Configuration of a Thermotropic Polyester from Small-Angle Neutron Scattering

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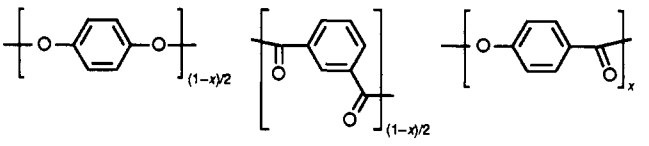
ABSTRACT: Small-angle neutron scattering has been used to ascertain the configuration of a random thermotropic terpolyester at three temperatures between the glass transition and the melting point on four fractions of different molecular weight. Specimens were prepared by casting films from solutions and subsequent annealing at selected temperatures for 1 h. All samples have a small amount of crystallinity, but at the lowest annealing temperature, 448 K, the molecules have a random-coil configuration. At the two higher annealing temperatures, 493 and 523 K, the molecules become increasingly stiff. This is observed as an increase in the persistence length from 9 Å at 448 K to ca. 44 Å at 523 K. The variation of the ratio $\langle s^2 \rangle_w / M_w$ with M_w for the two higher temperatures displayed the characteristics of a Kratky–Porod wormlike chain. Persistence lengths and shift factors were obtained from an extrapolation procedure based on an approximation for the dependence of the radius of gyration of a wormlike chain on the contour length and persistence length. The value of the persistence length obtained at 523 K is in good agreement with a value obtained from scanning tunneling microscopy elsewhere. These data suggest that the transformation to the nematic mesophase at temperatures above the melting point is aided by stiffening of the molecule at lower temperatures.

Introduction

Generally, the backbone of a thermotropic main-chain liquid-crystal polymer (MCLCP) is considerably less flexible than the more "conventional" vinyl polymers. For some MCLCPs this rigidity is maintained in dilute solution, leading to a rodlike configuration and the observation of depolarized light scattering from their solutions.[1] Other polymers, with rigid units in the main chain, including that studied here, do not display a rodlike configuration in dilute solution but in bulk; the combination of a relatively rigid and linear backbone together with the close packing of molecules favors the development of a mesophase melt, wherein the molecules are arranged in "domains" in which the mutual alignment and direction of chain axes are highly correlated.[2] A nematic phase is usually observed.[3] The solid-state molecular configuration of such molecules has been of considerable theoretical interest;[4-6] however, experimental investigation has been little reported. That which has been reported has focused on specimens aligned in a magnetic field;[6] examination of the quiescent melt or samples rapidly quenched from the high-temperature mesophase has yet to be reported. Furthermore, there appear to have been no experiments or speculations on the configuration of MCLCPs at temperatures below that at which they display liquid-crystalline mesophases nor on the possible configurational changes which may take place as the polymer approaches the transition temperature. Since the MCLCP is usually at a temperature well above its T_g before it reaches T_m, there is considerable long-range motion and therefore the molecule may rearrange its configuration relatively easily as conditions approach T_m.

The paucity of the experimental data is perhaps attributable to two sources. First, small-angle neutron scattering (SANS) is perhaps the only method of obtaining configurational properties of polymers in bulk (melt or solid); this requires the preparation of a deuterated polymer, and for MCLCPs this may be difficult. Second, many MCLCPs are aromatic polyesters, and at temperatures above the transition to the mesophase they undergo rapid transesterification, causing problems in the interpretation of SANS data to which we allude below. The degree of liquid crystallinity and consequently the ease of melt processing and ultimately the modulus of an MCLCP depend on the existence of sufficiently long straight sequences in the polymer. However, this aspect has to be balanced by the polymer having a melting point below the degradation temperature, and for this purpose nonlinear monomer units are often incorporated into the MCLCP polymer chain.

We report here the use of SANS to evaluate the radii of gyration of discrete fractions of a MCLCP which we designate LCP. This polymer has residues of hydroxybenzoic acid (HBA), hydroquinone (HQ), and isophthalic acid (IPA) randomly distributed along the molecule. The stoichiometric formula is



where $x = 0.36$.

The incorporation of IPA units introduces additional nonlinearity (i.e., in addition to that arising from the population distribution of rotational states about main-chain bonds) into the molecule which reduces the crystalline perfection and reduces the melting point but does not prevent the formation of a thermotropic mesophase. Dilute-solution properties of this polymer have been reported earlier,[7] and it was demonstrated that the polymer has random-coil behavior in dilute solution since no depolarized scattering was observed. Other aspects of this polymer which we have studied include quasi-elastic light scattering from dilute solutions,[8] kinetics of transesterification reactions[9,10] in the melt, and the crystalline reorganization during heating below the melting point.[11]

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The kinetics of the transesterification in the melt are rapid; the outcome of this reaction is that, although the average molecular weight of the specimen is not altered, the monomer segments become redistributed over all polymer molecules in the sample. For SANS experiments this means that the deuterated segments in the labeled molecules become distributed over all (both deuterated and hydrogenous) molecules to an increasing extent as the transesterification proceeds. Analysis of the results, in the absence of any knowledge of the transesterification reaction, would therefore indicate that the molecular weight of the deuterated MCLCP had decreased. Although there is no such degradation of the polymer, the deuteriolabeled sequences are no longer correlated with each other after transesterification and moreover this loss of correlation increases as the time of transesterification increases. Consequently, there is no prospect of obtaining the configuration of these polymers in the nematic mesophase; therefore, we report here on the configuration of LCP at three temperatures between T_g and T_m, in the absence of transesterification.

Experimental Section

Preparation of Deuterated LCP. Deuteriohydroquinone was prepared by repeated refluxing of hydrogenous hydroquinone in a 2% (v/v) solution of deuteriosulfuric acid in deuterium oxide. After each reflux period (6 h), the hydroquinone was recovered by cooling the solution in ice and filtering off the crystals. The extent of the deuteration was checked by comparing the ESR signal with that reported by Yao and Heller.[12] After five separate refluxings, complete deuteration was obtained. The procedure of Komiyama and Hiroi[13] was adopted to prepare deuteriohydroxybenzoic acid. This involved the use of β-cyclodextrin hydrate as an inclusion catalyst; the yield of this reaction was ca. 40–45% of the theoretical, and analysis by NMR indicated a level of deuteration of 98 atom %. Attempts to synthesize deuterioisophthalic acid by low-pressure oxidation of deuterio-*m*-xylene met with no success. Consequently, the deuteriolabeled LCP polymer used here contains hydrogenous isophthalic acid residues. Deuterium LCP (dLCP) was prepared from these monomers by a dispersion polymerization method.[14] A fully hydrogenous polymer (hLCP) was prepared under exactly the same conditions.

Small-Angle Neutron Scattering. Each of the polymers prepared as described above was fractionated by the solvent precipitation procedure described elsewhere.[8] Molecular weights were obtained by solution light scattering, and dLCP fractions were combined with hLCP fractions of the same molecular weight. The mixed polymers were dissolved at a concentration of 2% (w/v) in a mixture of 95% (v/v) trifluoroacetic acid and 5% (v/v) dichloromethane; the solution was then poured into a shallow dish made of poly(tetrafluoroethylene) (PTFE). Solvent was allowed to evaporate for 24 h, after which time the resultant pliable sheets were removed and disks (20 mm diameter) cut from them. Each of these disks was placed between glass plates and vacuum dried for 1 week, over which time the temperature was slowly raised to 373 K. Typically, the resultant films had thicknesses between 0.1 and 0.2 mm.

All the SANS data reported here were obtained using the D11 diffractometer at the Institut Laue-Langevin, Grenoble, France. The incident neutron wavelength was 8 Å, and a sample to detector distance of 10 m was used; hence, the range of the scattering vector covered by the area detector was $4 \times 10^{-3} \leq Q/\text{Å} \leq 2.5 \times 10^{-2}$. Initial experiments were made on specimens with a range of concentration of dLCP between 1% and 5% (w/w). However, Zimm plots of the data (vide infra) showed that the second virial coefficient for this system was zero; therefore, for subsequent experiments a fixed dLCP concentration of 5% (w/w) was used. SANS experiments were performed on samples which had been annealed for 1 h at temperatures of 448, 493, and 523 K and subsequently quenched to ambient temperature, at which temperature all SANS experiments were carried out. The annealed samples were prepared by stacking several of the films prepared as described above in a heated infrared sample preparation die. During annealing the films were not compressed, but the jaws of the press were placed in light contact with the die elements to prevent any adventitious buckling of the films during annealing. After annealing, since the individual films which made up the stack were not fused together, their thicknesses could be checked; no changes in thickness on annealing were noted. Earlier work on the transesterification kinetics of this terpolyester had shown that transesterification could not be detected at the temperatures used here,[9] consequently, the SANS results obtained are not complicated by this process. This contrasts with SANS data for a different polyester system recently reported.[29] All scattering data were corrected to the same thickness and transmission; background scattering was subtracted using the scattering from hLCP alone.

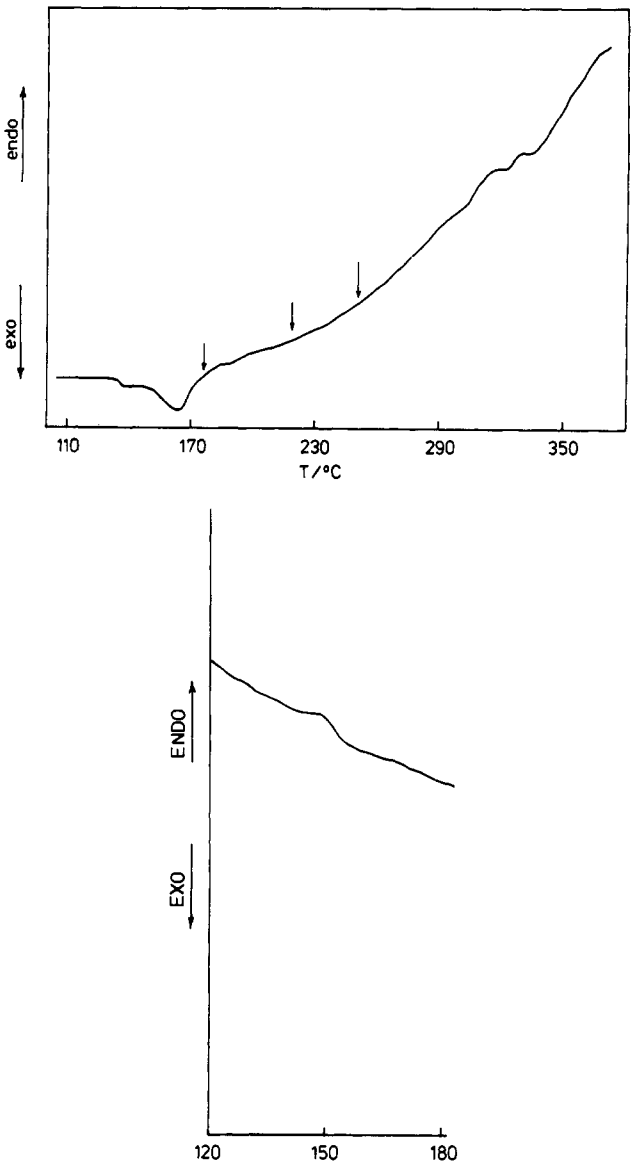

Figure 1. DSC thermogram for LCP. Temperatures at which SANS samples were annealed at are marked on the thermogram by arrows. Enlargement of the DSC thermogram in the region of T_g.

Results and Discussion

The DSC thermogram for LCP is shown in Figure 1a; the T_g is evident and is centered at 403 K. On the scale of this diagram the transition attributed to the T_g appears to be exothermic and contradicts the general observations for other polymers. However, on a larger temperature scale (Figure 1b), the initial part of the thermogram is endothermic but rapidly becomes exothermic in nature[30]

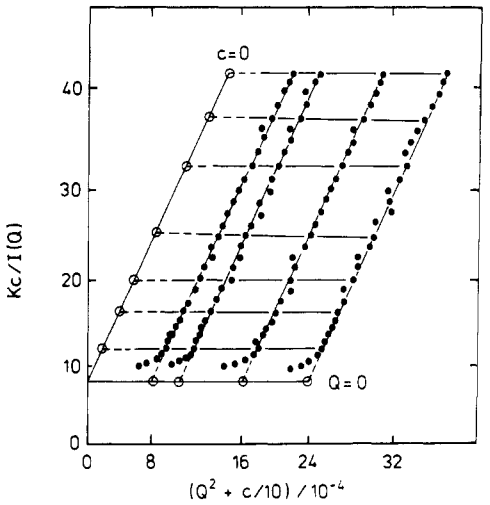

Figure 2. Zimm plot for dLCP in hLCP annealed at 523 K for 1 h.

Table I
Weight-Average Molecular Weights and Radii of Gyration from SANS

	$\langle s^2\rangle_w{}^a/10^3$ Å^2		
$M_w/10^3$	448 K	493 K	523 K
103.0 ± 9	4.44	5.62	7.57
81.0 ± 7	3.73	4.82	5.49
63.0 ± 7	2.69	3.18	4.08
55.0 ± 7	2.41	2.78	3.40

[a] The average statistical error on the values of $\langle s^2\rangle_w$ obtained from extrapolation to zero concentration of deuterium LCP is 8%.

and is immediately followed by a crystallization exotherm. In this region, the growth of small spherulites is observed in the initially transparent specimen when it is viewed on a hot-stage microscope. At the completion of this exotherm, there are no further transitions until the melting point at ca. 545 K intervenes; the polymer then transforms to a nematic mesophase and remains in that state until degradation takes place at ca. 620 K. The lowest annealing temperature used corresponds to the completion of the crystallization exotherm while the highest temperature is some 20 K below T_m, thereby avoiding any possibility of transesterification. A typical Zimm plot obtained is shown in Figure 2; extrapolations to $Q = 0$ (where $Q = (4\pi/\lambda)\sin\theta$, λ = neutron wavelength and 2θ = scattering angle) and $c = 0$ enabled calculation of the weight-average molecular weight, M_w, the z-average mean-square radius of gyration, $\langle s^2\rangle_z$, and the second virial coefficient, A_2. From the slope of the $Q = 0$ line, it is evident that A_2 is zero within experimental error, and thus at the temperatures used the mixture of dLCP in hLCP forms an "ideal solution" with no excess thermodynamic properties. Weight-average molecular weights and weight-average radii of gyration obtained from SANS data are given in Table I. Correction of the z-average values of the mean-square radius of gyration obtained from the Zimm plots to weight-average values was made using the correction procedure of Kurata and Stockmayer;[15] i.e.

$$\langle s^2\rangle_w = \langle s^2\rangle_z (h+1)/(h+2) \qquad (1)$$

with $1/h = (M_w/M_n) - 1$. For M_w/M_n a value of 1.2 was used, this value being an average of all values obtained for a larger number of similar fractions from a CONTIN analysis of autocorrelation functions from photon correlation spectroscopy on dilute solutions of LCP. This value of the polydispersity was confirmed by size-exclusion chromatography on some of the fractions using the trifluoroacetic acid/methylene dichloride mixture referred to above as the eluting solvent. Separate dilute-solution light scattering measurements on one of the hLCP fractions before and after heating showed that no degradation had taken place on heating for 1 h at the highest temperature used here. All of the molecular weights and radii of gyration reported here are obtained from SANS data.

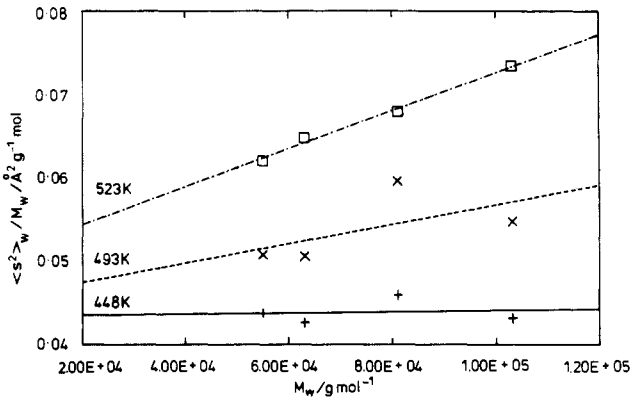

Figure 3. Values of $\langle s^2\rangle_w/M_w$ as a function of M_w for LCP fractions annealed at the temperatures indicated.

Table II
Values of K and α for the Relation $\langle s^2\rangle_w = KM_w{}^\alpha$

T/K	α	K
448	1.0_2	0.036
493	1.18	0.007
523	1.26	0.003_6

The relationship between the molecular weight and the mean-square radius of gyration is given by the empirical equation

$$\langle s^2\rangle_w = KM_w{}^\alpha \qquad (2)$$

Figure 3 shows $\langle s^2\rangle_w/M_w$ as a function of M_w and clearly indicates that, for the lowest temperature, $\alpha = 1$ but at the two higher temperatures $\alpha > 1$. Values of $\alpha = 1$ are characteristic of Gaussian coils in their unperturbed state; additionally values of $A_2 = 0$ are also symptomatic of molecules being on their unperturbed "ideal" state. Consequently at 448 K we conclude that LCP has a random-coil-like configuration and is in its unperturbed state. Furthermore, the value of $(\langle s^2\rangle_w/M_w)^{1/2}$ (0.21 Å mol$^{1/2}$ g$^{-1/2}$) obtained from the data for the fractions annealed at 448 K is in reasonable agreement with that calculated from the value of $(\langle r^2\rangle_0/M_w)^{1/2}$ obtained from dilute-solution light scattering data reported earlier (0.32 Å mol$^{1/2}$ g$^{-1/2}$). The values of K and α in eq 2 have been calculated by least-squares analysis of double-logarithmic plots of the mean-square radius of gyration as a function of the molecular weight, and these are tabulated in Table II. At the two higher temperatures the value of α is considerably increased, indicating an increase in the molecular dimensions. This increase cannot be attributed to an expansion of the molecule via excluded-volume effects since the value of the second virial coefficient remains unaltered at zero for these higher temperatures. Evidently some change in the configurational nature of the molecule is taking place. Large values of α are associated with polymer molecules having a rodlike configuration, and for true rigid-rod molecules then we expect $\langle s^2\rangle \propto M_w{}^2$; consequently for the temperatures of 493 and 523 K, LCP appears to be in some intermediate state between a random coil and a rigid rod. Such intermediate behavior has been described by broken-rod models,[16,17] but their use and application to experimental data is by no means straight-

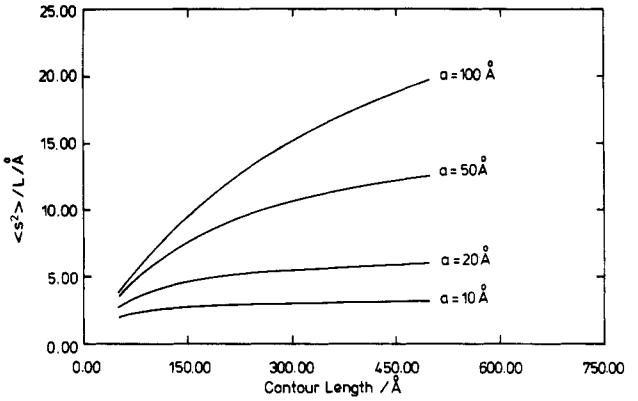

Figure 4. Dependence of $\langle s^2 \rangle / L$ on contour length, L, calculated for a Kratky–Porod wormlike chain for the values of the persistence length noted.

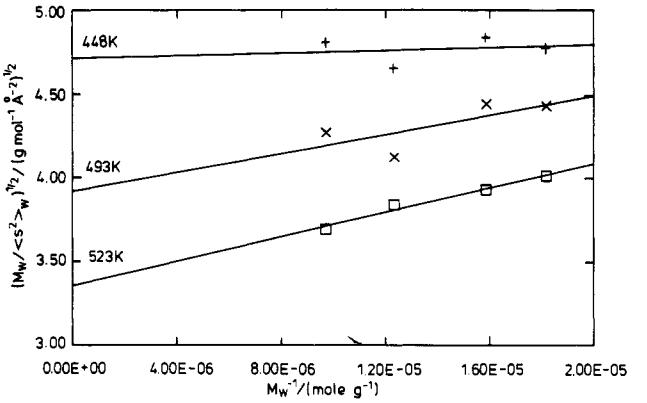

Figure 5. Murakami plots for LCP annealed at the temperatures shown using radii of gyration and molecular weights obtained from SANS.

forward. Of considerably more value in the present case is the use of wormlike chains as models for the configuration of LCP. The simple form of this model, the Kratky–Porod wormlike chain, has been known for some time[18] and is a continuous version of a freely rotating chain wherein the backbone has continuous curvature but the direction of curvature at any point in the backbone trajectory is random. Fundamental parameters of this model are the contour length, L, and the persistence length, a, the latter parameter being defined by Flory[19] as the average sum of the projection of all bonds $j \geq i$ on bond i, where bond i is remote from the chain ends, in an indefinitely long chain of bonds. Hence, for a chain of N bonds of length l with a supplementary bond angle, φ, then

$$L = \lim_{\substack{N \to \infty \\ l \to 0}} Nl \tag{3}$$

$$a = \lim_{\substack{\varphi \to 0 \\ l \to 0}} (l/(1 - \cos \varphi)) \tag{4}$$

The attractive feature of the Kratky–Porod model is that, by adjusting the value of a, random-coil and rigid-rod configurations may be described by one model. Subsequently, this model has been expanded and discussed in considerably greater detail by Yamakawa and coworkers, who have described the *helical* wormlike chain.[20-23] This model has random coils, rigid rods, and Kratky–Porod wormlike chains as special cases, and the molecule is now described by four parameters, the persistence length, the constant curvature and torsion of the characteristic helix, and Poisson's ratio. Even with the customary assumption that the last parameter is zero, the helical wormlike chain is far too sophisticated for application to the data we have available here and therefore we have restricted ourselves to the original Kratky–Porod wormlike model. For this model[24]

$$\langle s^2 \rangle = (aL/3) - a^2 + (2a^3/L)[(1 - a/L)(1 - \exp(-L/a)] \tag{5}$$

Since $L \propto M$, then $\langle s^2 \rangle / L$ is qualitatively equivalent to the experimentally determined quantity $\langle s^2 \rangle_w / M_w$. Values of $\langle s^2 \rangle / L$ calculated from eq 5 for selected values of a and for a range of values of L are plotted in Figure 4 as a function of L. The noteworthy point is that, as the persistence length increases, the dependence of $\langle s^2 \rangle / L$ shows an increasingly positive deviation from a line of zero slope. This is exactly the behavior we observe in Figure 3 for the experimental data obtained by SANS; however, there is no evidence in the experimental data for the curvature predicted in Figure 4. This is due to the limited range of molecular weights studied here; marked curvature only becomes apparent for values of L which would correspond to molecular weights of 5000 and below for LCP. The lowest molecular weight we used was ca. 55 000. In principle, values of a and L could be obtained by fitting eq 5 to the data of Figure 2; however, the small number of data points makes this an unwise procedure, and therefore we have resorted to the linear extrapolation procedure of Murakami et al.[25] Their approximation to eq 5 is

Table III
Persistence Lengths and Shift Factors for LCP in the Solid State from Murakami Plots

T/K	a/Å	M_L/Å^{-1}
448	9.0 ± 3	66.8 ± 8
493	31.2 ± 5	159.4 ± 8
523	44.3 ± 5	165.9 ± 8

$$(M_w/\langle s^2 \rangle_w)^{1/2} = (3M_L/a)^{1/2}[1 + 3aM_L/2M_w] \tag{6}$$

The factor M_L is the shift factor and is the polymer molecular weight divided by the contour length, L. All the data plotted according to eq 6 and the linear least-squares fits are shown in Figure 5, and the values of a and M_L obtained are given in Table III. From these data and this analysis, it appears that LCP specimens prepared by casting from dilute solution retain the dilute-solution Gaussian coil configuration for temperatures just greater than that where the crystallization exotherm is completed. At higher temperatures the persistence length increases with temperature; i.e., the molecule stiffens and becomes more rodlike. Over a temperature range of 75 K the persistence length increases by a factor of 5; however, we are unable to say whether this increase in persistence length, and therefore increasing rigid-rod character, continues into the nematic melt phase since transesterification reactions rapidly take place above the melting point of 543 K. Yamakawa[26] has tabulated values of M_L and a for a variety of polymers. Values of M_L range from ca. 9 Å^{-1} for poly(ethylene oxide) to 215 Å^{-1} for schizophyllan, the majority of values being in the range 20–40 Å^{-1}. High values of M_L are associated with polymers which are generally accepted as being truly rodlike, e.g., DNA and poly(γ-benzyl L-glutamate) in dimethylformamide. High values of M_L indicate a large number of monomer units per unit contour length and therefore could be indicative of helical structures being present in the molecule since this is the most efficient way of obtaining large values of M_L. However, we believe that such structures are highly unlikely for this random terpolyester. The values of M_L

we have obtained for LCP fractions annealed at 493 and 523 K are considerably higher than the average of the values quoted by Yamakawa, whereas the value for the fractions annealed at 448 K is marginally higher than those quoted for syndiotactic forms of vinylic polymers. Other work[11] has shown that, at temperatures in this region and on prolonged annealing (24–72 h), LCP undergoes a crystalline reorganization which appears to consist of organized regions of hydroquinone and isophthalic acid residues. Although, no evidence for such reorganization could be observed for the short annealing times used here, the large values of M_L may presage the crystalline reorganization which becomes evident on annealing for long times. Confirmation of this speculation requires a detailed correlation of SANS data with crystalline diffraction patterns, and such data are unavailable for LCP as yet.

The values of the persistence length obtained are not remarkably high. At 448 K the value of 9 Å is of the same order of magnitude as the values quoted for poly(dimethylsiloxane), poly(ethylene oxide), and other vinyl polymers. (N.B., Yamakawa actually gives values of the stiffness factor which is equal to $2a$.) Since the persistence length is twice the Kuhn statistical segment length, the values obtained indicate that the statistical step length increases from ca. 5 Å to ca. 22 Å over the temperature examined. On average the monomer unit length in LCP is 6.5 Å, and hence at the lowest temperature the statistical segment is identified with a monomer unit which is commensurate with the exhibition of random-coil-like behavior observed in the variation of $\langle s^2 \rangle_w$ with M_w and remarked on earlier. This observation also suggests that there is considerable independence of rotation about each of the ester linkages which make up the main-chain backbone. At the highest temperature it appears that there are three to four monomer units in the statistical unit of LCP. At the two higher temperatures the increased values of the persistence length of 30–45 Å are on a par with the syndiotactic forms of conventional vinylic polymers such as poly(methyl methacrylate) and poly(vinyl chloride) in their syndiotactic form but are considerably less than the values of 500 and 1500 Å for DNA and poly(γ-benzyl L-glutamate), respectively. However, it is abundantly evident that annealing LCP at the higher temperatures has stiffened the molecules considerably and increased the rodlike character of the molecule.

Recently Krömer et al.[27] have reported on a solution characterization of a thermotropic polyester consisting of 70 mol % HBA and 30 mol % 2-hydroxy-6-naphthoic acid. They obtained a value of 120 Å for the persistence length by a numerical analysis of the values of the radius of gyration and the hydrodynamic radius. Since this polymer would be considerably more rigid than LCP due to the naphthoic residues in the main chain, the considerably larger value of the persistence length is not surprising. Values of persistence length have been reported for other main-chain aromatic polyesters, and these are highly scattered.[1,29,30] Not only do the values depend on the chemical constitution of the polymers but also they depend on the techniques used. Moreover, there is considerable variation within that obtained by one technique. Quoted values range from 10 to 400 Å, with the majority in the region 35–90 Å; our values here are consistent with this range, the lower values we observe being attributable to the fact that the polymer is not within the mesophase range. Donald et al.[28] have performed a series of scanning tunneling microscopy experiments on LCP and related materials where x is varied. In each case the polymer was

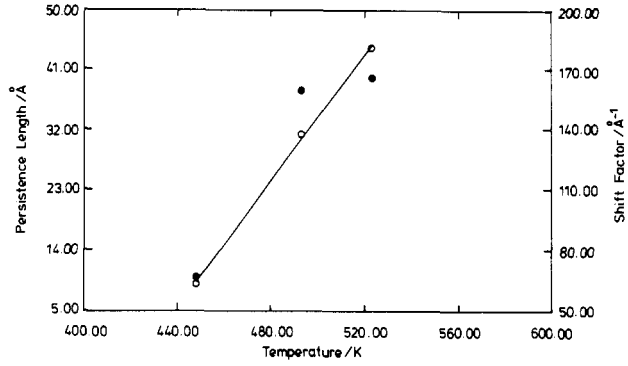

Figure 6. Temperature dependence of the persistence length and the shift factor obtained from Murakami plots of SANS data: (○) persistence lengths; (●) shift factors.

taken above its melting point (where rapid transesterification takes place, and thus the polymer becomes unamenable to configurational investigation by SANS) and allowed to cool before being examined in the scanning tunneling microscope; the persistence length was obtained as the distance over which the molecules were linear. For $x = 0.36$ a value of 40 ± 5 Å was obtained which is in excellent agreement with the values reported here at 493 and 523 K. The temperature dependences of both a and M_L are shown in Figure 6. It appears that the persistence length has a linear dependence with temperature, and extrapolation of this behavior into the melt suggests that the persistence length approaches a value of ca. 65 Å; however, since the molecule undergoes a first-order phase transition at T_m, it is unsafe to assume that this linear dependence is maintained. It is also noteworthy that the shift factor has a considerably different value at 448 K compared to the two higher temperatures; this is due to the molecule having a random-coil configuration at that temperature, whereas at the higher temperatures configurational changes have taken place, leading to the coil having a more wormlike nature, and hence there is little change in the shift factor once this configurational change has taken place.

At this point some remarks regarding the nature of the sample are appropriate. We have referred to our earlier work[7] on the dilute-solution properties of LCP which showed that a random-coil configuration prevailed in solution. To compare with the dilute-solution results, the samples were prepared by evaporation of solutions of LCP. The films eventually obtained have a very small amount of crystallinity which increases on heating above T_g and is responsible for the crystallization exotherm seen in Figure 1.[11] The increase in crystallinity is observed as a growth in size of the existing spherulites in the samples, and the maximum crystallinity observed never exceeds 12%. However, the crystals will limit the extent of configurational reorganization at temperatures below T_m, and therefore the values of the persistence length obtained here are probably smaller than would be obtained in the absence of crystallinity. The agreement between our values of a and those obtained by Donald et al.[28] from scanning tunneling microscopy on cooled melts is perhaps due to the statistics of the distribution of persistence lengths. The values from SANS will be weight-average values since weight-average radii of gyration were used in the evaluation of the persistence length; the scanning tunneling microscopy values are *number*-average values, and thus there will be a greater emphasis on the smaller values in the distribution of persistence lengths.

Conclusions

A random aromatic thermotropic copolyester containing residues of hydroxybenzoic acid, hydroquinone, and isophthalic acid in the main chain has been cast into solid plaques from 2% solutions of the polymer. Although only four fractions have been examined here, the molecular weight range covered is at least 3 times that generally available in polyesters; furthermore, the absolute values of the molecular weight are considerably higher than normally used in the examination of the configurational properties of polyesters. The conclusions made here are confined to temperature ranges where there is a complete absence of transesterification reaction. On heating, a T_g is observed at 403 K which is followed immediately by a crystallization exotherm. At the completion of this exotherm, the value of $\langle s^2 \rangle_w / M_w$ is constant over a molecular weight range of 55 000–103 000; combining this with the observation of a value of zero for the second virial coefficient in the Zimm plots derived from SANS data, it was deduced that the polymer has a Gaussian random-coil configuration at 448 K. At higher temperatures, the second virial coefficient retained a value of zero, but the value of $\langle s^2 \rangle_w / M_w$ displayed an increasing dependence on the molecular weight of the polymer. It has been shown that this is the behavior expected for a Kratky–Porod wormlike chain with an increasing value of the persistence length. Values of the persistence length at temperatures of 493 and 523 K are 31 and 44 Å, respectively. Although larger than commonly encountered, these values indicate that the molecules do not have a particularly stiff rodlike structure; however, the values of the shift factor obtained are larger than would be expected from simple calculations based on molecular weights and bond lengths. It has been speculated that crystalline reorganization observed elsewhere, but not quantified, may be a possible source of these high values of M_L. The values of the persistence length were in excellent agreement with those obtained by scanning tunneling microscopy, but this was probably fortuitous given the different modes of preparation of the samples. The observation of the stiffening of the molecule below T_m suggests that the transformation to a nematic phase is facilitated by this "preordering" of the segments which make up the terpolyester studied here. The aromatic copolyesters could not be studied in the nematic melt due to the occurrence of transesterification reactions which randomizes the distribution of labeled sequences over all molecules present in the system.

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References and Notes

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(30) We note in passing that others have also observed exothermic T_g values; see: Krigbaum, W.; Tanaka, T. *Macromolecules* **1988**, *21*, 743.

Registry No. HBA/HQ/IPA (copolymer), 112482-60-7; neutron, 12586-31-1.