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Novel aspects of microstructure of liquid crystalline copolyesters as studied by microhardness: influence of composition and temperature

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The microhardness of a series of random copolyesters of 4-hydroxybenzoic (HBA) and 2-hydroxy-6-naphthoic acid (HNA) has been investigated as a function of composition and temperature. The results reveal that, at room temperature, the microhardness of non-oriented materials deviates from the linear additivity of the hardness of single homopolymers. Such a deviation is shown to be mainly related to changes in the molecular packing of the rigid chains. This packing, and as a consequence microhardness, can be characterized by an average cross-sectional area which includes crystalline and non-crystalline regions. The fact that the microhardness behaviour and the temperature dependence of the cross-sectional area are closely related is emphasized. An analytical expression embracing the coefficient of thermal softening, β, and the thermal expansion coefficient of the cross-sectional area, α_A, is proposed. © 1997 Elsevier Science Ltd.

(Keywords: microhardness; liquid crystalline copolyesters; structure)

INTRODUCTION

Copolyesters of 4-hydroxybenzoic (HBA) and 2-hydroxy-6-naphthoic acid (HNA) have lately been receiving particular attention, as they exhibit a thermotropic liquid crystalline phase from which highly oriented fibres can be produced. Transmission electron microscopy (TEM)[1–3], scanning electron microscopy (SEM)[3–5], small angle X-ray scattering (SAXS)[3,6], wide angle X-ray diffraction (WAXD)[6–14] and differential scanning calorimetry (d.s.c.)[8,15,16], have been used to study the morphology and microstructure of these systems, as well as the nature of the melt. Dielectric properties, dynamic mechanical behaviour, experimental and theoretical longitudinal chain moduli and nuclear magnetic resonance (n.m.r.) studies of these random copolyesters have also been reported[17–20]. A recent magnetic susceptibility study offers valuable information on the molecular relaxation at the mesophase[21].

It is well known that microhardness is directly related to the microstructural changes in semicrystalline and amorphous polymers[22–24]. On the other hand, hardness is connected to the macroscopic mechanical properties of materials[22–25]. Recent papers highlight the dependence of microhardness upon crystallinity, crystal thickness and polymorphic crystal forms in random liquid crystalline copolyesters containing flexible spacers[26,27]. In the present paper we wish to re-examine these concepts in the case of rigid copolyesters which show substantial differences from flexible polymers. It is known that SAXS maxima have been detected only in P(HBA/HNA) copolyesters of lower molecular weight (degree of polymerization, DP $\leq$ 125)[6]. However, for higher molecular weights (DP $\sim$ 250), the packing of rigid molecular rods in the material does not give rise to any SAXS maxima. In addition, the measured crystallinity of the copolyesters shows very little dependence upon thermal treatments. A value of crystallinity close to 0.2 has been obtained in all cases (*Table 1*). This result indicates the overwhelming contribution of much more abundant non-crystalline regions, which should be taken into account when analysing a mechanical property such as microhardness. However, the observed parallel changes of crystal structure, orthorhombic or pseudohexagonal, on the one hand, and microhardness variations on the other, highlight in the present study the intimate connection between both crystalline and non-crystalline phases. In fact, the evidence of small crystals in random copolyesters with rigid rod molecular structures, imposes for the remaining non-crystalline regions a degree of order which will keep adjacent molecules in a more or less parallel arrangement (nematic glass).

EXPERIMENTAL

Specimen preparation

P(HBA/HNA) samples of high molecular weight (DP $\sim$ 250), supplied by Hoechst Celanese Corporation with molar ratios 30/70, 58/42 and 75/25, were compression moulded and quenched from the melt as described elsewhere[7]. Films 0.25 mm thick were obtained. The microcrystals are disoriented in the plane of the film with the molecular axis parallel to the film surface. Samples were annealed for 24 h at temperature of 240°C for P(HBA/HNA) 30/70 and 75/25 and 220°C for the molar

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Table 1 X-ray crystallinity (w_c) of the P(HB/HN) copolyesters, quenched from the melt and thermally annealed

P(HB/HN)	w_c (quenched)	w_c (annealed, 24 h)
0/100	0.65	–
30/70	0.19	0.20
58/42	0.19	0.20
75/25	0.20	0.20
100/0	0.80	–

ratio 58/42. The temperature dependence of the samples without annealing was studied in the whole range of compositions. The annealed samples were investigated at room temperature, except for sample 75/25, which was also studied as a function of temperature. The microhardness of the homopolymers PHB and PHN was also measured at room temperature to examine the influence of the comonomer ratio. The PHN homopolymer was supplied by Prof. Kricheldorf (University of Hamburg) in powder form with two different morphologies: needle-like and slab-like crystals. Details of the synthesis and characterization of PHN are described elsewhere[28]. The influence of the crystal morphology and sample preparation on microhardness has been reported in a separate publication[29]. The PHN sample with slab-like morphology was compression moulded (75 kN) for 3 min at 400°C. The latter morphology was selected for having a lower melting point than the needle-like crystallites. The PHB homopolymer was supplied by Prof. H. G. Zachmann (University of Hamburg) in the form of an ~ 0.25 mm thick film.

Microhardness measurements

Microhardness was measured at room temperature using a Vickers tester. The microhardness, H, is calculated from

$$H = K\frac{P}{l^2} \tag{1}$$

where P is the applied force in Newtons, l is the diagonal length of the indentation in metres, and $K = 1.854$ is a geometrical constant related to the angle between non-adjacent faces of the squared pyramidal diamond. The length of the indentation diagonal was measured up to ±1 μm with an optical microscope. Loads of 0.10, 0.25, 0.5 and 1 N were used. The slope of the plot P vs L^2 gives the value of the microhardness. Each hardness measurement corresponds to 10 indentations. The estimated error is less than 2%. In order to minimize the creep of the material under the indenter, a loading cycle of 0.1 min was chosen.

The temperature dependence of microhardness was measured using a heating stage. The temperature was calibrated at the surface of the samples by determining the melting point of several standards. Conducting paste was distributed between the sample and the hot stage to improve thermal conductivity. Experiments involving temperature variations for a given sample were performed with a fixed load of 0.1 N.

Wide angle X-ray diffraction measurements

X-ray scattering patterns at room temperature for the quenched and annealed samples of P(HB/HN) 30/70, 58/42 and 75/25, as well as the PHN homopolymers were obtained. X-ray diffractograms were recorded with a Rigaku vertical goniometer attached to a Rigaku high power X-ray generator with rotating anode (Ni-filtered Cu–K$_\alpha$ radiation) using 40 kV and 140 mA. Scans were made in the angular range between 10 and 40° (2θ) at a goniometer speed of 1° min^{-1}, using a time constant of 1. For the determination of the orthorhombic unit cell dimensions the 110 and 200 diffraction peaks were used. The experimental profiles of the 110 and 200 reflections were fitted to Lorentz curves. For the correction of instrumental broadening effects, a silicon sample was used. The size of the coherently diffracting domain values, D, was directly calculated from the integral breadth of each reflection as described elsewhere[7]. The data from the PHB sample are taken from reference[30]. The temperature dependence of the lattice spacing and other X-ray diffraction data for P(HB/HN) 30/70, 58/42 and 75/25 compression moulded samples have been reported elsewhere.

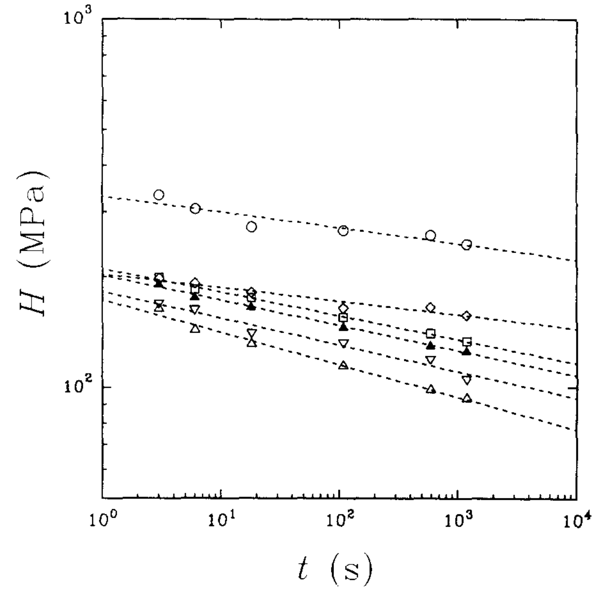

Figure 1 Log–log plot of the microhardness as a function of loading time for the quenched P(HB/HN) samples: ○, 0/100; □, 30/70; ▽, 58/42; △, 75/25; ◇, 100/0. Solid symbols correspond to annealed 75/25

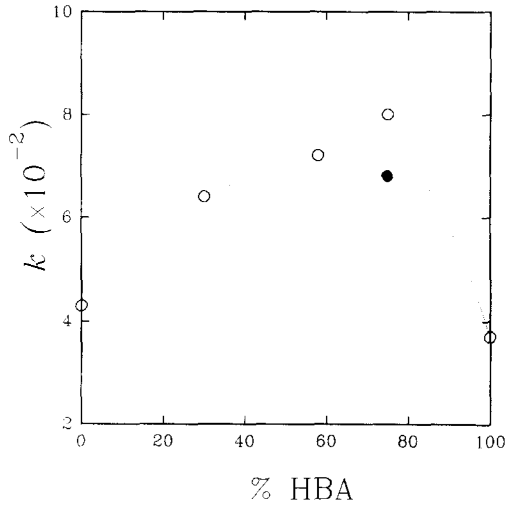

Figure 2 Plot of the creep constant as a function of HBA content. Open symbols, quenched samples; solid symbols, annealed sample

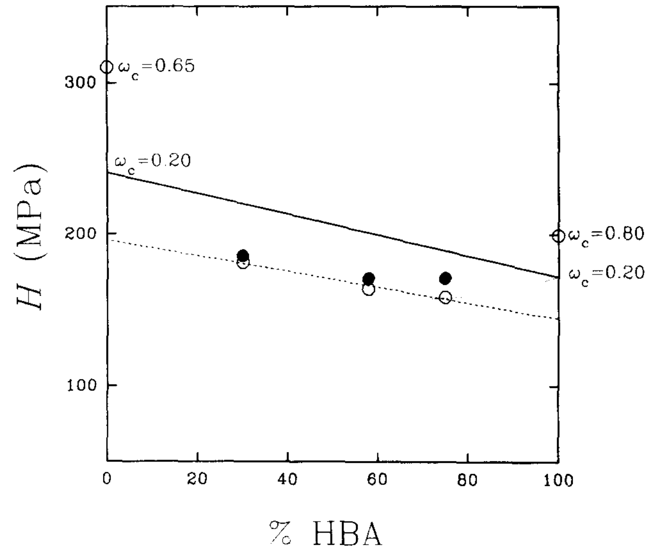

Figure 3 Experimental values of microhardness as a function of comonomer composition for the P(HB/HN) copolyesters. Open symbols, quenched samples; solid symbols, annealed samples. The solid straight line corresponds to the additivity law of single homopolymers normalized to a crystallinity of $w_c = 0.2$. The H data for the homopolymers and their corresponding w_c values are included. The dashed curve represents a proposed variation of H values for the copolymers in contrast to a linear variation (dashed straight line)

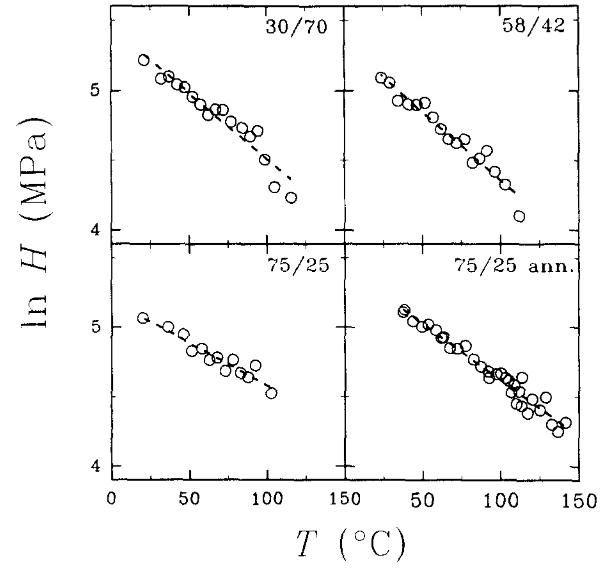

Figure 4 Temperature dependence of microhardness for the quenched samples: 30/70, 58/42, 75/25; and the annealed one: 75/25

RESULTS

Influence of composition on microhardness

Figure 1 shows the microhardness variation as a function of loading time under the indenter for the various samples. This behaviour follows a law of the type

$$H = H_{0.1} t^{-k} \qquad (2)$$

where $H_{0.1}$ is the hardness value at a given reference time (0.1 min) and the slope k of the straight lines in *Figure 1* provides a quantitative measure of the rate of creep under the indenter. *Figure 2* shows the variation of the creep constant k for the series P(HB/HN) as a function of comonomer composition. It is seen that for the samples quenched from the melt, there exists a high deviation from a linear behaviour, the lowest k values, 3.7 and 4.3×10^{-2}, corresponding to the homopolymers PHB and PHN respectively, while the highest k value is obtained for the copolymer 75/25 (8.0×10^{-2}). Annealing of the latter material at 240°C during 24 h, leads to a clear decrease of the creep constant.

Figure 3 represents the plot of microhardness as a function of comonomer composition for a given loading time of 0.1 min. Hardness and degree of crystallinity, ω_c, are usually related according to the expression[22]:

$$H = \omega_c H_c + (1 - \omega_c) H_{nc} \qquad (3)$$

where H_c and H_{nc} are the intrinsic hardness values of the crystalline and non-crystalline phases. Inmost cases, a controlled variation of the crystallinity permits the calculation of H_c and H_{nc} through equation (3). However, as mentioned above, the crystallinity of our samples cannot be substantially changed even if we use widely different preparation methods such as quenching from the melt or long time annealing. Irrespective of the treatment used, values of ω_c near 0.2 were always obtained. *Table 1* shows the calculated crystallinity values for all P(HB/HN) copolyesters. In order to plot comparable results, we have normalized the values of microhardness of the homopolymers to a crystallinity value of 0.2. To do this, one of the two missing values, H_c or H_{nc}, should be known in equation (3). Let us, then, first assume a linear behaviour of microhardness with comonomer composition (dashed straight line in *Figure 3*). The intercept of this line with the vertical axes would give the microhardness values for the two homopolymers having $\omega_c = 0.2$. From these intercept values we may attempt to calculate the corresponding H_{nc} values for PHB and PHN. By using equation (3), H_{nc} values of 127 and 144 MPa are respectively obtained. These values are lower than those of the disordered phase of PET and PEN ($H_{nc} = 163$ MPa for PET and $H_{nc} = 210$ MPa for PEN), homopolymers of quite similar monomer units but with a higher degree of molecular flexibility[20]. Therefore, it does not seem reasonable to assume lower H_{nc} values for the nematic glass of our rigid homopolymers in contrast to the amorphous phase of PET and PEN. We may consider, then, the H_{nc} values of PET and PEN as a lower limit for our PHB and PHN homopolymers. Using these H_{nc} values together with equation (3), the corresponding H values for $\omega_c = 0.2$ were computed for both homopolymers. These H values are represented in *Figure 3* as the intersection of the solid straight line with the vertical axes. This solid line corresponds to the linear additivity law of microhardness values given by the two homopolymers, with an assumed crystallinity of 0.2. It is clear that the H values for the copolyesters are lower than those calculated from the additivity law (solid line). After annealing at high temperature, a slightly increased microhardness value is observed for all samples. This is more evident in the 75/25 copolyester (see *Figure 3*).

Temperature dependence of microhardness

Figure 4 shows the dependence of microhardness with temperature, T, for the quenched copolyesters P(HB/HN) 30/70, 58/42 and 75/25, and for the thermally annealed 75/25. At temperatures close to the glass transition temperature (T_g) (above 100°C), there is a large viscoelastic recovery of the material and no indentations are observed after load removal. Above

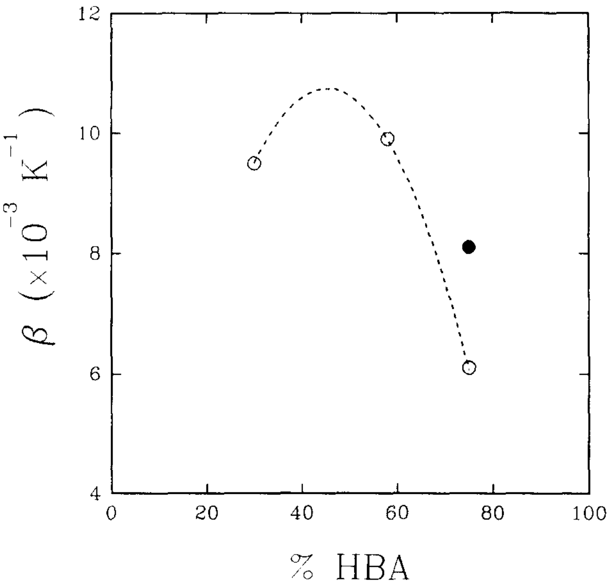

Figure 5 Plot of the thermal expansion coefficient of the copolyesters P(HB/HN) as a function of HBA content. Open symbols, quenched samples; solid symbols, annealed sample

T_g, the microcrystals are probably mechanically stable at the strains involved in micro-indentation and the non-crystalline regions have enough molecular mobility, in the nematic-like state, as to contribute to a complete recovery of deformation. In the temperature range below 125°C, H follows an exponential decrease as a function of T given by

$$H = H_0 e^{-\beta T} \tag{4}$$

where H_0 is the hardness of the material at a temperature of 0 K and β is the so-called coefficient of thermal softening. *Figure 5* shows the β coefficient for the investigated copolymers as a function of comonomer composition. It is to be noted that these values (ranging from 9.9 to $6.1 \times 10^{-3}\,\mathrm{K}^{-1}$ for 58/42 and 75/25 respectively) are of the same order of magnitude as that of copper measured at high temperature (>400°C)[31].

DISCUSSION

Microstructure

When discussing the microhardness of P(HB/HN) copolyesters, it is convenient to emphasize the fact that 80% of the material is located in non-crystalline regions. However, by taking into account that many molecules have to be attached to one or more crystalline segments, it seems reasonable, owing to chain rigidity, that the overall packing of the molecular chains across the material is influenced by the three-dimensional distribution of crystallites. Let us start the discussion of the results by analysing the more abundant information which is obtained from the crystalline phase. Apart from the degree of crystallinity, which has been shown to remain nearly constant, two other main parameters must be taken into account: crystal size and molecular packing[26,27].

Microhardness is known to be dependent on the average crystal thickness of the sample[26]. In our case, no SAXS maxima were observed for the non-oriented samples of P(HB/HN) quenched from the melt or after thermal treatment. As previously suggested[3], the absence of SAXS maxima can be due to the lack of contrast between the electron density of the crystalline and the non-crystalline phases. Thus, the coherence length of the lattice in the 110 and 200 directions of the orthorhombic unit cell can be used as a measure of the lateral size of the microcrystals. Values of $D_{110} \sim 190$ Å and $D_{200} \sim 50$ Å are obtained independently of copolyester compositions. For the hexagonal phase of the 75/25 sample we have: $D_{110} = D_{200} = 120$ Å. For the homopolymers, however, the D-values are about 50 Å larger in both directions. The difference of D_{hk0} values between the homopolymers and copolymers is negligible, as it would contribute to an increase in the microhardness values of PHB and PHN of 4% at the most[26].

Molecular packing

Once the influence of crystallinity and crystal thickness is discarded, one is bound to consider that changes in microhardness are mainly due to variations of the average molecular packing within the crystalline and the non-crystalline phases. The packing of the chains in the polymer and, therefore, the changes in cohesive energy of the crystals, have been shown to play a role in determining the hardness value[32]. Thus the closer molecular packing of crystalline polymers (PE, PEEK) with increasing crystallization temperature leads to an increase in H[32,33].

From previous work[7] it is known that, at room temperature, P(HB/HN) 30/70 and 58/42 show an orthorhombic crystal structure with an angle γ between the diagonals of the unit cell of 114° for the copolyester 30/70 and 117° for the 58/42 composition (*Table 2*). Annealing at high temperature leads to a lattice structure with angles $\gamma = 110°$ for the 30/70 sample and $\gamma = 115°$ for the 58/42 copolymer, although no significant change in the cross-sectional area of the unit cell is observed. On the other hand, the copolymer P(HB/HN) 75/25 shows a pseudohexagonal structure at room temperature. On annealing, this structure is gradually transformed towards an orthorhombic phase with a more dense molecular packing[6]. Both homopolymers, PHB and PHN, show a well defined orthorhombic crystal structure at room temperature[30,34].

Having this in mind, the results of *Figure 1* and *Figure 2* suggest that creep is favoured in those materials which show a crystalline molecular packing close to an hexagonal symmetry. The most compact molecular packing shown by the homopolymers yields the lowest creep constant values k. Annealing of the 75/25 copolymer means a transformation towards an orthorhombic symmetry which is reflected in a parallel decrease of k.

The dashed curve in *Figure 3* represents the experimental values of microhardness as a function of comonomer composition of constant crystallinity and crystal thickness. Our results show that the H values for the copolyesters are lower than those calculated from the additivity law (solid line), while those of the annealed samples show a slight tendency to smaller deviations.

The molecular packing in the crystal phase can be described in terms of the molecular cross-sectional area ($a \times b/2$), a and b being the intermolecular parameters of the orthorhombic unit cell. *Figure 6* shows the value of the cross-sectional area for both series (quenched from the melt and annealed samples) as a function of

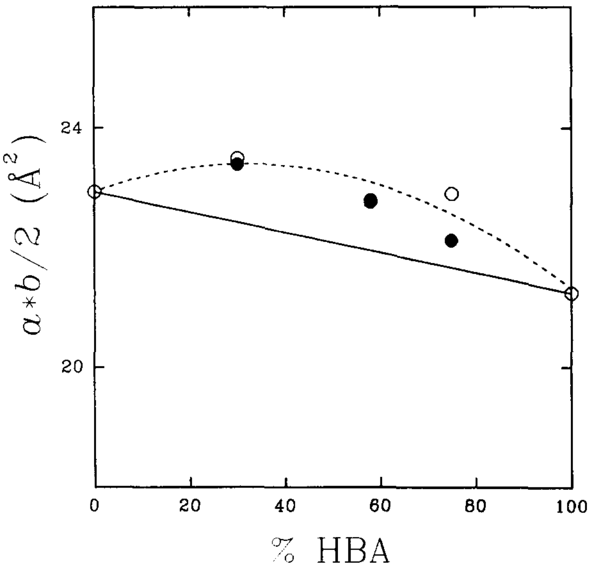

Figure 6 Molecular cross-sectional area ($a \times b/2$) of the crystal phase as a function of comonomer composition. Same symbols as in *Figure 3*

Table 2 γ angle of the crystalline unit cell, at room temperature, for the P(HB/HN) copolyesters

P(HB/HN)	γ (°, quenched)	γ (°, annealed, 24 h)
30/70	114	110
58/42	117	115
75/25	120	108

comonomer composition. The deviation of microhardness values from the additivity law can now be directly related to the corresponding deviation of the values of the cross-sectional area of the crystalline phase from a linear plot. The deviation from the hexagonal symmetry (decrease in γ) when annealing the samples (see *Table 2*) is reflected in a small increase in the microhardness values (see *Figure 3*). The largest H increase corresponding to the HBA rich copolymer corresponds to a clear decrease in the cross-sectional area (*Figure 6*).

Since the microhardness decrease with temperature is concurrent with the lattice expansion, the thermal variation of microhardness can be related in a first approximation to the cross-sectional area of the molecules in the crystalline phase (*Figure 7a*). A linear variation of the microhardness with the crystalline cross-sectional area is obtained in all cases. However, the microhardness of the 75/25 copolymer, quenched and annealed, is described by two different well separated lines. This means that the two different crystal packings in the 75/25 material give rise to the same microhardness. This is possible if the microhardness variation of the non-crystalline regions follows the opposite trend to the microhardness of the crystals.

The non-crystalline phase in these materials essentially consist of rigid rod molecules with cylindrical symmetry along their chain axes. Therefore, the cross-sectional area of the molecules in the non-crystalline phase could be considered to be approximately equal to $\pi \times (d/2)^2$; i.e. proportional to the squared intermolecular distance d^2. *Figure 7b* shows the variation of microhardness with d^2 in the non-crystalline material. The d-value was derived from the X-ray scattering maximum of the non-crystalline halo after application of the Ehrenfest relation[35]. It can be immediately observed that while annealing produces a contraction of the molecules within the crystal lattice, it results in an expansion of the average intermolecular distance in the non-crystalline phase. The superposition of two opposite effects explains the small increase of microhardness observed on quenching. Thus, while the crystalline regions become harder, the microhardness of the non-crystalline regions decreases not so markedly, giving an overall small increase. This molecular behaviour can be envisaged in the following way: after annealing the molecules in the microcrystals become better packed into an orthorhombic structure, probably inducing some of the molecular non-crystalline segments closely attached to them to contract in the same way. However, the rest of the non-crystalline material appears to remain expanded, after the annealing treatment, to fill the resulting free space. This compensation mechanism yields the very low bulk thermal expansion coefficient experimentally observed for these materials[36].

In order to account for the double contribution of crystalline and non-crystalline phases, let us next introduce an average cross-sectional area of the molecules, A:

$$A = w_c \frac{a \times b}{2} + (1 - \omega c)\pi\left(\frac{d}{2}\right)^2 \qquad (5)$$

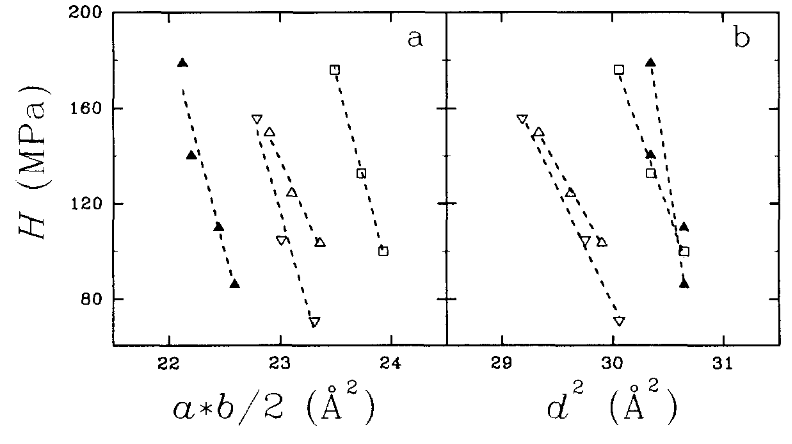

Figure 7 Dependence of the microhardness with the cross-sectional area of the molecules; (a) in the crystal phase; (b) in the non-crystalline regions. □, 30/70; ▽, 58/42; △, 75/25. Solid symbols, annealed 75/25

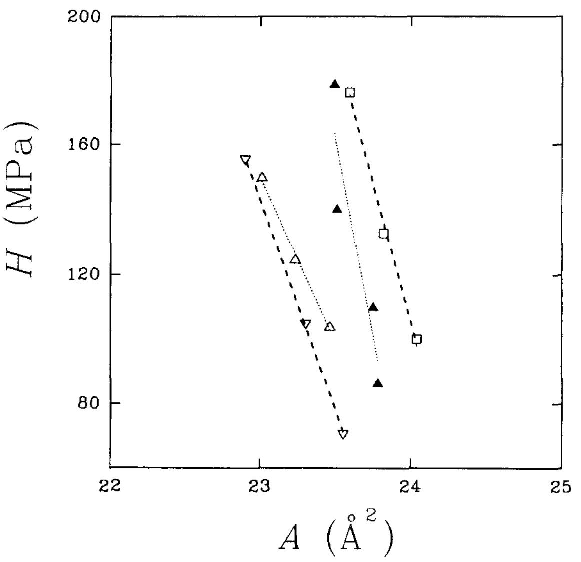

Figure 8 Linear dependence of H with the average cross-sectional area A of the molecules for the various copolyesters. Same symbols as in *Figure 7*

Table 3 Comparison of experimental values of the two sides of equation (6) for the P(HB/HN) copolyesters

P(HB/HN)	Thermal treatment	$H_0\beta$ (MPa °C^{-1})	$\frac{\delta H}{\delta A} \times \frac{\delta A}{\delta T}$ (MPa °C^{-1})
30/70	Quenched from the melt	1.13	1.27
58/42	Quenched from the melt	1.06	1.06
75/25	Quenched from the melt	0.76	0.77
75/25	Annealed at 240°C, 24 h	0.92	1.03

Figure 8 illustrates the linear dependence of H with the average cross-sectional area A for the various copolyesters. The two lines corresponding to the 75/25 copolyester are now much closer, with all the experimental points clearly separated from those of the other two materials. A unique curve has not been found probably due to the simplicity of the model and the errors in the calculation of the intermolecular non-crystalline distance. However, the dependence of microhardness with temperature can, as a first approximation, be directly related to the variation of the defined average cross-sectional area.

Thermal softening and expansion coefficient

Since the softening of the material is related to the thermal expansion of the molecules in both phases, one may attempt to correlate the coefficient of thermal softening with the thermal expansion coefficient of the average cross-sectional area. The variation of H with T can be written as:

$$\frac{\delta H}{\delta T} = \frac{\delta H}{\delta A} \times \frac{\delta A}{\delta T} \tag{6}$$

In this expression, $\delta H/\delta T$ can be approximated to $H_0\beta$, in the range of temperatures studied, provided the value of β is small. The quantity $\delta H/\delta A$ is, furthermore, the slope of the plots in *Figure 8*. On the other hand $\delta A/\delta T$ is proportional to the thermal expansion coefficient of the average cross-sectional area A (α_A). We have calculated both sides of equation (6) and the results are collected in *Table 3*. Results show a good correlation between $H_0\beta$ and $\delta H/\delta A \times \delta A/\delta T$. Consequently, the coefficients β and α_A can be related by:

$$\beta = \frac{\bar{A}}{H_0} \times \frac{\delta H}{\delta A}\alpha_A \tag{7}$$

where $\bar{A}$ is the average value of A over the range of temperatures studied. It is noteworthy that equation (7) offers the possibility to derive the thermal expansion coefficient of a polymer from microhardness measurements. Of course, the constant $\bar{A}/H_0 \times \delta H/\delta A$ is a parameter which is material dependent.

CONCLUSIONS

Microhardness values, at room temperature, of non-oriented P(HB/HN) copolyesters as a function of composition show a clear deviation from the linear additivity law of single components. Such a deviation is shown to be mainly related to changes in the packing of the rigid molecules. Degree of crystallinity and crystal size, on the contrary, remain constant with composition and do not have any significant contribution to the microhardness value. The packing of the molecules, and therefore H, can be characterized by an average cross-sectional area, which includes crystalline and non-crystalline regions. The slightly higher microhardness values found in annealed materials as compared with the quenched ones is proposed to be due to an increase of H_c together with a concurrent decrease of H_{nc}. Finally, the parallel temperature dependence of, both, microhardness and average cross-sectional area, leads to an analytical expression which relates the coefficient of thermal softening to the thermal expansion coefficient of the cross-sectional area of the materials.

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