Changes in molecular conformations in poly(ethylene terephthalate) produced by crystallization and drawing as determined by neutron scattering

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Poly(ethylene terephthalate) (PET) was synthesized in deuterated and nondeuterated forms from ethylene glycol and dimethyl terephthalate. Deuterated and nondeuterated PET were then blended by coprecipitation from 1,1,1,3,3,3-hexafluoro-2-propanol solution and subsequent melt-pressing under vacuum with quenching to prevent crystallization. Some of the samples prepared were then either isothermally crystallized or oriented by cold-drawing. The single-chain structure of PET under these conditions was determined by neutron scattering. The noncrystalline and the semicrystalline samples were investigated in both the small- and the intermediate-angle regions. The scattering in the Guinier region from both sets of samples exhibited a linear Zimm plot with slight increase in the radius of gyration upon crystallization. The presence of a long period of ~13 nm was evident in the scattering from the crystallized homopolymer blanks. A plateau indicative of a coil-type molecular structure was observed for both the noncrystalline and the semicrystallization samples in a Kratky plot presentation of the scattering from the intermediate-angle region. The small-angle scattering from the cold-drawn samples indicated that the necking process was nonaffine.

(Keywords: poly(ethylene terephthalate); crystallization; drawing; neutron scattering)

INTRODUCTION

Through the use of deuterium labelling, neutron scattering has been found to be extremely effective for determining the structure of polymer molecules in the condensed matter state. When deuterium is substituted for hydrogen for a given fraction of the polymer molecules present in a sample, a system is obtained where chemically identical molecules have vastly different scattering lengths; from the small angle neutron scattering (SANS) profile of such a system, the structure factor for a single chain can be calculated. In this study, the molecular morphology of poly(ethylene terephthalate) (PET) has been determined under three different conditions: (1) in the glassy state; (2) in the semicrystalline state; and (3) after cold-drawing.

Previous studies[1,2] have shown that investigations on condensation polymers such as PET can often be complicated by the occurrence of chain-transfer reactions in the melt. Thus, after melting a blend of deuterated and nondeuterated PET up to 3 min at 280°C, a blockcopolymer of both species has been obtained with an average molecular weight of a block lying in the range 900–10 000 g mol^{-1}, depending on the melting time while the molecular weight was ~23 000 g mol^{-1}. The small blocks had almost unperturbed dimensions, as predicted by Flory[3]. However, owing to transesterification, the dimensions of larger molecules could not be determined.

Therefore a new technique of preparation has been developed in the present work. It was found that the blend cast from solution contains small crystals that melt at a temperature of only 250°C and that the material stays for some time in the molten state before formation of new crystals of larger thickness and the usual melting point of 272°C. Using this result, amorphous films were prepared by pressing the blend for 20 s at 250°C and then quenching it in ice–water. Under these conditions only a small amount of transesterification occurred, namely less than one occurrence per molecule on average[2].

The changes in the conformation of the single PET molecule as a result of crystallization are of primary interest in this study. To determine the structure of a polymer molecule in a crystallized sample the SANS profile must be taken over a wide range of the scattering vector **q**. In the wide **q** region changes in the molecular morphology over a short distance are considered; from the scattering profile in the small **q** region, values for the radius of gyration and the molecular weight of the overall chain are obtained.

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In addition to the effect of crystallization on the molecular conformations, the molecular structure resulting from different orientation processes as determined by SANS is of great interest. With SANS, the microscopic and macroscopic draw ratios can be compared for PET samples which have been oriented under different experimental conditions.

Neutron scattering experiments on poly(ethylene terephthalate) were performed also by McAlea *et al.*[4]. They were able to prevent transesterification completely by pressing the powder at only 100°C. It was shown that the molecules had unperturbed dimensions. However, the samples prepared in this way were partly crystalline; the influence of crystallization and drawing on the conformations was not investigated.

EXPERIMENTAL

Synthesis of poly(ethylene terephthalate)

PET was synthesized in both its deuterated and nondeuterated forms by transesterification of dimethyl terephthalate and ethylene glycol followed by melt condensation. As catalyst 0.138 wt% manganese(II) acetate and 0.042 wt% antimony(III) oxide were used in combination. As deuterated dimethyl terephthalate was not commercially available it was obtained from the reaction of 1,4-dibromobenzene with n-butyllithium and carbon dioxide to yield terephthalic acid, which was converted to the dimethyl ester by conversion with a commercially available BF$_3$–methanol reagent. The ester product (yield ~95%) was then purified by twice recrystallizing from methanol and distilling under vacuum. Further details are given in previous publications[1,5].

The molecular weights of both the deuterated and nondeuterated material were then determined by gel permeation chromatography in 1,1,1,3,3,3-hexafluoro-2-propanol. For deuterated PET a weight average molecular weight of $M_w = 4.6 \times 10^4$ g mol^{-1} was obtained and for nondeuterated PET, $M_w = 4.0 \times 10^4$ g mol^{-1}.

Preparations of SANS samples

Since the deuterated and nondeuterated components must be statistically mixed at a molecular level in SANS samples, these components are usually mixed together by codissolution followed by solvent removal by, e.g. reprecipitation, freeze drying or solvent casting. Since it is one of few solvents in which PET does not degrade, 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) was used for the blending process. Four mixtures were prepared, which contained 0%, 50%, 70% and 100% deuterated PET. After deuterated and nondeuterated PET in the appropriate ratio were dissolved in HFP, the solution was filtered through a 0.2 mμ filter. One sample set was prepared by film casting from the solution. The other sets were produced by a melt-pressing process (*Figure 1*): the PET solution was added dropwise to methanol (nonsolvent), and the resulting precipitate was then dried in a vacuum oven.

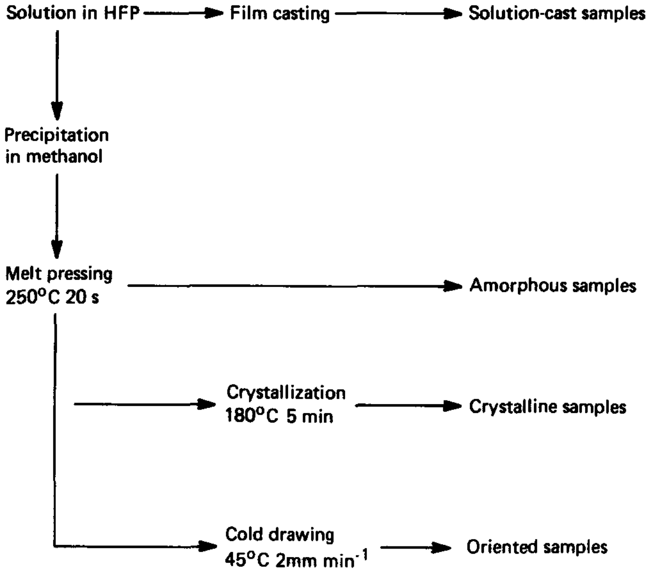

Figure 1 Sample preparation procedures

The blend powder was then transformed into a film suitable for SANS by melt-pressing at 250°C for 20 s (10 s at contact pressure and 10 s at 100 kbar), a process that was carried out under vacuum to prevent degradation. To prevent crystallization, samples were quenched in ice–water immediately after pressing. Three sets of four samples were prepared in this manner; two of the three sets were then subjected to further treatment. To determine the molecular morphology resulting from crystallization, one set of samples was annealed at 180°C for 5 min in a vacuum oven. A second set of samples was cold-drawn at 45°C and a strain rate of 2 mm min^{-1} (corresponding to 10% min) to determine the molecular conformation resulting from the necking process.

Small-angle neutron scattering measurements

SANS measurements were carried at the Institute Laue-Langevin, Grenoble, on the D11 and D17 small angle diffractometers. The instrumental set up is given in *Table 1*.

The SANS data were then normalized to the absolute intensity scale using 1 mm water as the calibration standard. After the transmission correction, a correction for incoherent scattering and background due to density fluctuations was applied to the intensities of all blend specimens, which was obtained by taking a weighted average of the scattering for the pure nondeuterated and deuterated PET[6]. The single chain scattering function $P(\mathbf{q})$ and the weight average degree of polymerization Z were derived from the following expression for the absolute scattering intensity[7]

$$R(\mathbf{q}) = x(1-x)(a_H - a_D)^2 N Z^2 P(\mathbf{q}) \tag{1}$$

where x is fraction of deuterated species present, a is the neutron scattering length per monomer repeat unit of either the deuterated (D) or the nondeuterated (H) species, N is the number of molecules per unit volume, and $\mathbf{q}$ is the scattering vector, proportional to the sine of the scattering angle. The results are presented as the normalized scattering intensity,

$$S(\mathbf{q}) = \frac{R(\mathbf{q})}{ZNx(1-x)(a_H - a_D)^2} \tag{2}$$

For samples which have undergone transesterification, the single-chain scattering function obtained is that for a D or H block instead of that for the entire molecule.

Table 1 Instrumental set-up and samples investigated

Instrument	D11 Detector position centered	D17 Detector position centered	D17 Detector position offbeam 14°
Wavelength/nm	1.0	1.2	1.2
Sample–detector distance/m	10.6	2.8	1.4
q range covered/nm^{-1}	0.05–0.20	0.1–0.7	0.2–2.5
Solution-cast sample	†	+	–
Amorphous sample	+	+	+
Crystalline sample	+	+	+
Oriented sample	+	+	–

+ Sample investigated
– Sample not investigated
† Measurement stopped because of strong void scattering

The z-average radius of gyration, R_{gz}, is then obtained from the small **q** dependence of the single chain scattering function given by

$$P(\mathbf{q})^{-1} = 1 + (R_{gz}^2\mathbf{q}^2/3) + \ldots \quad (3)$$

If the polydispersity of the sample is known and a Schulz–Flory distribution is assumed, then it is possible to convert the z-average square of the radius of gyration to a weight average value, R_{gw}^2, by

$$R_{gw}^2 = R_{gz}^2(1+U)/(1+2U) \quad (4)$$

where U is the polydispersivity $M_w/M_n - 1$. For polymers that are both polydisperse and possess a coil-like structure, the Debye formula for the single-chain scattering function is modified to give[8]

$$P(\mathbf{q}) = 2(1 + Ux(\mathbf{q}))^{-1/U} - 1 + x(\mathbf{q})/(1+U)x(\mathbf{q})^2 \quad (5)$$

where

$$x(\mathbf{q}) = R_{gz}^2\mathbf{q}^2/(1+2U)$$

Values for both the polydispersity, U, and the weight average radius of gyration, R_{gw}, can then be obtained from fitting the preceding equation to the neutron scattering data in the intermediate **q** region.

RESULTS AND DISCUSSION

Isotropic PET blends

The scattering in the Guinier region from all sets of samples investigated (*Figures 2, 3* and *4*) exhibited a linear Zimm plot with a slight increase in the radius of gyration, R_{gz}, upon crystallization from 6.5 nm to 7.2 nm (see *Table 2*). The molecular weight values of just over 27 000 obtained for both samples represent approximately a 40% reduction in the block length owing to the occurrence of transesterification during melt-pressing. If the polydispersity of a polycondensation type polymer $U = 1$ is assumed, values for the ratio of the radius of gyration R_{gw} to the square root of the molecular weight are obtained for both the noncrystalline and crystalline samples of 0.032 nm and 0.036 nm, respectively.

This invariance of R_{gw} can be explained by the solidification model[9,10], where it is assumed that crystallization occurs only by straightening suitably oriented sequences of a coil without a long-range diffusional process. This should be valid especially in the case of rapid crystallization—as investigated by this experiment—whereas slow crystallization might occur in other processes. Therefore it is preferable to investigate further the radius of gyration and its changes under slow crystallization conditions.

Because of the strong forward scattering caused by voids the solution-cast samples could not be investigated in the smallest **q** range. Nevertheless, assuming the same polydispersity of one, the Zimm plot (*Figure 4*) can be extrapolated to $\mathbf{q} = 0$ and the molecular properties can be evaluated in the usual manner, but with greater uncertainty. The molecular weight of 46 900 is identical to the value obtained by gel permeation chromatography, which indicates that no transesterification has occurred; the ratio of the radius of gyration to the square root of the molecular weight is 0.035 nm, in the same region as for the melt-pressed samples.

In the intermediate-angle neutron scattering profiles from the crystallized homopolymer blanks, the presence of a long period of about 13 nm was evident (*Figure 5*). For both the noncrystalline and semicrystalline samples, a Kratky plot presentation of the intermediate angle scattering intensity (*Figure 6*) exhibited a plateau indicative of a coil-like structure. (Although a polymer chain may be folded in a lamella, it is still possible that it exhibits quasi-Gaussian behaviour in certain ranges of **q**.) By analysing the intermediate-angle scattering data for the noncrystalline sample with the modified Debye

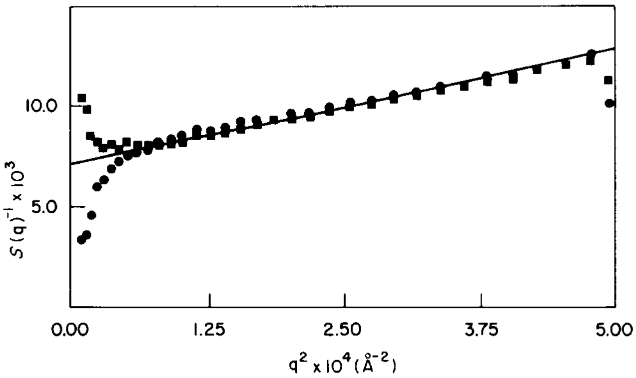

Figure 2 Zimm plots of noncrystalline PET blends (melt pressed and quenched). % Deuterated PET: (■), 50; (●), 70

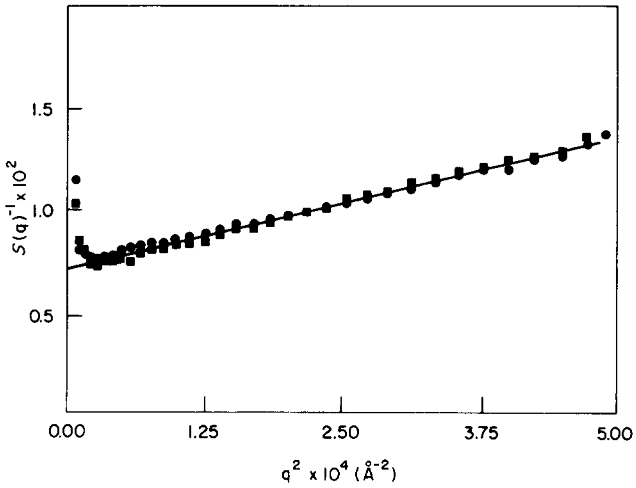

Figure 3 Zimm plots of melt pressed and quenchend PET blends after crystallization (300 s, 180°C). % Deuterated PET: (■), 50; (●), 70

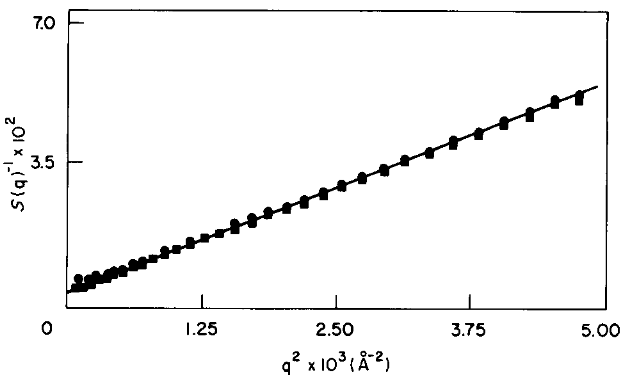

Figure 4 Zimm plot of solution-cast PET blends. % Deuterated PET: (■), 50; (●), 70

Table 2 Radius of gyration R_{gz}, molecular weight M_w, polydispersity U and ratio $R_{gw}/M_w^{0.5}$

				$R_{gw}/M_w^{0.5}$ (nm)	
	R_{gz} (nm)	M_w	U	Guinier region	Kratky plot
Amorphous, solution-cast	9.3	46 900	-	0.035	-
Amorphous, melt-pressed	6.5	27 300	0.96	0.032	0.034
Crystallized 5 min 180°C	7.2	27 500	-	0.036	0.035
Drawn, parallel	12.4	27 300	-	-	-
Drawn, perpendicular	2.6	26 000	-	-	-

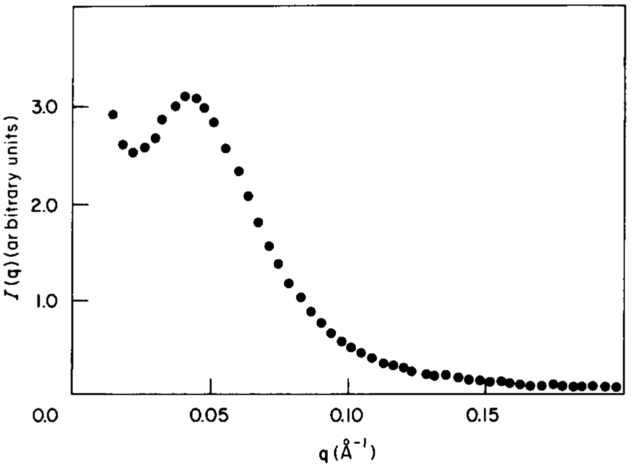

Figure 5 SANS of deuterated PET blank after crystallization (300 s, 180°C)

equation, a polydispersity value of $U = 0.96$ was calculated (*Figure 7*), which is in good agreement with the anticipated value for PET of 1.0. From the height of the observed plateaus, values for the ratio of the radius of gyration to the square root of the molecular weight were obtained for both the crystallized sample and the noncrystalline sample of 0.035 nm and 0.034 nm, respectively, in good agreement with the small-angle data, where a slightly expanded radius of gyration was observed upon crystallization.

Oriented PET blends

The SANS was observed from PET samples (*Figure 8*) that had been cold-drawn at 45°C at 2 mm min^{-1}. A macroscopic draw ratio of 4.9 was obtained for PET under these conditions. The instrumental set-up was that used for investigation of the isotropic samples. The radial symmetric collimation was kept the same to ensure the same instrumented resolution and avoid additional correction[11].

The neutron scattering data were then analysed by segmenting the detector in pie-shaped slices with an angle μ relative to the direction of draw. The calculation of the absolute intensities was the same as in the isotropic case. Only equation (3) changes to

$$p^{-1}(Q,\mu) = 1 + R_{gz}^2(\mu)Q^2 + \ldots \qquad (6)$$

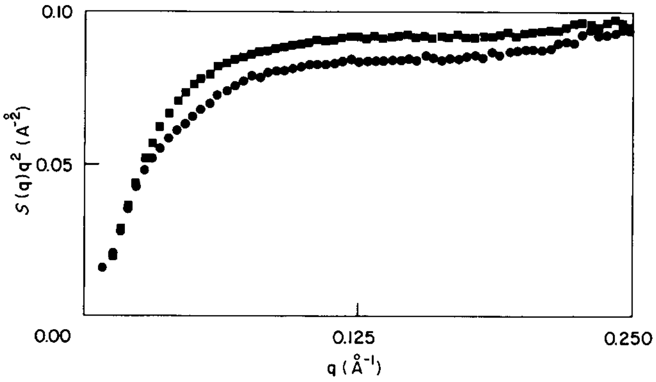

Figure 6 Kratky plots of noncrystalline (■) and semicrystalline (●) PET blends (melt-pressed and quenched)

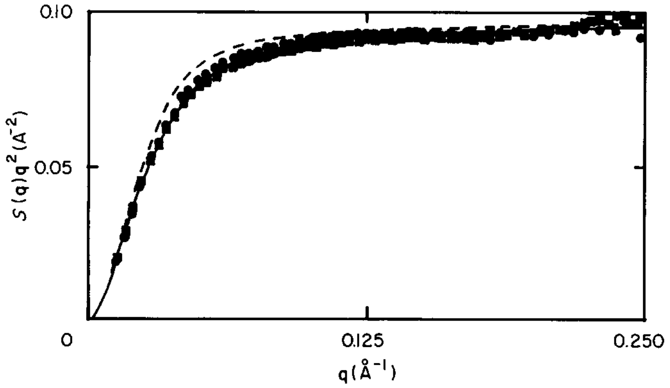

Figure 7 Kratky plot of the amorphous melt-pressed blends compared with theoretical values (Debye equation) for different polydispersities, U. %Deuterated PET: (■), 50; (●), 70. Calculated: (– – –), $U = 0$; (———), $U = 0.96$

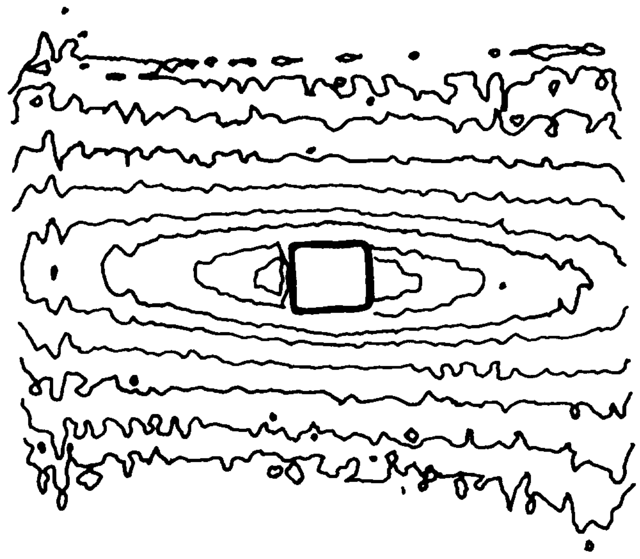

Figure 8 Contour intensity plot of SANS from cold-drawn PET blend (50:50, H:D), for 0.008 Å^{-1} < q < 0.07 Å^{-1}. The direction of orientation in the diagram is vertical

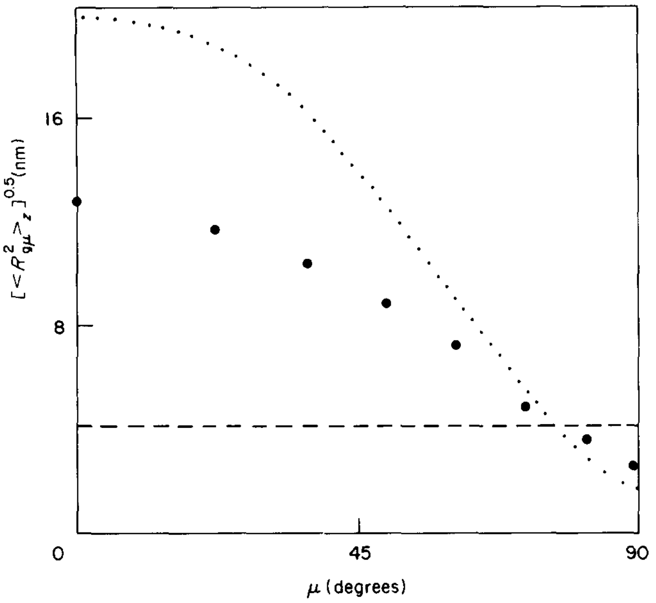

Figure 9 SANS determined component of radius of gyration versus the angle μ relative to the drawn direction for cold-drawn PET blends. (·····), calculation assuming affine deformation; (– – –), radius of gyration $R_{gz}/\sqrt{3}$ of the isotropic sample; (●), oriented samples

employing the expression $R^2_{gz} = R^2_{gzu} + R^2_{gzv} + R^2_{gzw}$ (where u, v, w are the main axes in the molecular coordinate system). The molecular weight remains constant as expected (*Table 2*). The radius of gyration exhibits a dependence on $\cos^2 \mu$ (*Figure 9*); in the draw direction it becomes $R_{gzw} = 12.4$ nm, perpendicular $R_{gzu} = 2.8$ nm. The molecular draw ratio[11]

$$MDR = (R_{gzw}/R_{gzu})^{2/3}$$

was evaluated to be 2.8. In *Figure 9*, the SANS determined radius of gyration values in one direction has been compared with both that obtained for the unoriented sample and those predicted in the case where the polymer chain deforms in proportion to the macroscopic extension of the sample (the affine case). The failure of the PET molecules to deform affinely could easily result from factors such as chain slippage during draw.

CONCLUSIONS

For noncrystalline PET the radius of gyration is slightly smaller than that predicted by Flory[8]. The radius of gyration increased slightly upon crystallization at 180°C as was observed in both the small and intermediate angle scattering. Cold-drawn samples of noncrystalline PET with a macroscopic draw ratio of 4.9 exhibited a molecular draw ratio of 2.8 thus deforming markedly less than affinely at the microscopic level.

In the intermediate-angle region the scattering curve of the amorphous sample shows a plateau, which can be explained by a random-coil conformation of the molecules. The similarity of the scattering profile of the crystallized PET sample indicates that the individual molecules remain in a rather disordered state after undergoining crystallization with such a large degree of undercooling. The observation of a long period of 13 nm for the nonblended, crystallized samples, indicates that the folded chain nature of the individual molecules should be evident in a region of larger **q** than those measured in this study.

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