Chain Conformations in Copolyesters of PET and PHB As Determined by Small-Angle Neutron Scattering

E. Olbrich, D. Chen, and H. G. Zachmann*

Institut für Technische und Makromolekulare Chemie, Universität Hamburg, Bundesstrasse 45, 2000 Hamburg 13, FRG

P. Lindner

Institut Laue Langevin, BP 156X, F-38042 Grenoble Cedex, France

Received December 18, 1990

ABSTRACT: Small-angle neutron scattering (SANS) experiments were performed on blends of deuterated and nondeuterated copolyesters of poly(ethylene terephthalate) (PET) and poly(*p*-hydroxybenzoic acid) (PHB). The PET content varied between 80 and 60 mol %, the sample containing 60 mol % being liquid crystalline. Depending on the time of melting during sample preparation, transesterification took place to various degrees resulting in samples in which the molecules contained deuterated and nondeuterated blocks of various lengths. The average degree of polymerization and radius of gyration of these blocks were measured and the length of the statistical element *b* was calculated as a function of composition. The transition from the amorphous to the liquid-crystalline state did not lead to an additional increase in *b*. From this it was concluded that, in the nematic state, the molecules are not elongated. From the length of the statistical element, the average degree of polymerization of the PHB sequences could be estimated.

I. Introduction

Small-angle neutron scattering (SANS) has been successfully applied to determine the molecular conformations in amorphous and semicrystalline polymers. Usually the degree of polymerization and the radius of gyration of the molecules are measured. It was shown that the molecules in the bulk form Gaussian coils with a radius of gyration being the same as in a Θ solvent.[1,2] In the polymers investigated the radius of gyration does not change during crystallization.[3,4] This was explained by Lieser et al.[3] in terms of a solidification model which was first proposed as a possible model for crystallization by Wunderlich[5] and Ewers et al.[6]

A comparatively new question is that of the molecular conformations in a liquid-crystalline polymer. The chains are lying almost parallel within a nematic or smectic domain. Therefore, one could assume that the molecules are highly extended in such domains. However, preliminary investigations[7] indicated that the molecules have the radius of gyration of unperturbed chains, at least in the case of nematic phases formed by semiflexible chains.

During annealing of polyesters, transesterification reactions take place. When performing SANS studies on blends of deuterated and nondeuterated polyesters, one has to consider these reactions which lead to block copolymers consisting of deuterated and nondeuterated blocks. As the chemical polydispersity cancels the correlation hole effect,[8] the average degree of polymerization Z_W and radius of gyration $\langle R_G^2\rangle_z^{1/2}$ of the deuterated and nondeuterated blocks are obtained in the same way as Z_W and $\langle R_G^2\rangle_z^{1/2}$ of whole molecules in a blend of deuterated and nondeuterated material.[9] Therefore, by means of SANS, it was possible to measure both the rate of transesterification and the molecular radius of gyration in poly(ethylene terephthalate) (PET).[9-15] A theory for the kinetics of the transesterification reaction was also developed.[9,16]

In the work presented in this publication we have investigated the following question: How does an increasing amount of stiff units in a copolymer consisting of flexible and stiff units change the average radius of gyration $\langle R_G^2\rangle_z^{1/2}$? Of special interest was the change of $\langle R_G^2\rangle_z^{1/2}$ occurring when the concentration of the stiff units reaches the critical value at which the copolymer becomes liquid crystalline. In addition, the relation between $\langle R_G^2\rangle_z^{1/2}$ and the average degree of polymerization of the blocks of the different units is discussed. Copolyesters of PET and poly(*p*-hydroxybenzoic acid) (PHB) containing different amounts of PHB were investigated. The PET units form the flexible parts in each molecule; the PHB units form the stiff parts.

II. Theory

The reduced scattering intensity $i(q)$ is defined as the measured differential scattering cross section $\mathrm{d}\Sigma/\mathrm{d}\Omega(q)$ divided by the number density of monomers N, by the contrast factor $(a_H - a_D)^2$ where a_H and a_D are the coherent scattering lengths of the nondeuterated and the deuterated monomers, respectively, and by $x_D\,(1 - x_D)$, where x_D is the fraction of deuterated chains:

$$i(q) = (\mathrm{d}\Sigma/\mathrm{d}\Omega)/(N(a_H - a_D)^2 x_D(1 - x_D)) \qquad (1)$$

In mixtures of deuterated and nondeuterated polymers $i(q)$ is given by

$$i^{-1}(q) = (1 - x_D)/Z_D P_D + x_D/Z_H P_H \qquad (2)$$

where Z_D and Z_H are the weight-average degrees of polymerization and P_D and P_H are the structure factors of deuterated and nondeuterated chains, respectively. q is the scattering vector given by $(4\pi/\lambda)\sin(\theta/2)$, θ being the scattering angle. This equation was derived by de Gennes[17] as a random-phase approximation of blends of deuterated and nondeuterated chains. Leibler and Benoit[8] have shown that this equation may also be applied for copolymers of deuterated and nondeuterated chains if the polydispersity M_W/M_N of these chains is approximately 2 and $qR_G \approx 1$.

The samples investigated consist of four different monomeric units, namely deuterated PET, nondeuterated PET, deuterated PHB, and nondeuterated PHB. After correction of their coherent scattering lengths with respect to the different molar volumes,[18] it becomes obvious that

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the contrast between the deuterated units and the nondeuterated units is an order of magnitude higher than the contrast between equally labeled PET and PHB units. Therefore, to a good approximation the coherent scattering lengths of the deuterated units can be averaged to

$$a_D = x_{PET}a_{PET,D} + (1 - x_{PET})V_{PET}/V_{PHB}a_{PHB,D} \quad (3)$$

where x_{PET} is the volume fraction of PET and V_{PET}/V_{PHB} is the ratio of the partial molar volumes of the PET and the PHB monomers. When we do this, the apparent degree of polymerization Z as determined by neutron scattering is given by $Z = n_{PET} + V_{PET}/V_{PHB}n_{PHB}$, where n_{PET} and n_{PHB} are the number of PET and PHB monomers per molecule, respectively. The ratio V_{PET}/V_{PHB} was calculated from density measurements to be 1.75. In a similar way the coherent scattering lengths of the nondeuterated monomers of both components can be averaged to

$$a_H = x_{PET}a_{PET,H} + (1 - x_{PET})V_{PET}/V_{PHb}a_{PHB,H} \quad (4)$$

Finally, the number of monomers per unit volume N is given by $N = \rho/N_Lm_0$, where ρ is the sample density and m_0 is the average mass of PET-sized volume elements. m_0 can be calculated from the masses of the PET and PHB units by means of the equation

$$m_0 = x_{PET}(x_Dm_{PET,D} + (1 - x_D)V_{PET}/V_{PHB}m_{PHB,D}) + (1 - x_{PET})(x_Dm_{PET,H} + (1 - x_D)V_{PET}/V_{PHB}m_{PHB,D}) \quad (5)$$

where $m_{PET,D}$ is the mass of a deuterated monomer PET unit and so on.

From the angular dependence of the reduced intensity $i(q)$ the average degree of polymerization of the deuterated and nondeuterated block, Z, and the z average of the square radius of gyration $\langle R_G^2\rangle_z$ can be determined. As the structure factors of the deuterated and the nondeuterated chains are the same, we can write $P_D = P_H = P$, and eq 1 becomes

$$i(q)^{-1} = (ZP(q))^{-1} \quad (6)$$

with $Z = Z_DZ_H/(x_DZ_D + (1 - x_D)Z_H)$.

In the case of Gaussian chains $P(q) = 2/u^2(u - 1 + e^{-u})$ with $u = q^2\langle R_G^2\rangle_Z$ and we obtain

$$i(q)^{-1} = Z^{-1}(1 + q^2\langle R_G^2\rangle_Z/3 + ...) \quad (7)$$

In a Gaussian chain consisting of n_S freely jointed segments l_S $\langle R_G^2\rangle$ is given by $\langle R_G^2\rangle = \langle h^2\rangle/6$ and the average square end to end distance $\langle h^2\rangle$ is equal to $n_Sl_S^2$. To replace n_s and l_s by the number of monomer units Z and the length of a monomer unit l_0, one takes into consideration that $n_Sl_S = Zl_0$ and obtains

$$\langle h^2\rangle = Zb^2 \quad (8)$$

with $b^2 = l_0l_S$. b is called the length of a statistical element. From this it follows that

$$<R_G^2> = Zb^2/2 = M_Wb^2/6m_0 \quad (9)$$

III. Experimental Section

Nondeuterated copolyesters of PET and PHB containing 80, 70, and 60 mol % mol % PET were synthesized from PET and p-acetoxybenzoic acid as described by Jackson and Kuhfuss.[19] The PET used for this synthesis was obtained from dimethyl terephthalate and ethylene glycol as described in a previous publication.[20] As it is known from other investigation,[19,21] the copolyester containing 60 mol % PET is partially liquid crystalline while the other ones are isotropic.

The deuterated materials were synthesized in the same way as the nondeuterated ones, starting from deuterated dimethyl terephthalate, ethylene glycol, and p-hydroxybenzoic acid. However, the time for transesterification of the dimethyl terephthalate with the ethylene glycol had to be increased from 2 to 4 h as this reaction obviously proceeds more slowly in the deuterated material than in the nondeuterated one. The times of transesterification of PET with PHB under argon had to be also increased from 30 min to 1 h.

Table I
Mole Percent of PHB, Intrinsic Viscosities, and Apparent Molecular Weights for the Copolyesters Investigated

fraction of PHB as charged, mol %	20	30	40
fraction of PHB as determined by H NMR, mol %	19	27	38
intrinsic viscosities, dL/g	0.458	0.419	0.481
molecular weight calculated by eq 1	17 300	15 200	18 500

The deuterated monomers were obtained in the following ways: Ethylene glycol was purchased from Hempel Co.; dimethyl terephthalate was synthesized from deuterated terephthalic acid, purchased also from Hempel as described earlier.[15] For the synthesis of deuterated p-hydroxybenzoic acid a new method was developed: Deuterated phenol is treated with KOD (deuterated potassium hydroxide) dissolved in D_2O at room temperature. After distillation at 80 °C in vacuo, one obtains deuterated potassium phenoxide. The phenoxide is dried for 1 h at 100 °C in vacuo and then ground and again dried for 4 h at 150 °C in vacuo. Then it is treated with potassium carbonate in carbon monoxide at 240 °C for 7 h under pressure (50 bar) in an autoclave. After cooling to room temperature, the material is dissolved in D_2O and acidified with deuterated sulfonic acid. The precipitated deuterated p-hydroxybenzoic acid is filtered off and dried. To purify the product, the dried powder is dissolved in ether and filtrated. Then the ether is evaporated in a rotary evaporator. Finally, the purified material is dried again and sublimated at 160 °C in vacuo.

The synthesized material was characterized by viscosimetry. The intrinsic viscosities were measured in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and apparent molecular weights were calculated from these viscosities by means of the relation

$$[\eta] = 5.2 \times 10^{-4}M_W^{0.695} \quad (10)$$

which is valid for PET,[22] the viscosity being given in dL/g. The results are shown in Table I.

To obtain blends of deuterated and nondeuterated copolyesters for the SANS measurements, the deuterated and nondeuterated material of each copolyester was dissolved in HFIP and then coprecipitated by ethanol. The concentration of the solution was 8.8 wt %; the fraction of deuterated material was 50 mol %. The solutions of the copolyesters containing 20 and 30 mol % PHB were completely clear. In contrast, the solution of the copolyester containing 60 mol % PET was slightly turbid. In all three cases, the precipitation was performed from the solution as it was obtained without filtration. The precipitated powder was dried for 120 h at 40 °C in vacuo. Then 0.2 mm thick amorphous films were produced by melt pressing in vacuo followed by quenching in ice water. The melt pressing was performed at three different temperatures above the melting point, i.e., 240, 250, and 260 °C for the copolyester containing 20 mol % PHB, 230, 250, and 260 °C for the copolyester containing 30 mol % PHB, and 250, 260, and 270 °C for the copolyester containing 40 mol % PHB. The melting time was varied between 10 and 1000 s. Neutron scattering experiments were performed at the Institut Laue Langevin (ILL) in Grenoble using the D17 diffractometer with a sample to detector distance of 2.8 m and a neutron wavelength λ of 12 Å. The wavelength resolution (fwhh) was 10%. The data were collected on a 64 × 64 two-dimensional position sensitive detector. The two-dimensional data were circular averaged by ILL-supported routines.[23] After normalization to an absolute intensity scale as described by Kugler et al.,[9] we obtained the differential scattering cross section $d\Sigma/d\Omega(q)$. The incoherent background and the coherent background arising from density fluctuations and voids were removed by a weighted subtraction of the scattering of a totally deuterated and a totally nondeuterated sample which were obtained under the same conditions as the H,D-mixture sample. This procedure

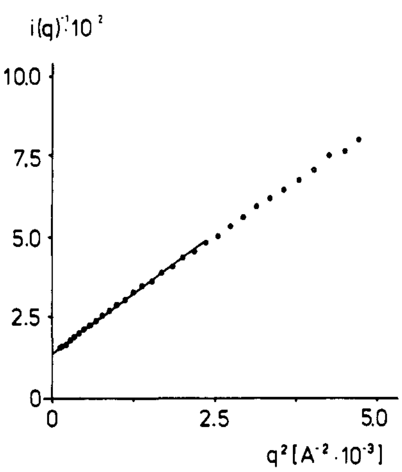

Figure 1. Zimm plot of the reduced intensity $i(q)$ corrected with respect to incoherent scattering and density fluctuation scattering for a copolyester containing 80 mol % PET melt pressed for 10 s at 250 °C.

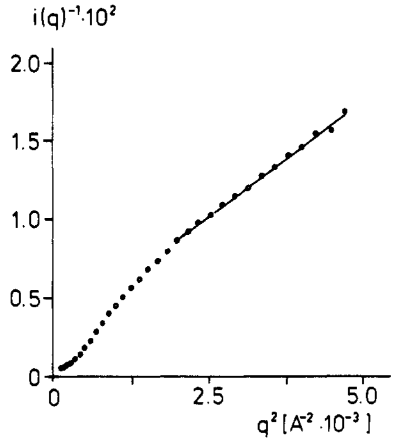

Figure 2. Zimm plot of the reduced intensity $i(q)$ corrected with respect to incoherent scattering and density fluctuation scattering for a copolyester containing 60 mol % PET melt pressed for 10 s at 250 °C.

was proposed by Gawrisch et al.[24] Finally, the reduced intensity $i(q)$, given by eq 1, is calculated and $i(q)^{-1}$ is plotted against q^2.

IV. Results

Figure 1 shows the Zimm plot of the reduced small-angle neutron scattering intensity of the copolyester containing 80 mol % PET. Before plotting, the scattering arising from density fluctuations and voids as well as the incoherent scattering was subtracted as described under Experimental Section. As one can see, a straight line is obtained. A similar straight line was found for the copolyester containing 70 mol % PET. In contrast, as shown in Figure 2, in the case of the liquid-crystalline copolyester containing 60 mol % PET the results lead to a straight line at larger scattering angles only, while at small scattering angles the intensity is proportional to q^{-4}, indicating that particle scattering predominates.[25] This may be due to some undissolved PHB clusters which may also cause the turbidity of the solution of this copolyester. This particle scattering, obviously, cannot be correctly subtracted when we perform the corrections described under Experimental Section.

From the scattering curves the average degree of polymerization Z and the average radius of gyration $\langle R_G^2\rangle_z^{1/2}$ of the deuterated and the nondeuterated sequences were determined according to eq 8. The Z average of the square of the radius of gyration is converted to its weight average by means of the relation[26] $\langle R_G^2\rangle_z/\langle R_G^2\rangle_W = (1 + 2U)/(1 + U)$, where U is the polydispersity $M_W/M_N - 1$. According to previous results[9] and theoretical considerations U was assumed to be 1. Due to transesterification, these parameters decrease with increasing melting time. As an example, Figure 3 shows the decrease of Z for the copolyester containing 70 mol PET.

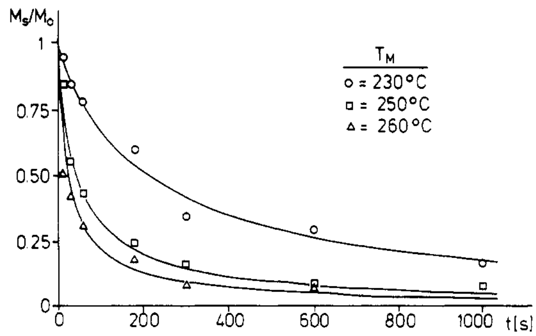

Figure 3. Degree of polymerization Z of deuterated and nondeuterated sequences divided by the degree of polymerization of the whole molecule as a function of melting time for a copolyester containing 70 mol % PET. Parameter: Temperature of melting T_M.

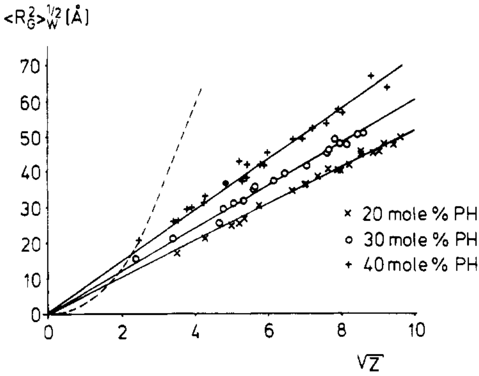

Figure 4. Radius of gyration $\langle R_G^2\rangle_w^{1/2}$ of deuterated and nondeuterated sequences as a function of the square root of their degree of polymerization Z. The dotted line represents the function for a rodlike molecule.

As a consequence of the transesterification process, which in principle is not wanted in investigations of chain conformations, we obtained results for a great variety of sequence lengths and radii of gyration by applying different melting times and temperature. Figure 4 represents the weight-average radius of gyration $\langle R_G^2\rangle_W^{1/2}$ as a function of the square root of the average degree of polymerization $Z_W^{1/2}$ of the deuterated and nondeuterated sequences for the three copolyesters investigated. One can recognize that the radius of gyration increases linearly with $Z_W^{1/2}$ as expected in the case of Gaussian coils.

Figure 5 shows the ratio $(\langle R_G^2\rangle_W/M_W)^{1/2}$ as a function of composition. M_W is the weight average of the deuterated and nondeuterated blocks. With increasing amount of PHB this ratio increases. In addition, in Figure 5 the length b of the statistical element, obtained from this ratio by applying eq 9, is represented. It is interesting to note that the incorporation of the stiff PHB units does not lead to an increase of b if the fraction of these units is 20 mol % only. The value obtained for the homopolymer PET in a previous publication[9] is also indicated in the figure.

V. Discussion

1. Chain Conformations in the Liquid-Crystalline State. Figure 4 shows that, at constant degree of polymerization Z, the radius of gyration becomes larger when

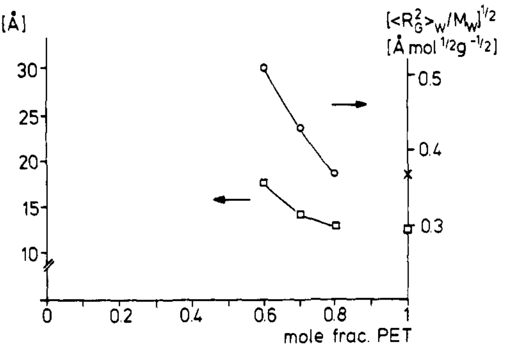

Figure 5. Guinier ratio $(R_G{}^2/M_W)^{1/2}$ and length of a statistical element b as a function of composition of the copolyesters.

the fraction of PHB increases. This can be explained by the fact that the PHB units are stiffer than the PET units. In the transition from the isotropic to the liquid-crystalline state, only the usual and no additional increase in $\langle R_G{}^2\rangle^{1/2}$ is observed. This result is in conflict with the assumption of completely extended chains in the liquid-crystalline domains, as such conformation would lead to much larger values of $\langle R_G{}^2\rangle^{1/2}$. In addition, the increase of the radius of gyration with the square root of the degree of polymerization is linear for the liquid-crystalline copolyester too. This means that, in the nematic state too, the chains obey Gaussian statistics, at least at a larger scale. If the chains were completely extended, $\langle R_G{}^2\rangle^{1/2}$ would be proportional to $Z^{1/2}$ as indicated by the dotted line in Figure 4, which obviously was not found.

We therefore assume that the conformations of the chains in the nematic phase are similar to those in a semicrystalline polymer. In these polymers, each chain, far from being extended, often bends and may go through several crystalline and noncrystalline regions. Bending may occur by forming ideal folds or loose loops. Similarly, within the nematic domains, the molecules may show sharp folds or more extended orientational disorder corresponding to the loose loop in the semicrystalline material. According to our model the transition from the isotropic to the nematic state takes place by straightening of some parts of the molecules without changes in the overall conformation, in the same way as described in the solidification model of crystallization.[3,5,6]

A model in which the molecules form sharp loops was discussed by de Gennes.[27] However, also more extended regions of orientational disorder may be possible. Probably all questions which were discussed in connection with ideal folds and loose loops in polymer crystals can be raised again with respect to structure in nematic domains of semiflexible chains.

2. Dependence of the Length of the Statistical Element on Composition. Figure 5 shows that the length of the statistical element b of the copolyester containing 80 mol % PET does not exceed the value measured on pure PET despite the presence of the stiff PHB units. Thus, an introduction of only a small amount of stiff units does not alter the chain conformation significantly. Higher amounts of PHB lead to an extension of the Gaussian coil.

How can this be explained? If we apply the freely jointed segment model for the copolymer and assume that both components are flexible chains having the b values b_{PET} and b_{PHB}, respectively, according to eq 8 we obtain for the average square of the end to end distance $\langle h^2\rangle$ of a copolymer chain

$$\langle h^2\rangle = n_{\mathrm{PET}}b^2{}_{\mathrm{PET}} + n_{\mathrm{PHB}}b^2{}_{\mathrm{PHB}} \qquad (11)$$

Table II
Comparison of the Experimentally Determined Values of the Lengths of PHB Blocks with the Values Calculated by Assuming a Statistical Distribution of the PET and PHB Monomers

fraction of PHB, mol %	20	30	40
Z_{PHB} as calculated for a statistical distribution	1.3	1.4	1.7
Z_{PHB} experimental from ref 25	2.5	2.1	10.3
Z_{PHB} experimental by eq 14	3.1	8.4	13.2
Z_{PHB} experimental by eq 16	0.2	4.3	9.0

Here n_{PET} and n_{PHB} are the number of PET and PHB monomers per molecule. They are given by the sum of the degrees of polymerization of all PET blocks $\sum\nu_{\mathrm{PHB}}$, respectively. This yields an average b value

$$\langle b^2\rangle = \langle h^2\rangle/n = x_{\mathrm{PET}}b^2{}_{\mathrm{PET}} + (1 - x_{\mathrm{PET}})b^2{}_{\mathrm{PHB}} \qquad (12)$$

where x_{PEt} is the mole fraction of PET given by n_{PET}/n and $n = n_{\mathrm{PET}} + n_{\mathrm{PHB}}$ is the average degree of polymerization of the copolyester. As b_{PHB} obviously has to be larger than b_{PET}, eq 11 leads to a monotonic increase of $\langle b^2\rangle$ with increasing PHB content. This is in contrast to the experimental result. Therefore, we have to modify our assumption.

We assume that the PHB blocks are completely stiff rods. Let ν_{PHB} be the number average of the degree of polymerization of the PHB sequences. Then, the average length of a PHB block is $\nu_{\mathrm{PHB}}\, l_{0,\mathrm{PHB}}$, and in each deuterated or nondeuterated block there are, on the average, n_{PHB}/ν sequences present. Thus, we obtain

$$\begin{aligned}\langle h^2\rangle &= n_{\mathrm{PET}}b^2{}_{\mathrm{PET}} + (n_{\mathrm{PHB}}/\nu_{\mathrm{PHB}})(\nu_{\mathrm{PHB}}\, l_{0,\mathrm{PHB}})^2 \\ &= n_{\mathrm{PET}}b^2{}_{\mathrm{PET}} + n_{\mathrm{PHB}}\nu_{\mathrm{PHB}}l_{0,\mathrm{PHB}}{}^2 \qquad (13)\end{aligned}$$

and

$$\langle b^2\rangle = \langle h^2\rangle/n = x_{\mathrm{PET}}b^2{}_{\mathrm{PET}} + (1 - x_{\mathrm{PET}})\nu_{\mathrm{PHB}}l_{0,\mathrm{PHB}}{}^2 \qquad (14)$$

In this case $\langle b^2\rangle$ may also decrease with increasing PHB content because ν_{PHB} may vary. As a matter of fact, one can use eq 14 to calculate the average degree of polymerization of the PHB block, ν_{PHB}, from the measured values of $\langle b^2\rangle$ as eq 14 can be rearranged to

$$\nu_{\mathrm{PHB}} = (\langle b^2\rangle - x_{\mathrm{PET}}b^2{}_{\mathrm{PET}})/((1 = x_{\mathrm{PET}})l_{0,\mathrm{PHB}}{}^2) \qquad (15)$$

The results for ν_{PHB} obtained by eq 14 using the values $b_{\mathrm{PET}} = 1.32$ nm (as measured on the homopolymer PET) and $l_{0,\mathrm{PHB}} = 0.63$ nm (as calculated by means of the usual values of atomic distances), are listed in Table II. For comparison the values obtained from SANS in a previous investigation on a copolyester in which only the PET was deuterated[12] together with the values calculated for a random copolymer ($\nu_{\mathrm{PHB}} = x_{\mathrm{PET}}{}^{-1}$) are given. As one can see, the average degree of polymerization is larger than is expected in a random copolymer. In both kinds of measurements the deviations are largest in the case of the copolyester containing 60 mol % PET. However, the agreement between the two investigations is not complete. The values obtained in this work are somewhat larger than those of the former samples. This is not surprising because it is quite reasonable to assume that the deviation from randomness varies from sample to sample, especially if differently deuterated monomers are used, as it is here the case.

We have also tried to evaluate the results by using a slightly different model. It seems to be questionable whether a stiff sequence of PHB can be considered to be freely jointed with the two adjacent PET units. Therefore, we have added to each PHB sequence a PET monomer unit of length $l_{0,\mathrm{PET}}$ and have considered this composite sequence to be a freely jointed segment instead of the PHB sequence. Equation 14 is then changed to yield

$$\langle b^2 \rangle = \langle h^2 \rangle / n = (x_{\mathrm{PET}} - (1 - x_{\mathrm{PET}})/\nu_{\mathrm{PHB}}) b^2{}_{\mathrm{PET}} + (1 - x_{\mathrm{PET}})/\nu_{\mathrm{PHB}} (\nu_{\mathrm{PHB}} l_{0,\mathrm{PHB}} + l_{0,\mathrm{PET}})^2 \quad (16)$$

By use of this equation ν_{PHB} was also calculated, and the results are given in the last row of Table II. The values obtained are somewhat smaller than those found by eq 14.

VI. Conclusions

The introduction of stiff PHB units into a flexible PET chain increases the value of $(\langle R_G{}^2 \rangle_W / M_W)^{1/2}$ and therefore the length of the statistical element b, as expected. When a fraction of 40 mol % PHB is reached and the material becomes liquid crystalline, no additional contribution to this increase of this ratio is observed which could be attributed to an elongation of the chains in the nematic domains. In addition, in the liquid-crystalline material the average radius of gyration increases proportionally to the square root of the degree of polymerization in the same way as in the isotropic amorphous state. From this it is concluded that the chains in the nematic domains are not completely elongated; stretched parts of the chain alternate with folds similar to the conformations in a semicrystalline material.

Measurements of the radius of gyration may also be used to determine the average degree of polymerization of the PHB sequences. It was found that this degree of polymerization is about twice as large as expected for random copolymers.

Acknowledgment. This work has been funded by the German Minister for Research and Technology (BMFT) under Contract No. 03-ZA2HAM.

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Registry No. (*p*-Acetoxybenzoic acid)(dimethyl terephthalate)(ethylene glycol) (block copolymer), 134152-91-3; (deuterated dimethyl terephthalate)(deuterated ethylene glycol)-(deuterated *p*-hydroxybenzoic acid) (block copolymer), 134177-30-3; deuterated *p*-hydroxybenzoic acid, 126840-16-2; deuterated phenol, 13127-88-3; potassium carbonate, 584-08-7.