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Structural relaxation of an oriented thermotropic liquid crystalline copolyester assessed by infrared spectroscopy and X-ray diffraction

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Samples of approximately uniform degree of orientation based on poly(hydroxybenzoic acid (73 mol%)-*co*-hydroxynaphthoic acid (27 mol%)), known as Vectra A950, were obtained by sectioning injection-moulded specimens. The degree of chain orientation was assessed by X-ray scattering and infrared spectroscopy. A comparison of the data obtained by the two methods enabled the angles between the chain axis and the transition moment vectors for the infrared absorption bands at 1474 cm^{-1} (22°) and 890 cm^{-1} (90°) to be assessed. The oriented samples showed, depending on the particular thermomechanical history used, either an increase or a decrease in chain orientation on annealing at temperatures below and above the crystal melting range. Constraining factors, the application of an external force to keep the samples at constant length or the presence of stabilizing crystallites, favoured an increase in chain orientation presumably through the annihilation of disclinations. Slow and gradual heating favoured recrystallization, i.e. the transformation of pseudohexagonal crystallites to the thermally more stable orthorhombic crystallites and possibly also to crystal modification II of poly(hydroxybenzoic acid). These form new physical cross-links which prevent shrinkage of the sample. Unconstrained oriented nematics containing no stabilizing crystallites showed a rapid approach (decrease for the highly oriented samples) to a universal value for the Hermans orientation function of ~0.3 at temperatures above 290°C. This behaviour, distinctly different from that of small-molecule nematics, shows some similarity with the behaviour of oriented flexible-chain polymers. © 1997 Elsevier Science Ltd.

(Keywords: liquid crystalline polymers; orientation; relaxation)

INTRODUCTION

Thermotropic main-chain liquid crystalline polymers have found a use as engineering plastics due to their good general properties and in particular to their superior mechanical properties, which approach those of short-fibre reinforced thermoplastics. These nematic polymers readily orient during conventional melt processing, and the oriented structure is preserved for extensive periods of time also at temperatures above the crystal melting point[1].

This paper presents data on the effect of various heat treatments on the state of orientation of an oriented copolyester of hydroxybenzoic acid (HBA) and hydroxynaphthoic and acid (HNA) known as Vectra. Most of the previous studies[2-4] were carried out on samples after they had been annealed and quenched to room temperature, and this leaves some doubt about the preservation of the structure during the cooling process. The orientation has been assessed by infrared spectroscopy and X-ray scattering, which permit a real-time recording of global orientation. A comparison is also made between the results obtained by the two methods. A hitherto unreported increase in chain orientation occurred in oriented samples when they were given a particular thermal treatment whereas the same samples, when given another thermal treatment, showed the more expected and earlier reported[4] behaviour with a decrease in orientation on annealing. Rapid heating of oriented injection-moulded samples of Vectra to temperatures between 280 and 290°C led to an instantaneous partial loss of orientation accompanying crystal melting[4]. However, an appreciable degree of chain orientation, 0.3–0.4 according to the Hermans orientation function, remained after the material had been heated above the melting region of the initial crystallites[4].

The samples used in this study were obtained from injection-moulded specimens. It is known that thin injection-moulded specimens exhibit a skin–core morphology with a highly oriented outer layer and a less oriented core[5-9]. Specimens of a thickness of 6 mm or more exhibited a more complex morphology with a greater number of layers of different orientation[9].

Vectra is a polymer with a complex structural and thermal behaviour. It is semicrystalline with a crystallinity of 20–40%[10-12], although some authors[13] have reported crystallinities as high as 60%. Wilson *et al.*[12] using the rigorous Ruland method reported

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crystallinities close to 20% for a wide range of copolymers based on HBA and HNA, including the Vectra A composition. The X-ray diffraction pattern of Vectra is indeed very special, with aperiodic meriodional reflections and well-defined equatorial reflections[11,12,14–17]. The high crystallinty is unexpected considering the fact the Vectra is a statistical copolymer and as such should be non-crystalline. The crystal structure of Vectra has been a matter of debate since 1985. Windle *et al.*[18] proposed that the crystalline component consists of non-periodic layer crystallites which arise from a lateral matching of similar sequences of neighbouring non-periodic chains. Biswas and Blackwell[19] assumed, on the other hand, a model where three-dimensional order is achieved without lateral matching of adjacent chains.

Annealing of rapidly cooled Vectra at temperatures slightly above the melting range causes an initially complete crystal melting, but at a later stage, recrystallization occurs which proceeds for several hundred minutes at these temperatures[20,21]. These 'new' crystallites melted near 320°C, and X-ray diffraction revealed two different crystalline components, one originating from periodic HBA units and the other from aperiodic HBA–HNA segments. Heating above 320°C regenerated the material, and the described behaviour reappeared in the next thermal cycle[20,21]. It was proposed by these authors[20,21] that the recrystallization is a 'conventional' physical nucleation growth process. Kachidza *et al.*[22] made similar observations on Vectra after it had been annealed at temperatures close to the crystal–nematic transition, and then suggested that the high-melting-temperature crystals consisted of PHBA homopolymer. They proposed that this material was formed by transesterification, a process earlier denoted crystallization-induced ordering[23,24]. Annealing of ultra-oriented Vectra at 260–270°C led to the formation of crystallites with a melting point between 340 and 350°C[25,26], and evidence was presented for the occurrence of transesterification during annealing[26]. Wilson *et al.*[12] showed by X-ray diffraction that rapidly cooled HBA-rich poly(HBA–HNA) samples, also including the Vectra A950 composition, contained 20% of pseudo-hexagonal crystal phase, which on annealing at temperatures above 200°C underwent a transformation to a denser orthorhombic phase and to a crystal arrangement analogous to phase II of PHBA. It was argued by these authors[12] that the transformation of the pseudo-hexagonal phase to the orthorhombic phase should occur by nucleation and growth rather than by transformation twinning.

EXPERIMENTAL

The material studied was a commercial grade of a thermotropic liquid crystalline copolyester, Vectra A950 (Hoechst-Celanese, USA), with 73 mol% of 4-hydroxybenzoic acid and 27 mol% of 2-hydroxy-6-naphthoic acid. The samples were obtained by sectioning 4 mm thick, dumb-bell-shaped injection-moulded specimens. The injection moulding was carried out in a Netsal Neomat 70/75 using the following processing conditions: melt temperature, 320°C; mould temperature, 100°C; injection time, 0.2 s; and holding pressure, 3.5 MPa. The pellets were dried at 160°C for 4 h prior to the injection moulding. Samples with a cross-section of 8 × 6 mm and thicknesses of 12 ± 3 and 120 ± 10 μm were prepared by embedding the specimen in epoxy followed by sectioning at room temperature in a direction parallel to the direction of flow using a Jung Autocut 2055 (Leica) microtome at a rate of 150 mm s^{-1}. These conditions gave minimum shrinkage of the samples and a surface free from visible defects. The large surfaces of the microtomed sections were always parallel to the major surfaces of the dumb-bell specimens.

Infrared dichroism measurements were made in a Perkin-Elmer 1760 equipped with a resistive heating oven with a PID temperature control (Eurotherm 903) keeping the sample temperature constant within ±0.5°C (calibration was made with standard substances), a TGS detector and a Perkin-Elmer polarizer KRS5. Each spectrum was based on 10 scans and had a spectral resolution of 4 cm^{-1}. The main directions with minimum and maximum absorptions of a given band were found by rotation of the polarizer. One of them always coincided with the major flow direction in the mould (director). For each absorption band (i) a dichroic ratio (R_i) could be obtained according to $R_i = A_{i,\mathrm{II}}/A_{i,\perp}$, where $A_{i,\mathrm{II}}$ is the absorbance of band i parallel to the director and $A_{i,\perp}$ is the absorbance of band i perpendicular to the director. The polarizer angle could be adjusted with an accuracy of 0.5°. A few truly kinetic studies were conducted in a Perkin-Elmer 2000 equipped with a hot stage, an MCT detector and a polarizer controlled by the software. The spectral resolution was for reasons of acquisition time set to 8 cm^{-1}, and the data obtained were based on only three scans per spectrum.

X-ray scattering patterns of samples of thicknesses 12 ± 3 μm (samples were highly tilted with respect to the incident beam) and 120 ± 10 μm were taken in a Statton camera using Ni-filtered Cu$K\alpha$ radiation ($\lambda = 0.154$ nm) from a Philips PW 1830 generator, and in a Stadi/P equipped with a curved-position sensitive detector using strictly monochromatized Cu$K\alpha$ radiation. The X-ray scattering films obtained in the Statton camera were analysed in an image analysis system: Northern Light Model B90 light table, Dage MTI 70 series camera, DTK 486–33 MHz PC, software by Optimas Bioscan Inc., UN-Scorpion VGA-Framegrabber. The chain orientation expressed in terms of the Hermans orientation function (f), using the major flow direction as the director, was assessed in accordance with Engberg and Gedde[4] using the azimuthal angle dependence of the equatorial scattering at $2\theta \approx 19.5°$ ($d = 4.5$ nm).

Annealing experiments were performed by rapid heating, either at 200°C min^{-1} in a temperature-calibrated Perkin-Elmer DSC-7 or at 130°C min^{-1} in the resistive oven, to the annealing temperature, which was systematically varied between 250 and 310°C. The samples were cooled in the differential scanning calorimeter at 200°C min^{-1} after the isothermal treatment, whereas a cooling rate of 20–30°C min^{-1} was used in the resistive oven. The chain orientation was assessed by X-ray scattering and infrared spectroscopy before annealing, after annealing at the annealing temperature (only with infrared spectroscopy), and at 23°C after cooling from the annealing temperature. Stepwise heating experiments were conducted by rapid heating (130°C min^{-1}) to 250°C, holding the samples at that temperature for 10 min, after which the dichroism was determined in the infrared spectrometer, rapid heating (130°C min^{-1}) to 260°C, holding the samples at that

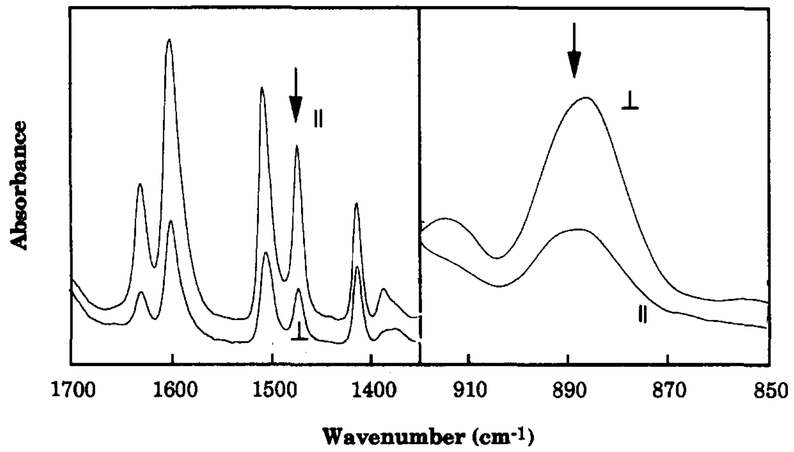

Figure 1 Infrared spectra recorded at 23°C of an oriented sample using infrared light polarized parallel to and perpendicular to the flow direction. Absorption bands at 1474 and 890 cm^{-1} used for the assessment of orientation are indicated in the figure. Note that the spectra are vertically shifted to enable comparison

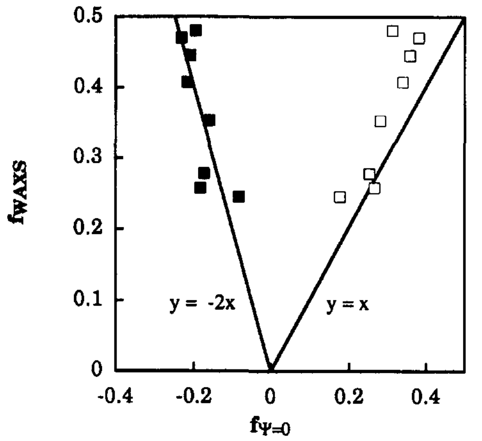

Figure 2 Determination of transition moment angles, by comparing f values obtained by wide-angle X-ray scattering and infrared dichroism, for the bands at 1474 cm^{-1} (□) and 890 cm^{-1} (■). The measurements were made at 23°C

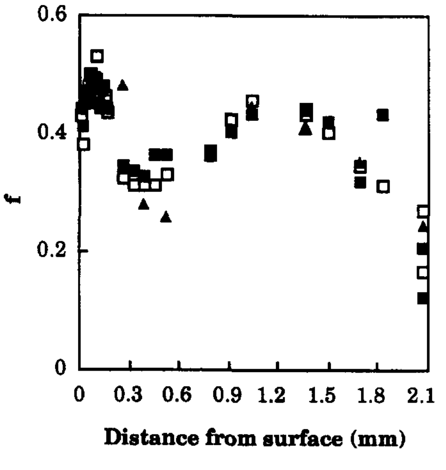

Figure 3 The Hermans orientation function (f) across the cross-section of an injection-moulded specimen obtained from infrared spectroscopy: 1474 cm^{-1} (□), 890 cm^{-1} (■) and wide-angle X-ray scattering (▲). The measurements were made at 23°C

temperature for 10 min, after which the dichroic ratio was determined in the infrared spectrometer, etc., at 10°C intervals up to 340°C. *In situ* measurements of infrared dichroism were also made during constant rate heating at 10°C min^{-1}.

Some samples were rigidly clamped between potassium bromide discs or in the d.s.c. pans. These samples showed only little or no change in shape after being annealed at temperatures above the melting point (290°C). Other samples were allowed to shrink freely during annealing using a spacer in the d.s.c. pan, often in combination with a silicone oil lubricant or by using a silicone-oil-lubricated specially built aluminium sample holder with a 40 μm thick countersink.

RESULTS AND DISCUSSION

The infrared spectra of an oriented Vectra sample with polarization directions parallel to and perpendicular to the director are shown in *Figure 1*. Two absorption bands were used to characterize the chain orientation, namely the 1474 cm^{-1} band due to C–C stretching vibrations in the naphthalene ring and the 890 cm^{-1} band assigned to C–H out-of-plane bending vibrations in the benzene ring[27–29]. The spectra displayed in *Figure 1* show that the absorbance associated with the 1474 cm^{-1} band is strongest along the director and that the 890 cm^{-1} band exhibits maximum absorbance in the perpendicular direction. Hence, the transition moment vectors of the vibrations should be respectively essentially parallel to (1474 cm^{-1}) and perpendicular to (890 cm^{-1}) the chain axis, which is in accord with previous reports[29].

The angles between the transition moment vectors and the chain axis were assessed with greater precision by comparing infrared dichroic ratio data and X-ray diffraction data according to equation (1), originally derived by Fraser[30], and *Figure 2*,

$$f = \left(\frac{R-1}{R+2}\right)\cdot\left(\frac{2\cot^2\psi + 2}{2\cot^2\psi - 1}\right) = f_{\psi=0}\cdot\left(\frac{2\cot^2\psi + 2}{2\cot^2\psi - 1}\right) \tag{1}$$

where f is the Hermans orientation function describing chain axis orientation, and ψ is the angle between the transition moment vector and the chain axis. The interference between the 1474 and 1502 cm^{-1} bands is negligible as judged by curve resolution into two Lorenz functions. Best linear fits of the data in *Figure 2* yield $\psi = 22°$ for the 1474 cm^{-1} band and 90° for the 890 cm^{-1}

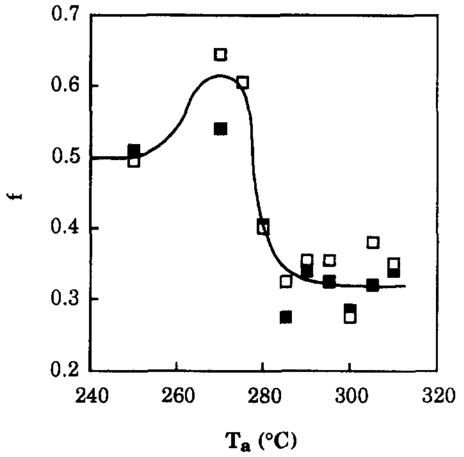

Figure 4 The Hermans orientation function (f) obtained from infrared spectroscopy (1474 cm^{-1} (□), 890 cm^{-1} (■)) for freely shrinking samples annealed for 6 s as a function of the annealing temperature (T_a). The infrared spectra were taken at 23°C after annealing

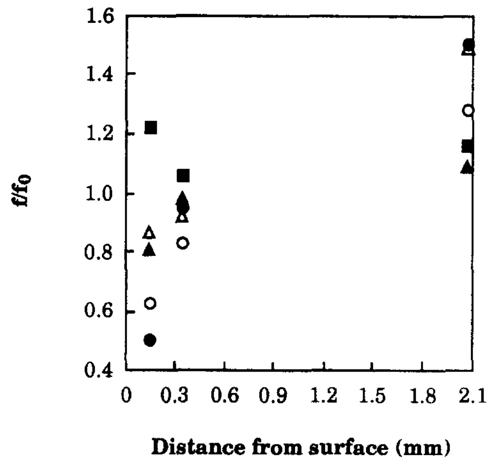

Figure 5 Annealing-induced changes in the Hermans orientation function (infrared spectroscopy results at 23°C using the 1474 cm^{-1} band; f/f_0, where f_0 is the Hermans orientation function of the depth before annealing) of freely shrinking samples as a function of the depth from the surface of the injection-moulded specimens using the following annealing temperatures and times: 270°C, 0.1 min (■); 280°C, 0.1 min (▲); 280°C, 1 min (△); 300°C, 0.1 min (●); and 300°C, 2 min (○)

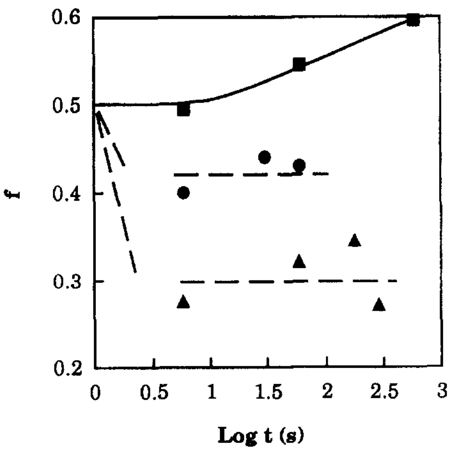

Figure 6 Annealing-induced changes in the Hermans orientation function (f; infrared spectroscopy results at 23°C using the 1474 cm^{-1} band) of freely shrinking samples as a function of the annealing time at the following annealing temperatures: 250°C (■), 280°C (●) and 300°C (▲)

band, which is in accordance with earlier published data[29].

Figure 3 shows the variation in chain orientation through the cross-section of the injection-moulded specimen. The chain orientations of samples from five different injection-moulded specimens were obtained, and the differences in chain orientation between samples taken at the same depth were insignificant. Data obtained by wide-angle X-ray scattering (WAXS) and infrared spectroscopy are generally in agreement. The orientation function shows two pronounced minima, one in the very centre of the 4 mm thick specimen and one 0.5 mm from the surface. The orientation of the near-surface material (150 μm thickness) is $f = 0.48$. The first maximum in orientation is located at about 100 μm from the surface. The core material also exhibited a significant degree of chain orientation, f being approximately 0.2. This multizone morphology is very similar to that observed in 6 mm thick ruler-shaped samples of poly(p-hydroxybenzoic acid-*co*-ethylene terephthalate)[9].

Oriented samples that were free to shrink, and with the initial Hermans orientation function $f_0 = 0.48$, increased their chain orientation on 6 s of annealing in the semicrystalline state, i.e. below 280°C (*Figure 4*). The samples were always heated by 200°C min^{-1} to the annealing temperature. Alderman and Mackley[31] showed that shear flow causes multiplication of disclinations in nematic Vectra. These structures may be frozen-in after rapid cooling below the glass transition temperature. The annealing leads to a greater mobility of the chains, enabling the annihilation of nearby pairs of disclinations of opposite sign and a consequent increase in the orientation. There is also a possible influence of a change of the banded structure that appears during shear and after the cessation of shear. The banded structure, which according to Viney *et al.*[32] is due to a 'gentle', serpentine trajectory of the molecules, may rearrange during annealing, causing a change in the degree of orientation.

Annealing at temperatures higher than 280°C caused a marked decrease in chain orientation from the initial value of $f = 0.5$ to 0.3, which is comparable with earlier published data obtained by X-ray scattering of other Vectra samples annealed at 290°C[4]. These results obtained by infrared spectroscopy were also principally confirmed by WAXS on short-time annealed samples. It may be suggested that the melting of the initially existing crystallites at 280–285°C caused a disintegration of physical cross-links in the nematic phase and randomization of adjacent chains. It is as if there is a molecular network in the nematic which gives a retraction similar to that found in oriented flexible-chain polymers.

Data for the annealing-induced reorientation of three groups of samples with different degrees of initial chain orientation are presented in *Figure 5*. Annealing at 270°C caused only moderate changes in chain orientation. Annealing at 280 and 300°C led to a pronounced decrease in chain orientation for the samples with the highest initial chain orientation ($f_0 \approx 0.5$), an almost invariant chain orientation for the samples with $f_0 \approx 0.3$ and a moderate increase in orientation for the samples with the lowest initial orientation ($f_0 \approx 0.2$). The orientation of the different samples with different initial orientations, from 0.2 to 0.5, thus approached after annealing at 280–300°C a value near 0.3 (*Figure 5*).

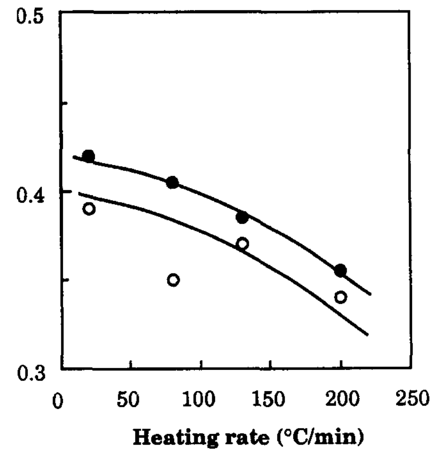

Figure 7 The Hermans orientation function (f; infrared spectroscopy results at 23°C using the bands at 1474 cm^{-1} (●) and 890 cm^{-1} (○)) of freely shrinking samples annealed at 290°C for 6 s as a function of the heating rate used prior to the isothermal annealing

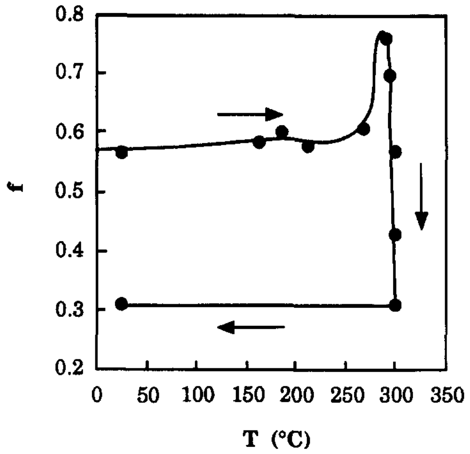

Figure 8 The Hermans orientation function (f; infrared spectroscopy results obtained at the temperature shown in the diagram, using the 1474 cm^{-1} band) as a function of temperature during a 10°C min^{-1} scan (first heating and then cooling as shown in the graph)

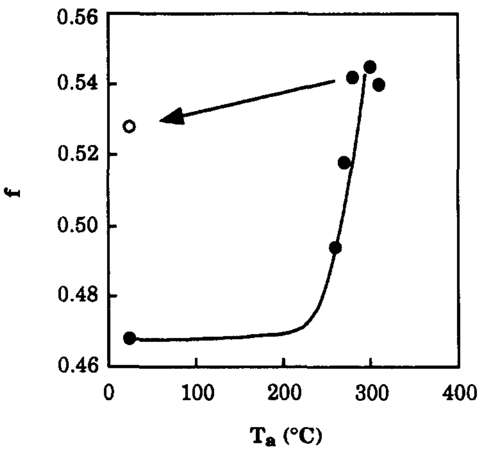

Figure 9 The Hermans orientation function (f; infrared spectroscopy results obtained at the annealing temperature shown in the diagram, using the 1474 cm^{-1} band) of a freely shrinking sample being stepwise heated between the annealing temperatures (T_a). The time spent at each isothermal annealing was 10 min. The orientation of a sample after cooling to 23°C is also shown (○)

It is thus as if a 'natural' universal degree of chain orientation exists, independent of the previous shear history, in the nematic melt above the crystal melting range. The degree of orientation, $f \sim 0.3$, seems low for a monodomain texture, which implies the presence of defects.

All hitherto presented data have been obtained by heat treatment in the d.s.c. apparatus and the chain orientation was determined by infrared spectroscopy at 23°C before and after annealing. Hot-stage infrared spectroscopy showed, however, that the dichroic ratios were the same before and after cooling from the annealing temperature.

The effect of annealing time on the chain orientation is strongly dependent on the annealing temperature (*Figure 6*). At low temperatures there is a progressive but retarding increase in orientation as a function of annealing time. A sample with $f_0 = 0.43$ exhibited after 18 h of annealing at 250°C a value of $f = 0.51$. Annealing at temperatures in or above the melting range led to a pronounced loss of orientation within the first 6 s, after which the degree of orientation remained essentially unchanged. Extensive (18 h) annealing at 270°C led to only marginal changes in chain orientation. These data are in agreement with earlier X-ray scattering data on similar Vectra samples[4].

The rate at which samples were heated to the annealing temperature affected the orientation relaxation at 290°C (*Figure 7*): a greater decrease in orientation occurred in samples that were rapidly heated to the annealing temperature. Continuous heating at 10°C min^{-1} of an oriented Vectra sample (free shrinkage) while continuously measuring the infrared dichroic ratio led to the development of further orientation, as shown in *Figure 8*. The degree of orientation remained approximately constant up to 270°C, above which the orientation function first increased dramatically and then decreased strongly, finally reaching a lower chain orientation at 300°C than was initially present. Cooling of the sample from the annealing temperature to room temperature caused no further change in chain orientation. Stepwise heating of a free-shrinking sample, involving a cycle with rapid heating (130°C min^{-1}) to a specified temperature and a 10 min isothermal period, led to a gradual increase in chain orientation (*Figure 9*). The data presented in *Figures 7* and *8* can be rationalized by a scheme in which the presence of crystallites, either of the original pseudo-hexagonal type or the later formed orthorhombic and phase II types[12], prevent the rapid, viscoelastic retraction of the nematic network. The dominant process is then thermally induced elimination of defects (disclinations), causing a gradual increase in the degree of orientation.

A number of samples were held at constant length during heating, and this restriction had a strong effect on the orientation relaxation behaviour (*Figure 10*). Stepwise heating to 340°C resulted in an accelerated, monotonous increase in orientation function with increasing temperature and a discoloured, degraded sample with unchanged dimensions after heating to 340°C. However, heating at a rate of 130°C min^{-1} to 290°C caused a similar increase in chain orientation, which is in sharp contrast to the outcome of a similar thermal treatment of a freely shrinking sample. It thus seems that this external constraint (holding the sample at constant length) has the same effect as the presence

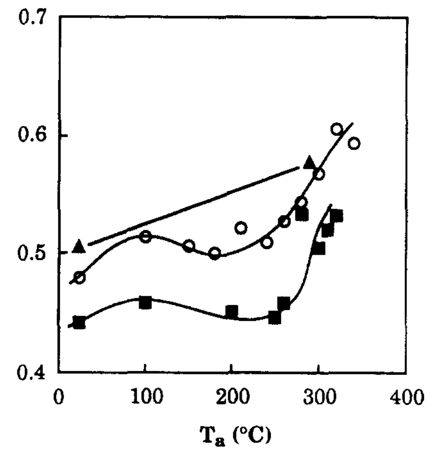

Figure 10 The Hermans orientation function (f; infrared spectroscopy results obtained at the annealing temperature shown in the diagram, using the 1474 cm^{-1} band) of samples held at constant length being stepwise heated between the annealing temperatures (T_a): between KBr discs (○), in a drilled d.s.c. pan (■). One sample was rapidly heated to 290°C and measured directly in the infrared apparatus (▲). The time spent at each isothermal annealing was 10 min

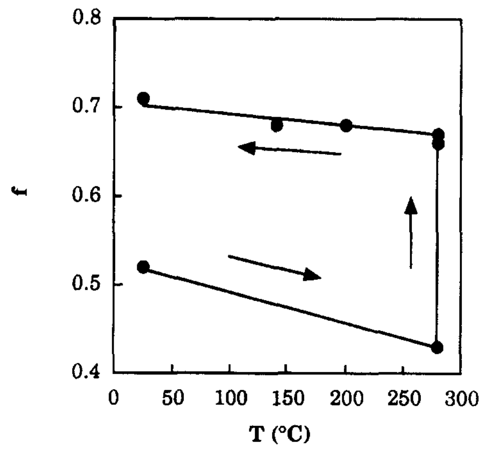

Figure 11 The Hermans orientation function (f; infrared spectroscopy results obtained at the actual temperature shown in the diagram, using the 1474 cm^{-1} band) of samples held at constant length being rapidly heated to 280°C, kept at that temperature for 30 min and finally cooled to 23°C

of crystallites. The viscoelastic retraction is prohibited, and the defect-eliminating process becomes dominant.

The effects of several more complex thermal histories were studied. A sample with $f_0 \approx 0.5$ was first rapidly heated to 290°C, and then held at that temperature for a few minutes while being allowed to shrink freely. This treatment caused a decrease in chain orientation function from $f = 0.5$ to 0.3. The sample was subsequently cooled to 23°C, reheated to 250°C and held at 250°C while changes in the infrared dichroism were recorded. The chain orientation remained constant during this treatment, which is strikingly different from the behaviour of a sample directly heated to and annealed at 250°C.

Oriented Vectra annealed under constrained conditions, either by the application of an external force keeping the samples at constant length or by the presence of crystallites, exhibited an increasing degree of orientation. Similar polymers undergo disclination multiplication during shear[31], and it is assumed here that the nematic structure prior to the heat treatments contained a substantial concentration of disclinations. The thermal treatment should in these cases lead to an increase in the mobility of the disclinations and thus increase the probability that disclination of the same strength and of different signs meet and annihilate. It has been shown that the concentration of disclinations decreases progressively during the annealing of globally isotropic, nematic polymers[33]. The disclination elimination causes a gradual increase in chain orientation. Slow or intermittent heating favours transformation of the metastable pseudo-hexagonal phase into the more stable orthorhombic phase and PHBA phase II[12,19,20]. These thermally more stable crystals constitute effective physical cross-links which prevent shrinkage of these samples. The recorded increase in the degree of orientation must then be due to perfection of the material between the crystallites (disclination annihilation). In both these cases the dimensions of the studied samples remained essentially unchanged after the thermal treatments, and also after annealing at temperatures as high as 340°C. Very high f values were approached after gradual heating, nearing those of the monodomains of small-molecule liquid crystals.

In unconstrained highly oriented nematics containing no stabilizing crystals there is a very rapid loss of orientation, within a time period of a few seconds, reaching a final value for the order parameter close to 0.3 at temperatures above 290°C. There is an accompanying corresponding change in the dimension of the samples. This behaviour is clearly different from the behaviour of small-molecule nematics, the latter showing a more gradual decrease in order parameter with increasing temperature close to the isotropization temperature[34]. The rapid retraction (loss of orientation) shows some similarity with the behaviour of flexible-chain polymers.

CONCLUSIONS

Oriented Vectra A samples showed, depending on the particular thermomechanical history used, either an increase or a decrease in chain orientation on annealing at temperatures below and above the crystal melting range. Constraining factors, the application of an external force to keep the samples at constant length or the presence of stabilizing crystallites, favoured an increase in chain orientation, presumably through the annihilation of disclinations. Unconstrained oriented nematics containing no stabilizing crystallites showed a rapid approach (decrease for the highly oriented samples) to a universal value for the Herman orientation function of ~0.3 at temperatures above 290°C. This behaviour, distinctly different from that of small-molecule nematics, shows some similarity to the behaviour of oriented flexible-chain polymers.

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