two stages. The first one consisted of the acetylation of the monomers with acetic anhydride, and the second of the melt alcoholysis, with the separation of byproduct acetic acid being made under reduced pressure.

For acetylation, sebacic acid, 4,4'-dihydroxybiphenyl and 2-hydroxy-6-naphthoic acid, in the selected molar ratio, were introduced in a pyrex reactor fitted with a reflux condenser and a vacuum outlet. After the catalyst addition (sodium acetate, 0.5-1% w/w), the solid mixture was carefully degassed under vacuum and pure nitrogen was admitted into the reactor. Then, a 18% molar excess of acetic anhydride was added, and the mixture heated to 140°C and refluxed for 5 h. At the end of this period, the temperature was raised to 170°C and acetic acid, together with the excess of acetic anhydride, was distilled off. The acetylated mixture was used for the second step without further purification. The acetylation of 4-aminobenzoic acid was carried out with a similar procedure in a separate vessel, because the acetylated derivative needed to be purified, by crystallization, from the diacetylated byproduct.

The mixture of acetylated monomers was introduced into a stirred stainless steel autoclave and the polycondensation was carried out with a computer controlled time-temperature profile. The temperature was gradually raised from ca. 220 to 250°C, over a period of 90 min, while acetic acid was distilled off under a flux of dry nitrogen. The temperature was then increased to 270-290°C (depending on the composition) in about 1 h, and left at the final value for 6 h. Finally, the pressure was gradually reduced to 0.01 mm Hg, and the reaction continued until the selected torque was reached (1-2 h).

The product polymer was then extruded through a die from the bottom of the autoclave with a nitrogen pressure of ca. 5 atm. The extrudate was cooled with water and pelletized. The polyesteramide was finally dried in a vacuum oven at 120°C for 10 h.

The inherent viscosity of the polymers, measured at 60°C in pentafluorophenol, at a concentration of 0.1 g/dL, ranged normally between 1 and 1.4 dL/g.

Techniques

X-ray diffraction (XRD) patterns were obtained with a Philips diffractometer, using the Ni-filtered CuKα radiation.

Differential scanning calorimetry (DSC) was carried out on a Mettler TA 4000 apparatus, under dry argon flow, with a rate of 20 °C/min. The samples (8-15 mg) were rapidly heated to 320°C, before the cooling (down to -60°C) and the heating (to 350°C) traces were scanned.

The rheological tests were carried out with a capillary rheometer, Rheoscope 1000 by CEAST, equipped with a capillary of 1 mm diameter and a length to diameter ratio L/D = 40. The shear viscosity measurements were made in a wide temperature interval.

Spinning tests were made using the same capillary viscometer, equipped with a conical die of 1 mm diameter and L/D = 0, the tensile module of the apparatus being used to draw down the filaments. The draw ratio (DR) could be continuously varied by changing the speed of the counter-rotating rolls; it was evaluated as the ratio between the cross sections of the die and of the filament. The extrusion shear rate was 24 s^{-1}. The stress-strain curves of the fibers were measured using an Instron mod. 1122 with an elongational rate of 0.5 min^{-1} and a gauge length of 10 cm. A minimum of seven measurements were made for each fiber, and the results were averaged.

Dynamic-mechanical testing was made on samples cut out from compression molded sheets, using a Rheovibron vicoelastometer, at a frequency of 110 Hz. The heating rate was about 1 °C/min.

RESULTS AND DISCUSSION

Structural Characterization

The XRD patterns of some SBAN copolyesteramides are shown in Figure 1. They are characterized by a relatively sharp peak (Bragg's spacing, d = 4.3÷4.5 Å) superimposed on a broader peak centered at approximately the same diffraction angle. The relative intensity of the two peaks depends on the copolymer composition. The d value is related to the average interchain distance perpendicular to the chain axis direction. The general absence of other discrete peaks is indicative of short-range order as well as of the lack of periodicity parallel to the chain axis, as expected for a copolymer with a random distribution of the comonomer units along the backbone.

Both the d value and the peak width increase significantly with the content of N units, as it could be expected considering the larger bulkiness of these units with respect to S, B and A units.

Additional discrete peaks may be observed in the XRD patterns of the copolymers with 46% of A and with 60% of N. They may be attributed to crystallization of A and N blocks, respectively, and suggest that homopolymeric blocks are present in these copolymers.

DSC analysis

The DSC thermograms of SBAN copolyesteramides are shown in Figure 2. They show a glass transition (Tg) at 110÷135°C, depending on the copolymer composition. The larger is the concentration of A units, the higher is the Tg value. This may be related to the probable formation of hydrogen bonds, due to the presence of amide linkages. As a matter of fact, replacement of A units with 4-hydroxy benzoic acid units results in a Tg lowering of about 50°C.

Two broad endotherms, characterized by relatively low enthalpy changes, appear above Tg. The transition temperature of the first one (in the 170÷200°C range) increases as the content of N decreases; that of the second one (in the 240÷310°C range) raises on

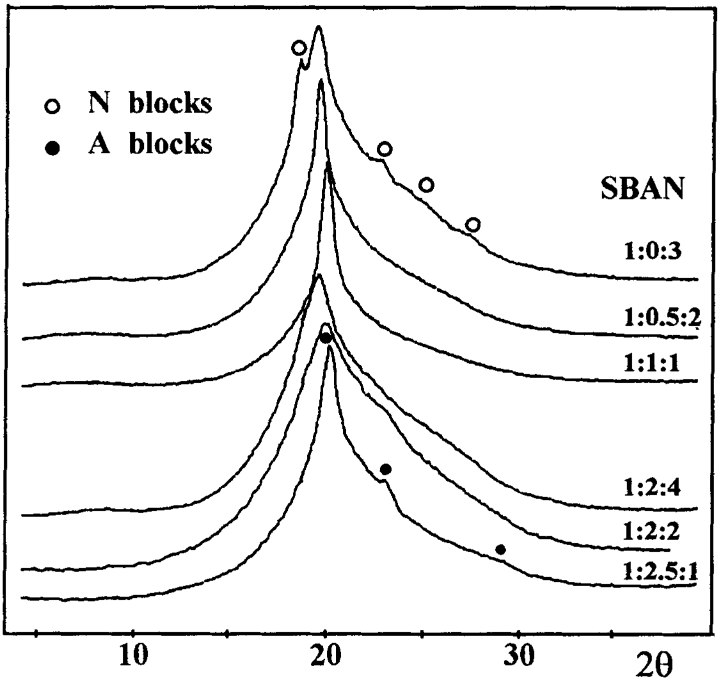

FIGURE 1 Powder X-ray diffraction patterns of SBAN copolyesteramides.

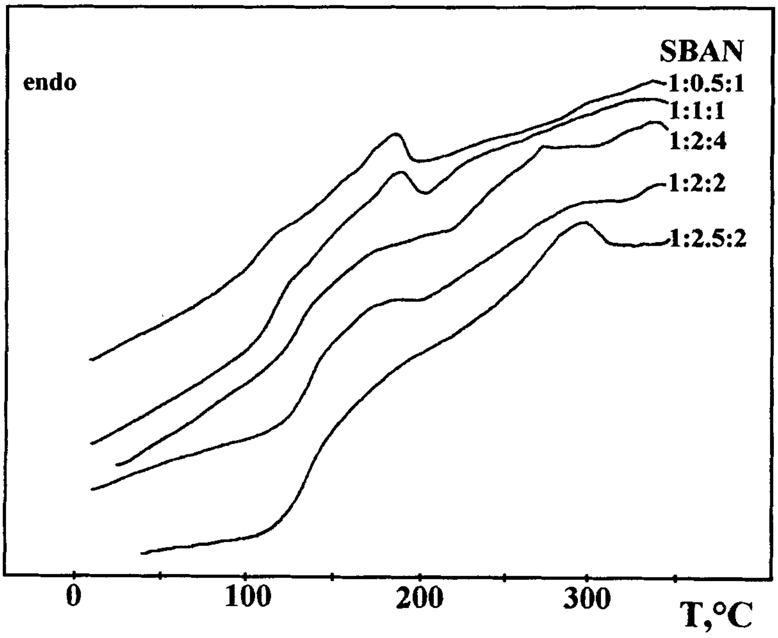

FIGURE 2 DSC heating traces of SBAN copolyesteramides.

increasing the content of N and, even more, of A units. According to the hot-stage optical microscopy observation, these endotherms should correspond to the crystal to nematic transitions. The DSC data, in line with the evidence coming from XRD analysis, point to a non-ideal randomness of some of the SBAN copolyesteramides.

Shear Viscosity

The viscosity curves of some SBAN copolyesteramides (1:0.5:2, 1:1:1, 1:2:2, and 1:2:4), measured at different temperatures, are shown in Figures 3. Some of these curves could

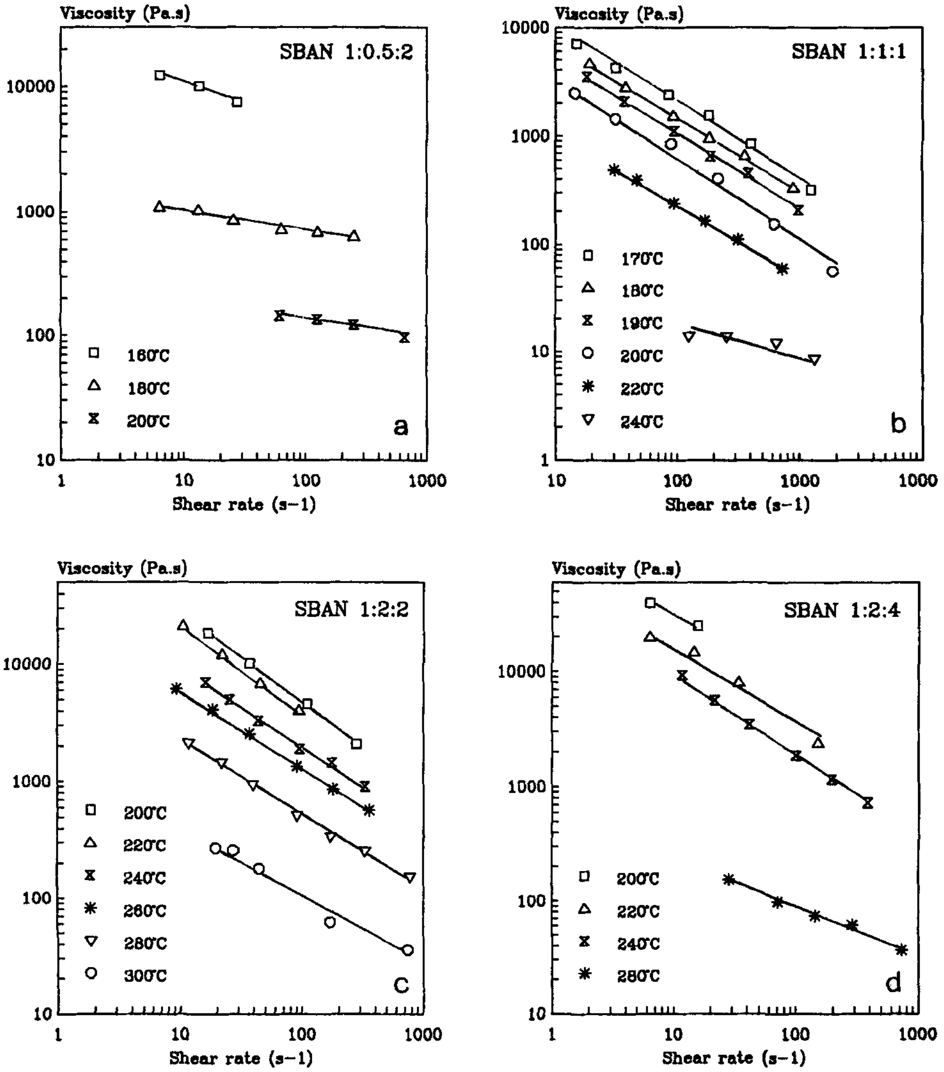

FIGURE 3 Viscosity curves of: a) SBAN 1:0.5:2; b) 1:1:1; c) 1:2:2; d) 1:2:4.

be measured even at temperatures very close to, or slightly lower than, the relevant crystal to nematic transition. This phenomenon had been already noticed for other LCPs,[8] and has been interpreted in terms of plastic flow.[16] In this case, however, it was not possible to carry out the measurements at temperatures well below the calorimetric melting points, as was the case with other semirigid LCPs of the SBH and SBHN types. Moreover, the viscosity range covered by these copolyesteramides is larger than that measured for SBH and SBHN polymers.[10] For example, SBAN 1:2:2 displays an appreciably higher viscosity than SBHN 1:2:2, when measured at the same temperature, despite of the fact that the two polymers have very similar melting points.[10]

To establish a fit correlation between the viscosity and the composition of the investigated LCPs is far from easy. However, upon increasing the relative content of A, and decreasing that of S/B, a viscosity increase is observed (cf., e.g., SBAN 1:0.5:2 with SBAN 1:2:4 and 1:1:2); on the other hand, an increase of the N content reduces the viscosity.

The behavior of SBAN copolyesteramides is distinctly non-Newtonian, except at the higher temperatures. On increasing the A content, the shear thinning behavior becomes more evident, and the Newtonian plateau is not revealed even at high temperatures. All these features can be explained considering the effect of intermolecular hydrogen bonds, due to the amide linkages, which limit the gliding ability of the macromolecules.

In previous works, some of the authors have shown that the thermal history of a semirigid LCP sample can influence its rheological behavior.[8,9] In particular, since the crystallization temperature ($T_{n\rightarrow k}$) may be appreciably lower than that of fusion ($T_{k\rightarrow n}$), the viscosity of the LCP can be easily measured even at temperatures lower than $T_{k\rightarrow n}$,

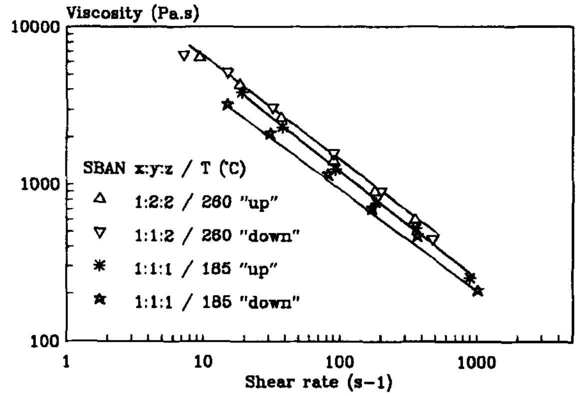

FIGURE 4 Viscosity curves of SBAN 1:2:2 (T = 260°C) and SBAN 1:1:1 (T = 185°C), measured with the "up" and "down" procedures (cf. text).

provided that the polymer has been previously melted. This demonstrates that the nematic phase may be quite stable, in these conditions. Thus, if the viscosity is measured at a temperature slightly lower than $T_{k \to n}$, different results are obtained according to whether the measurement temperature is reached upon heating ("up" procedure) or upon cooling ("down" procedure) the sample. This behavior was observed for some of the SBAN copolyesteramides, too. In Figure 4, the viscosity curves of two samples, SBAN 1:2:2 and SBAN 1:1:1, measured with the "up" and "down" procedures, are shown. It may be seen that the SBAN 1:1:1 polymer shows a lower viscosity, if the measurement is carried out at 185°C after preheating the polymer at 240°C ("down" procedure). SBAN 1:2:2, on the contrary, fails to show this behavior, and this is attributed to the very low crystallinity of this material.

Spinnability

Some of the SBAN copolyesteramides display good spinnability in a rather narrow temperature range. In Table II, the melting points of the investigated LCPs are reported, together with the minimum temperatures of spinnability. At temperatures lower than the indicated minimum values, the polymers displayed very high viscosity and the extrudate was too rigid to be wound round the bobbin, and broke like a brittle solid. In Table II, is also given an indication of the amplitude of the temperature range of spinnability of the

TABLE II Melting poins, spinnability, and fiber mechanical properties of the investigated copoliesteramides.

Polymer	$T_{k \to n}$ (°C)	Ts_{min} (°C)	ΔTs (°C)	DR_{max} (%)	E_{max} (GPa)	TS_{max} (MPa)
SBAN 1:0:3	160	-	-	-	-	-
SBAN 1:0.5:2	162	210	10	1600	65	550
SBAN 1:0.5:1	193	220	10	200	30	500
SBAN 1:1:3	195	240	10	25	25	100
SBAN 1:1:2.5	166	220	0	120	36	300
SBAN 1:1:2	184	240	20	1400	55	450
SBAN 1:1:1	196	250	10	7	2	70
SBAN 1:2:4	175	235	10	5	3	60
SBAN 1:2:3	180	240	10	30	7	80
SBAN 1:2:2	175	250	0	2	2	40
SBAN 1:2.5:1	295	-	-	-	-	-

different SBAN copolyamides. It may be seen that this interval is usually narrow, and does not exceed ca. 20°C. At temperatures above the spinnability range, the viscosity was too low and the polymer dripped. A range indicated in Table II as 0 means that the temperature could not be raised by 10°C above the minimum value without causing the polymer to drip.

Some of the SBAN polymers, such as SBAN 1:0:3 and SBAN 1:2.5:1, which have been shown to contain homopolymer blocks (cf. Figure 1), could not be spun at all. Others showed poor stretchability and gave extrudates which broke with moderate elongation, whereas some others could be easily spun and drawn to several hundreds percent of the natural length of the filament. An indication of the maximum draw ratio which could be used while spinning the different polymers is also given in Table II.

It may be seen that the spinnability changes dramatically with composition. Although it is not easy to establish a firm correlation between these two features, it seems that an increase of the content of A units beyond ca. 20% strongly depresses the spinnability. On the other hand, an increase of the ratio of S/B to N units seems to improve the polymer spinnability, provided that the molar content of A units remains below 20%.

Mechanical Properties

The tensile moduli (E_{max}) and the tensile strengths (TS_{max}) measured on SBAN fibers spun with the maximum draw ratio are collected in Table II. It is evident that remarkable mechanical properties were measured only when high draw ratios could be used. This is reasonable because, with semirigid LCPs, strong fiber elongations are needed in order to achieve satisfactory molecular orientation and, thereby, high modulus and strength. In particular, SBAN 1:0.5:2 and SBAN 1:1:2, which could be drawn to ca. 15 times their natural length, showed tensile moduli in the 60 GPa range, which is typical for wholly aromatic LCPs containing N units.[10] On the contrary, the samples that could not be spun with appreciable draw ratio were shown to possess tensile moduli very close to those of flexible isotropic polymers.

The dependence of the tensile modulus of SBAN fibers on the draw ratio is illustrated in Figure 5 for the 1:1:2 polymer. It may be seen that the modulus improvement is particularly marked in the 0÷100 DR range. For higher DR values, the modulus increase becomes smoother. This behavior is similar to that displayed by other semirigid LCPs and, in particular, by the SBHN polymers,[9,10] and differs markedly, on the contrary, from that displayed by wholly aromatic LCPs.[17-19] This difference has obviously been attributed to the presence of the flexible spacers, which need high draw ratios to become extended.

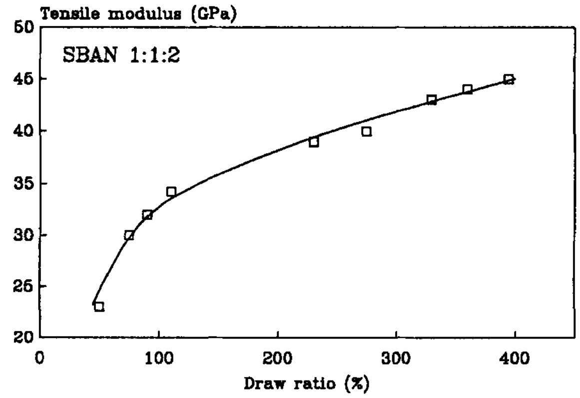

FIGURE 5 Tensile modulus of SBAN 1:1:2 fibers, as a function of the draw ratio.

Calundann ad Jaffe[20] established an empirical correlation between the values of the moduli of LCPs and their degree of aromaticity, i.e. the ratio of the number of sp2 hybridized carbons to the total number of atoms in the polymer chain, and found it to be approximately linear. The same dependence was found to hold for semirigid LC copolyesters, too. In Figure 6, the E_{max} values measured on fibers spun from SBAN 1:0.5:1, 1:0.5:2, and 1:1:2, are plotted vs. the degree of aromaticity. In the same Figure, the straight line reported for semirigid SBH and SBHN polymers is also plotted for the sake of comparison. It is evident that the E_{max} values of the SBAN LCPs are higher than those of SBH and SBHN polymers having the same degree of aromaticity. It is worth noticing, however, that the slopes of the straight lines are such that the E_{max} values of

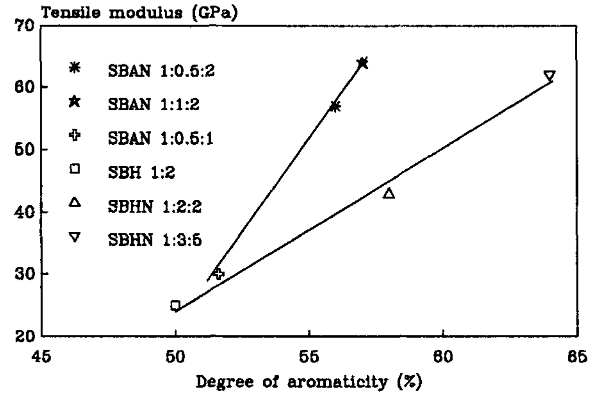

FIGURE 6 Maximum tensile modulus of different semirigid LCPs, as a function of the degree of aromaticity.

the SBAN copolyesteramides approach those of the SBH and SBHN copolyesters when the degree of aromaticity, and the content of A units become smaller. The increase of E_{max} with increasing the concentration of A is clearly to be attributed to the presence of hydrogen bonds which enhance the molecular interactions and thereby, the polymer stiffness.

Dynamic-Mechanical Properties

The storage modulus, E', and the loss modulus, E", of the compression molded specimens of SBAN 1:0.5:2 and SBAN 1:2:4 are plotted in Figures 7 and 8, respectively.

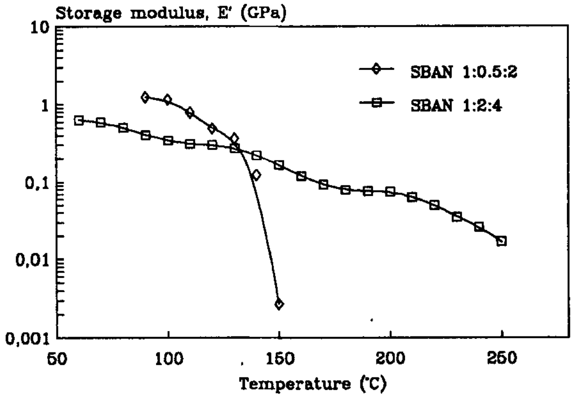

FIGURE 7 Temperature dependence of the storage modulus of SBAN 1:0.5:2 and SBAN 1:2:4.

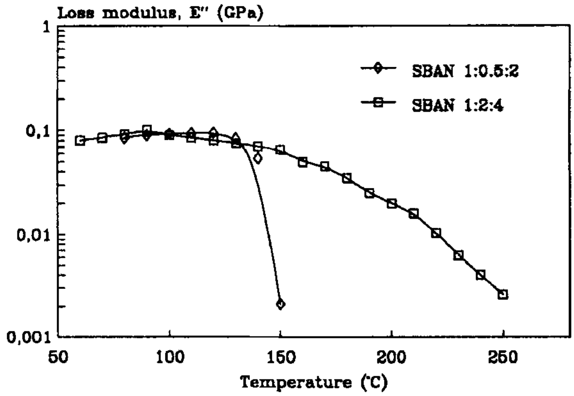

FIGURE 8 Temperature dependence of the loss modulus of SBAN 1:0.5:2 and SBAN 1:2:4.

The glass transition temperatures of these polymers, as measured from these plots, are in the 100÷120°C range, and correspond closely to the values found by calorimetry. It may be interesting to notice that the glass transition temperatures of the SBAN copolyesteramides (100÷135°C) are appreciably higher than those of similar semirigid LCPs of the SBH and SBHN types (65÷80°C).[10] The enhanced thermal resistance of the SBAN copolyesteramides was expected, as a result of the presence of the amide linkages in the backbone of these novel semirigid LCPs.

A comparison of SBAN 1:0.5:2 and SBAN 1:2:4 shows that the storage modulus of the latter decreases much less steeply with temperature. This is another indication that an appropriate concentration of A units in the main chain may have a beneficial effect on the thermal and thermomechanical behavior of semirigid LCPs.

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