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Studies of Chain Folding in Solution-Crystallized Poly(ethylene terephthalate)

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ABSTRACT: The relative conformer composition for poly(ethylene terephthalate) (PET) crystallized from a dilute solution in dimethyl phthalate as a function of temperature is studied with Fourier transform infrared spectroscopy. The trans isomer increases with crystallization temperature. Correlation of conformer composition and lamellar thickness for crystallized and annealed samples indicates that the fold structure contains between two and three gauche isomers and no trans contributions. These results are consistent with a regular adjacent reentry fold structure for solution-crystallized PET.

Introduction

Poly(ethylene terephthalate) (PET) crystallized from dilute solution is composed of aggregates of fibrillar crystals.[1,2,11] Fibrils radiate from a central nucleus and are composed of lamella-like structures. Wide-angle X-ray diffraction and electron microscopy have verified a chain-folded structure.[1] Infrared studies of the folding have been reported,[4] and more recently an infrared method has been described to measure the rotational composition in PET.[6] In this study the Fourier transform infrared (FTIR) and small-angle X-ray diffraction (SAXD) techniques are applied to solution-grown and annealed crystals with the goal of improving the present state of understanding of the disordered phase.

Background and Theory

Two parameters related to the fold structure are the long period and the relative conformer composition. For a given molecular weight and cilium length, a change in conformer composition alters the fold. In single crystals, where the amount of amorphous material is small, the magnitudes of the SAXD long period and the lamellar thickness become close. However, the quantities increasingly diverge as the intercrystalline regions become large. In poly(ethylene terephthalate), where the amorphous content is relatively high, the long period can be corrected to obtain the lamellar thickness. Illers and Hendus have developed such as relationship.[12] Assuming a two-phase structure (see Discussion) the lamellar thickness is related to the measured long period by the volume crystallinity as

$$\mathrm{LT} = L(\alpha)(\rho/\rho_c)$$

where L = long period, α = percent crystallinity, ρ = density, ρ_c = pure crystal density, and LT = lamellar thickness.

The interrelation of the lamellar thickness to the conformer composition depends on the morphological model chosen to describe the polymer structure. PET contains three conformational isomers: trans, gauche(+), and gauche(−). The two gauche conformers cannot be experimentally distinguished. The trans isomer is the major component in the crystalline phase. The gauche conformer is primarily contained in the folds and the amorphous phase as chain ends or tie molecules. We will derive the necessary equation to relate conformational composition to fold structure. Initially, we assume an ideal crystal model. Figure 1 defines useful parameters of the model. The total gauche can be represented by the degree of polymerization (DP) multiplied by the relative amount of gauche:

$$\text{total gauche} = (\mathrm{DP})(\%\ \text{gauche}) \tag{1}$$

The gauche conformers are possibly located in the folds, tie molecules, and chain ends. The combination of these species equals the total gauche contents as

$$\text{total gauche} = \mathrm{TMG} + \mathrm{CEG} + \mathrm{FdG} \tag{2}$$

where TMG = tie molecule gauche, CEG = chain end gauche, and FdG = fold gauche. The amount of fold gauche is equal to the number of crystal trans stems per molecule (i.e., the number of folds) times the number of gauche units per fold (n). The number of crystal trans segments per molecule is the crystal trans content, (DP)(% Txtal), divided by the number of trans molecules per stem (B).

$$\text{trans segments per molecule} = (\mathrm{DP})(\%\ \mathrm{Txtal})/B \tag{3}$$

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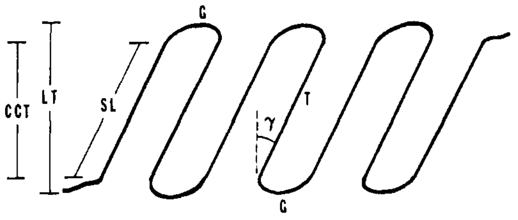

Figure 1. Molecular model of an ideal PET single crystal.

B is given by the lamellar thickness (LT) divided by the c-axis repeat distance (C) and the cosine of the angle between the chain axis and the fold surface (γ).

$$B = \mathrm{LT}/(C \cos \gamma) \tag{4}$$

The number of fold gauche units is expressed as the product of the crystal trans segments per molecule (eq 3) and the number of units in the fold (n). Substitution with n and eq 2–4 yields

$$\%\ \mathrm{G} = n\frac{\%\ \mathrm{Txtal}}{\mathrm{LT}/(C \cos \gamma)} \tag{5}$$

As with the gauche conformers, the total trans is represented by

$$\text{total trans} = (\%\ \mathrm{DP})(\%\ \text{trans}) \tag{6}$$

Trans structures are possible, located in the crystal and in the surrounding amorphous regions. This is written as

$$\text{trans} = \mathrm{Txtal} + \mathrm{Tam} \tag{7}$$

and

$$\%\ \mathrm{Tam} = \%\ \mathrm{CET} + \%\ \mathrm{TMT} + \%\ \mathrm{FdT} \tag{8}$$

where CET = chain end trans, TMT = tie molecule trans, and FdT = fold trans. Since we have the relationship % T + % G = 1, substitution yields the following:

$$\%\ \mathrm{Txtal} + \%\ \mathrm{Tam} + \%\ \mathrm{TMG} + \%\ \mathrm{CEG} + n\left(\frac{(\%\ \mathrm{Txtal})(C \cos \gamma)}{\mathrm{LT}}\right) = 1 \tag{9}$$

Equation 9 is the defining relationship for the conformational composition in terms of the lamellar structure of a chain-folded PET crystal. The formulation, although valid, is cumbersome for experimental application. For this reason we consider simplifications based on related experimental evidence. A thorough electron microscopic examination of solution-crystallized PET has revealed the absence of interlamellar material.[2] This establishes a low abundance of tie molecules and suggests their absence. With little or no tie molecules, trans and gauche conformations therein are correspondingly low.

The chain ends of the crystallized polymer assume trans or gauche conformations and affect the analysis as shown in eq 9. Location of the ends for solution-crystallized PET is in the interlamellar regions.[25] The contribution to the total conformer composition depends on their length. This issue has been addressed in another system for oligomeric nylon chains in solution.[5] The authors found the long period to remain constant as the length of chains increased. They suggested that if a chain was long enough to span the growing face of the crystal, it did so. We do not have direct evidence of this process in the system under study, but it is inferred from the nylon case and energetic considerations. We will analyze our data on this basis with the realization that the results depend on this issue.

The state of trans conformers in the fold structures is addressed later and found to be low or nonexistent.

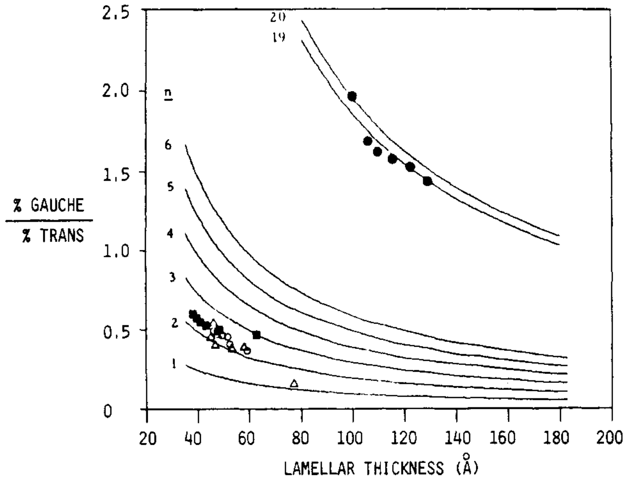

Figure 2. Plot of the conformer ratio as measured with infrared spectroscopy vs. the lamellar thickness. Solid lines are theoretical values per equation.[6] (-●-) Conformer ratio data of Lin and Koenig[6] and long period data of Yeh;[2] (-■-) conformer ratio data of this work and long period data of Yamashita;[3] (-○-) time-varied annealing data; (-△-) temperature-varied annealing data.

Equation 9 now reduces to the following form using % trans ≅ % Txtal + % Tam and % TMG + % CEG ≅ 0:

$$\%\ \text{trans} + n\left(\frac{(\%\ \text{trans})(C \cos \gamma)}{\mathrm{LT}}\right) = 1 \tag{10}$$

The second term in eq 10 is equal to the fold gauche and can be equated to the percent gauche in the sample. Rearrangement produces

$$\frac{\%\ \mathrm{G}}{\%\ \mathrm{T}} = n\left(\frac{C \cos \gamma}{\mathrm{LT}}\right) \tag{11}$$

Equation 11 is the defining relationship for the number of units in a single fold of solution-crystallized PET. Figure 2 shows the relationship between the conformer ratio and the lamellar thickness according to eq 11. Solid lines are the theoretical variation of the associated parameters. The number of gauche units in the chain fold is represented by n. In the present context this formulation is tested for solution-crystallized samples. The formulation can also be applied to annealed samples with the following considerations. The solution-crystallization process produces a highly ordered lamellar morphology. The effect of annealing on lamellae has been intensely studied and has yielded several underlying processes. It is well accepted that crystal perfection increases and defects are eliminated. Lamellar thickening occurs at the expense of the surrounding amorphous regions. Partial melting has been suggested as the mechanism for the thickening.[22] An increase in the melting point of annealed PET crystals is attributed to fold surface smoothing and lower surface free energies.[23] The changes upon annealing indicate that the PET crystals become increasingly appropriate for the formulation as developed in eq 10.

Experimental Section

Solution Crystallization. Amorphous PET with a viscosity-average molecular weight of 24 600 was dissolved in dimethyl phthalate at a concentration of 1.0%. The dissolution temperature in this solvent is ca. 200 °C. The solution was rapidly diluted in solvent-treated and preheated test tubes to produce a final concentration of 0.1% at the desired crystallization temperature. Tubes were capped to prevent the loss of solvent. Crystallization in the temperature range 45–155 °C occurred in a thermally regulated oil bath that was monitored to within ±0.5 °C. The time of crystallization was 31 h, ensuring completion of the process.

The crystallized polymer was separated from the bulk of the solvent by vacuum filtration at the crystallization temperature. Crystals prepared under these conditions have spherulitic morphology composed of aggregations of fibrillar ribbons.[1,2]

For IR analysis the wet crystals were formed into films less than 25 μm thick on salt plates. Plates were dried under vacuum for 3 days at 50 °C. Solvent removal was determined by the absence of characteristic DMP absorbances. The resulting sample spectra showed all absorbances within the Beer's law range. This nondestructive sample preparation technique allowed for the direct observation of unaltered structural features.

Annealing. Wet crystals were formed into films on KBr plates and dried under vacuum at 50 °C. Films were floated off plates on water and mounted on 100-mesh copper sheet screening for infrared analysis. Samples were isothermally annealed under vacuum between 180 and 247 °C as a function of time. After the selected time interval the samples were allowed to cool to room temperature.

Density. A density gradient column was prepared according to ASTM D1505.[13] A density range of 1.41–1.51 g/cm^3 was prepared with mixtures of carbon tetrachloride and *n*-heptane. The temperature of operation was maintained at 23.0 ± 0.1 °C by means of a thermoregulated water jacket. Eight standard glass floats (±0.0001 g/cm^3 at 23 °C) were placed in the column for calibration. Calibration coefficients for the column were an average of 0.999. Samples were dried for 3 days at 50 °C under vacuum before immersion in the column.

Fourier Transform Infrared Spectroscopy. Spectra were recorded on a Digilab FTS-20 infrared spectrometer at a resolution of 2 cm^{-1}. The wavenumber reproducibility was 0.01 cm^{-1}. A liquid nitrogen cooled detector ensured maximum signal detection. Both sample and reference beams were scanned 400 times to provide a high signal-to-noise ratio.

Small-Angle X-ray Diffraction. Patterns were recorded photographically on a Rigaku-Denki camera using pinhole collimation. The X-ray source was from a Rigaku-Denki generator producing Ni-filtered Cu Kα radiation of 1.54-Å wavelength. Film-to-sample distance was 29 cm. Patterns were scanned with an EDP scanning microscope.

Wide-Angle X-ray Diffraction. Tracings were recorded with a General Electric composite system consisting of an XRD-6 generator, an SPG-4 goniometer, and a sealed proportional counter tube detector. The radiation employed was Ni-filtered Cu Kα. Diffraction tracings were recorded by continuous scanning at a rate of 2°/min in a 5–38° 2θ range. Unoriented dry powder samples were mounted on glass slides for scanning.

Results

Conformational Content of PET. A quantitative determination of the relative conformer composition is possible by using Fourier transform infrared spectroscopy. Several successful applications to polymer systems have demonstrated the usefulness of the procedure.[6,8,14] In brief, first a separation of conformationally "pure" spectra is required by using the ratio method or spectral stripping. These spectra are then used as components in a least-squares curve-fitting algorithm. The best fit of the components to the spectrum of the mixture yields the relative conformer composition.

The ratio method for separation of conformational isomers has previously been applied to annealing studies of glassy PET.[6,8,9] In this work the authors have applied the procedure to solution-grown crystals of PET. Earlier work has suggested that use of the 973-cm^{-1} trans and the 898-cm^{-1} gauche absorbance bands for coefficient determination. Figure 3 shows the result of application of the ratio method to solution-quenched and solution-crystallized (135 °C) PET spectra. (A) is the spectrum of the "pure" trans conformer and (B) the "pure" gauche. The trans spectrum contains the bands typically assigned to this conformation (e.g., 1471, 1386, 988, and 972 cm^{-1}) and likewise for the gauche (e.g., 1370, 1041, 1019, and 898 cm^{-1}).

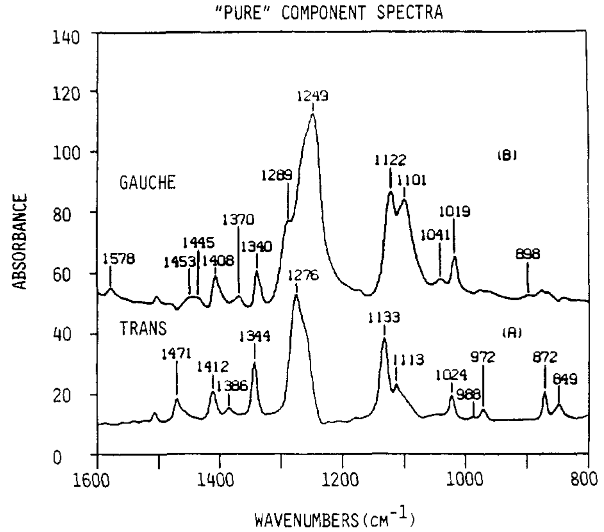

Figure 3. "Pure" spectra used in the curve-fit analysis: (A) spectrum of the "pure" trans conformational isomer; (B) "pure" gauche isomer.

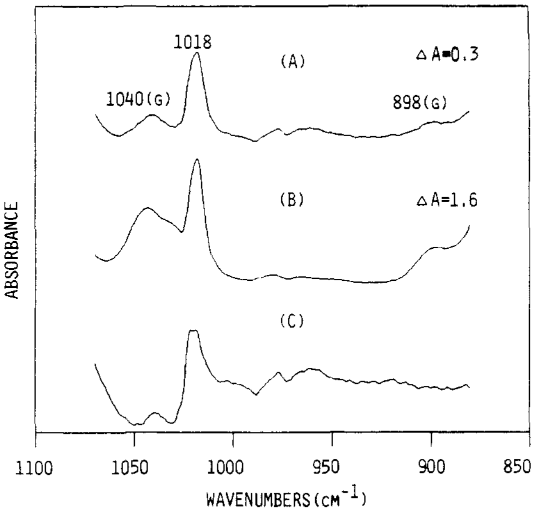

Figure 4. "Pure" gauche spectra (1075–875 cm^{-1}): (A) solution-crystallized gauche; (B) glass-annealed gauche; (C) difference spectrum.

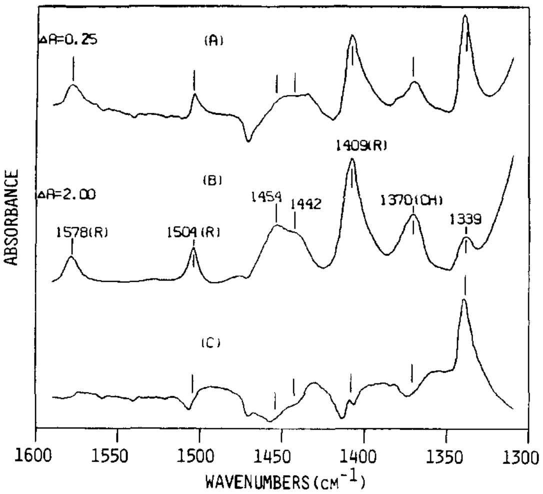

Figure 5. Same as Figure 4 in the 1590–1310-cm^{-1} region.

For purposes of comparison the ratio method was also applied to spectra of amorphous and heat-crystallized PET. The "pure" gauche spectra derived from PET crystallized in solution and heat-crystallized from the glassy state are shown in Figures 4 and 5. The solution-

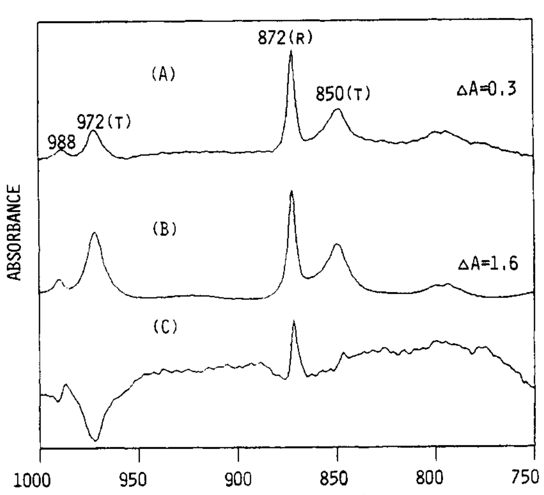

Figure 6. "Pure" trans spectra (1000–750 cm^{-1}): (A) solution-crystallized trans; (B) glass-annealed trans; (C) difference spectrum.

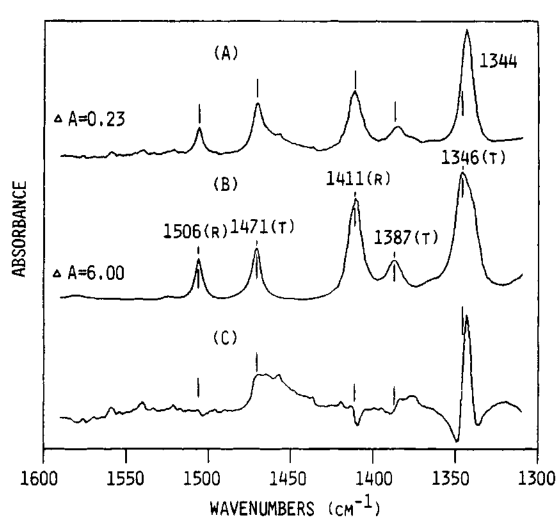

Figure 7. Same as Figure 6 in the 1590–1310-cm^{-1} region.

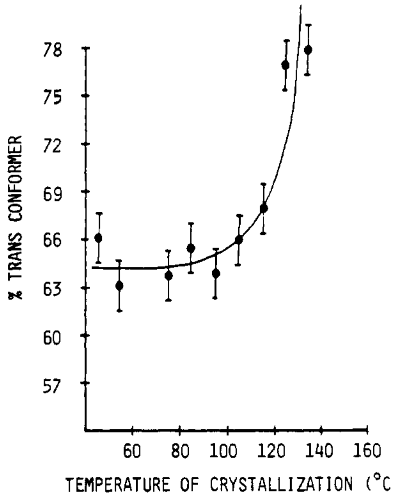

Figure 8. Relative amount of trans conformation as a function of the crystallization temperature.

crystallized spectra are shown in (A) and the annealed spectra in (B) of each figure. The given absorbance values are for the original mixtures before separation. Since the absorbances of the annealed spectra are outside the Beer's law range, interpretation is necessarily qualitative. The criterion for subtraction in Figure 4 is the reduction of the 898-cm^{-1} gauche mode to zero, and in Figure 5, the reduction of the 1578-cm^{-1} amorphous ring mode to zero. The subtraction spectrum 4C reveals 2 points. First, the ring (1018 cm^{-1}) and gauche –C–O– (1040 cm^{-1}) bonds are in different environments as evidenced by the opposite intensities and secondly, the –C–O– mode has a broader vibrational distribution in the annealed gauche. Figure 5C reveals substantial differences in the glycol segment of the molecule. A shift in the distribution of the CH_2 bending modes centered around 1445 cm^{-1} toward lower wavenumbers is indicative of a distortion of gauche conformations. Also in Figure 5C a considerable intensity increase is displayed in the 1339-cm^{-1} band. The band has often been assigned to a trans association of glycol segments. Since all other trans contributions have been removed from these "pure" gauche spectra via the ratio method, the increased intensity is not due to additional trans associations of the glycol segment. Therefore, changes in the terephthalic acid portion of the molecule are suggested as affecting vibrational changes in the glycol segment. Spectral evidence for alteration of ring vibrations in the "pure" gauche of the two sample preparations is apparent in the 1409- and 1808-cm^{-1} modes. The spectra of the "pure" trans isomers are shown in Figures 6 and 7 for solution-crystallized samples (A) and heat-crystallized glassy samples (B). The criteria for the subtraction spectra (C) are the 795-cm^{-1} ring mode in Figure 6 and the 1506-cm^{-1} ring mode in Figure 7. The difference in intensity ratios of the 972-cm^{-1} trans and 872-cm^{-1} ring bands of Figure 6 is indicative of a different environment for these modes in the two types of preparations. In addition, the subtraction shows an increased vibrational distribution in the annealed sample. This is characteristic of a decrease in order in the annealed crystals as compared to the crystals grown in solution. The same is true of the 1350–1340-cm^{-1} band in Figure 7C. In this case the annealed sample spectrum, Figure 7B, has a shoulder which corresponds to the maximum observed in the solution-crystallized spectrum, Figure 7A. This suggests that the annealed trans has two species, one of which is equivalent to the solution-crystallized vibration. Other spectral changes in Figure 7C indicate that the trans conformers of each sample reside in different vibrational environments.

With a separation of conformational isomers in hand it becomes a simple matter to apply a linear least-squares curve-fitting algorithm to determine the conformational composition. The technique allows for the use of an entire spectral region for the calculation of scaling coefficients. A substantial improvement of fit occurs when a straight base line is used as an additional component in the analysis. We have applied the technique to spectra collected from samples crystallized from dilute solution over a wide temperature range. The results are shown in Figure 8. The % trans levels off to ca. 63 at low temperatures of crystallization. Solution quenching the hot PET–solvent mixture into liquid nitrogen yields a % trans value of 62.7 substantiating the minimum in the temperature range under study. The data display an increase in the trans conformer content with temperature of crystallization. The kinetic theory of chain folding predicts a similar dependence of lamellar thickness on crystallization temperature. Yamashita has experimentally verified such an increase for PET crystallized in DMP in the same temperature range as the present study.[1] This suggests an interdependence of the amount of trans conformer and the long period.

Characterization of the Trans Content in the Amorphous Phase. Table I shows the wide-angle X-ray diffraction (WAXD) % crystallinity measurements as a function of temperature for the solution-crystallized sam-

Table I
Characterization of the Trans Content in the Amorphous Phase

temp, °C	F_c (WAXD)	F_g (IR)	F_a
45	63	0.34	+0.03
55	64	0.37	−0.01
65	64	0.36	0.0
75	65	0.36	−0.01
95	65	0.36	−0.01
115	67	0.32	+0.01
135	75	0.22	+0.03
155	69	0.29	+0.02

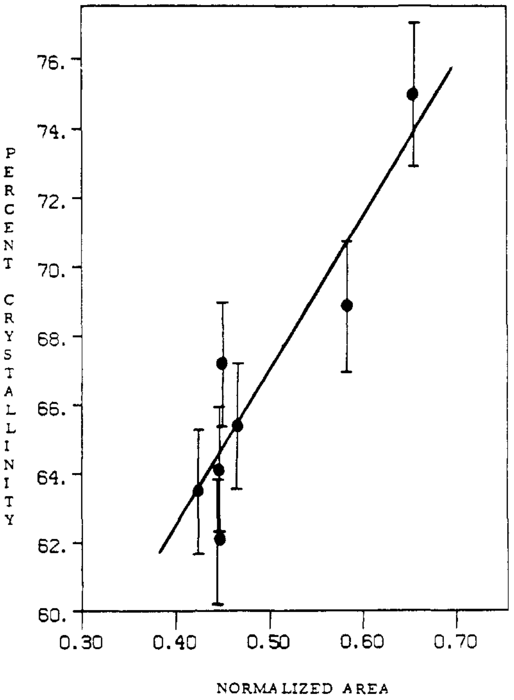

Figure 9. Correlation of the normalized area of the 875-cm^{-1} out-of-plane ring mode with the wide-angle X-ray measured % crystallinity. The 875-cm^{-1} band is normalized with the 1410-cm^{-1} band.

ples. The values are consistent in magnitude and trend with IR % trans conformer content. A linear correlation between FTIR and WAXD results is observed. The normalized area of the 875-cm^{-1} mode is shown to vary directly with the amount of crystallinity measured by WAXD as seen in Figure 9. The 875-cm^{-1} band is normalized against the 1410-cm^{-1} benzene ring band. The normalized absorbance of the 1410-cm^{-1} band has been shown to be constant with temperature.

However, the infrared analysis does not differentiate between trans conformers in the crystalline and amorphous phases.[6] The authors have demonstrated this on samples of PET annealed from the glass using spectral stripping. Quantification of the trans content with IR is a measure of trans conformers in both phases. Conversely, WAXD is sensitive only to the crystalline trans conformers. We have

$$F_c + F_g + F_a = 1 \qquad (12)$$

where F_c = fraction crystalline, F_g = fraction gauche, and F_a = fraction trans amorphous. This equation assumes the compatibility of infrared and WAXD data for this application. This has been demonstrated in a prior work.[24] A correlation of the WAXD-measured crystallinity with the IR-measured gauche content for crystalline PET yielded F_a in agreement with an IR-density correlation.[6] For example, the WAXD-measured crystallinity of an amorphous film is zero ($F_c = 0$), and the gauche content is ca. 85%. This gives an F_a value of 15% which is close to other independent estimates.

Table II
Conversion of the Long Period to the Lamellar Thickness by a Volume Crystallinity Treatment: Solution-Crystallized Samples

temp, °C	ρ	ρ/ρ_c	% trans	L,[a] Å	LT, Å
85	1.452	0.9616	65.6	64.0	40.4
95	1.453	0.9623	64.2	64.5	39.8
105	1.453	0.9623	66.2	65.0	41.4
115	1.458	0.9612	68.0	65.5	42.8
125	1.455	0.9636	77.1	68.0	50.5
130	1.460[b]	0.9669	76.0[b]	75.0	55.1
135	1.461	0.9675	78.0	97.0	73.2

[a] Reference 1. [b] Extrapolated from data.

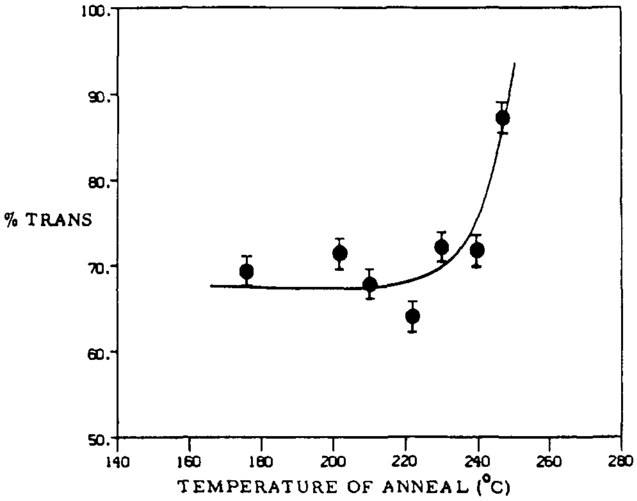

Figure 10. Relative amount of trans structure as a function of temperature of anneal for crystals solution grown at 45 °C. Samples were annealed for 1 h. Each data point results from a different sample.

Least-squares curve-fitting of infrared spectra provides F_g. Integration of WAXD curves gives F_c. Subtraction using eq 6 yields the amount of trans conformer in the amorphous phase for PET crystallized in solution. The last column in Table I shows the calculated values for the trans-amorphous fraction. The essentially zero values within experimental error establish that all trans structures are contained within the organized lattice of the crystal. Note that this also establishes the absence of trans structures in chain folds and tie molecules.

Correlation of the lamellar thickness and the gauche/trans ratio based on eq 11 is shown in Figure 2. The number of gauche units in a chain fold (n) is the variable parameter. The data for PET crystallized from dilute solution are plotted in Figure 2. Long-period measurements are taken from Yamashita[1] for PET crystallized under the same conditions. Lamellar thickness is obtained by multiplying the long period by the volume crystallinity factor. Table II shows the results of the treatment. Density of the crystalline region is 1.51 g/cm^3 from infrared analysis.[6] Figure 2 shows that the average number of gauche units in the fold (n) is greater than two and less than four for all crystallization temperatures. It is interesting to note that the average number of units per fold appears to increase with lamellar thickness (i.e., temperature). The average value calculated from the plot is n = 2.48.

Conformational Analysis of Annealed PET. The least-squares curve-fit algorithm has been applied to the spectra of annealed samples of solution-crystallized PET.

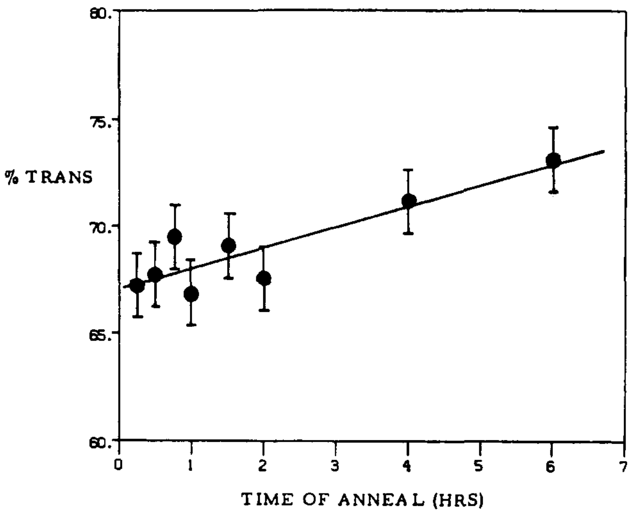

Figure 11. Relative amount of trans structure as a function of time of anneal for crystals grown at 45 °C. Data points result from different samples.

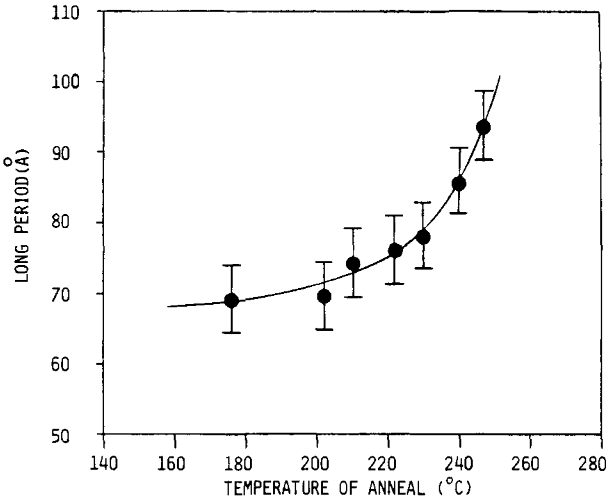

Figure 12. Long period as a function of temperature of anneal. Same sample treatment as in Figure 10.

Figure 10 shows a plot of the relative amount of trans conformer vs. the temperature of anneal for a sample solution crystallized at 45 °C. The samples have been annealed at their respective temperatures for 1 h. As the melting temperature is approached, the trans content increases asymptotically.

Figure 11 shows the trans content as a function of time of anneal at 230 °C for crystals grown at 45 °C. Data points originate from different original solution-crystallized samples grown at 45 °C. The linear increase in the trans content is in accordance with a gradually increasing lamellar thickness.

Small-Angle X-ray Diffraction. Small-angle X-ray diffraction patterns were obtained on unoriented and annealed solution-crystallized mats. The long spacings were calculated by assuming Bragg's law. Results for the long period as a function of temperature of anneal are shown in Figure 12. Samples are crystallized at 45 °C and annealed at the respective temperature for 1 h. Error bars are the 95% confidence limits in peak maximum estimation. The long period is shown to increase sharply as the melting temperature (ca. 260 °C) is approached. This effect occurs in many polymer systems[3] including solution-crystallized and annealed PET.[1,11]

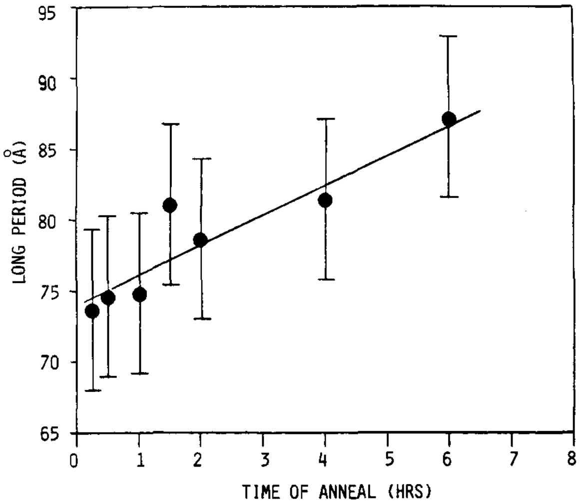

Figure 13. Long period as a function of time of anneal at 230 °C. Same sample treatment as in Figure 11.

Table III
Conversion of the Long Period to the Lamellar Thickness by a Volume Crystallinity Treatment: Annealed Samples

temp of anneal, °C	time of anneal, h	L, Å	ρ, g/cm^3	% trans	LT, Å
176	1	69.1	1.420	69.4	45.1
202	1	69.6	1.416	71.6	46.7
210	1	74.2	1.416	67.9	47.2
222	1	76.1	1.417	64.1	45.8
230	1	78.0	1.418	72.3	53.0
240	1	85.6	1.420	71.9	57.9
247	1	93.6	1.421	87.3	76.9
230	0.25	73.6	1.411	67.2	46.2
230	0.50	74.6	1.415	67.7	47.3
230	1.0	74.8	1.415	66.8	46.8
230	1.5	81.1	1.416	69.1	52.6
230	2.0	78.6	1.416	67.6	49.8
230	4.0	81.4	1.416	71.2	54.3
230	6.0	87.2	1.416	73.1	59.7

Results of the long period vs. the time of anneal are shown in Figure 13. Samples were crystallinized in solution at 45 °C and annealed at 230 °C. The long period increases linearly with time of anneal. Diffraction patterns of samples annealed for times greater than 6 h lost the discrete unoriented ring character and were not used in this analysis.

Correlation of FTIR and SAXD Measurements. Solution-crystallized samples grown at 45 °C were annealed in two ways. The time (at 230 °C) and the temperature of annealing were varied. Table III shows the conversion of long period to lamellar thickness for these samples. Correlation of the lamellar thickness and the conformer content of annealed samples is shown in Figure 2 (open symbols). Time of anneal (open circles) has no effect on the value of n. In other words, the structure of the fold remains constant. On the other hand, annealing for 1 h as a function of temperature produces a change in the fold structure (open triangles). The number of gauche units in the chain fold (n) drops to one when the gauche to trans ratio becomes low. This corresponds to an annealing temperature of 247 °C. In addition to the fact that the fold structure is changing at high temperatures, adjacent reentry is implied by a one-unit-fold structure.

The correlative analysis is also applied to PET heat-crystallized from the glass in Figure 2. Conformational content data of Lin and Koenig[6] and long period data of Yeh[2] are plotted for PET annealed from the glass for 300 min at temperatures between 130 and 200 °C. Here the long-period data are not corrected for the volume fraction

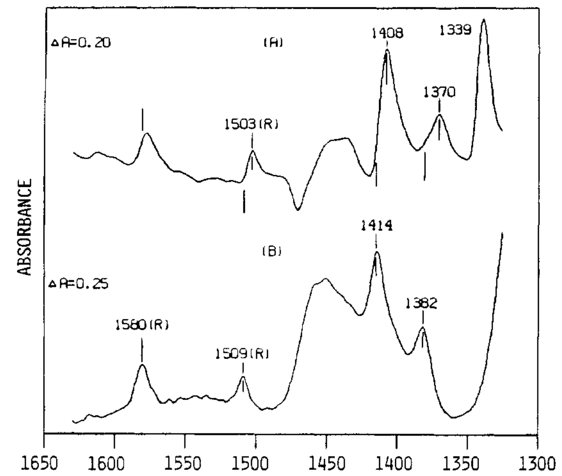

Figure 14. Spectra of (A) "pure" gauche of solution-crystallized PET and (B) cyclic trimer in trifluoroacetic acid with the solvent subtracted.

of crystallinity. In the temperature range under consideration, the fold material does not significantly change. A value of $n = 19$–20 indicates a large amount of nonadjacent reentry, loose loop folds, or tie molecules. Since the temperature range under consideration does not give the morphology assumed in eq 9, the data are presented in Figure 2 for comparative purposes.

Discussion

In order to apply the long-period reduction by the volume crystallinity factor, a two-phase system must exist. In the unit cell of crystalline PET all conformers are trans. However, the glassy polymer contains mainly gauche conformers and a small amount of trans. This suggests a heterogeneous or multiphase system. On the other hand, highly crystalline PET contains no trans conformers in the amorphous regions.[6] In other words, the amorphous regions are composed solely of gauche species. The crystals under study here are believed to contain little, if any, trans conformers in the amorphous phase, as previously noted. This suggests a homogeneous amorphous phase. Additionally, PET solution crystallizes in a well-developed lamellar morphology. As a consequence the crystals can be analyzed as a two-phase system.

The correlation of FTIR and SAXD data indicates the fold structure in solution-crystallized PET is composed of two to three gauche units. Other lines of evidence support a three-gauche-unit fold. First, space-filled molecular modeling of two adjacent crystal stems and an associated fold confirms the steric feasibility of an adjacent reentry three-gauche-unit fold structure. The model requires the carbonyl groups to be in the cis position and out of the plane of the benzene rings. Modeling of a two-gauche-unit fold indicates that the structure cannot adjacently reenter the lattice. However, nonadjacent reentry is possible with two units.

Second, the occurrence of about 1% cyclic tris(ethylene terephthalate) is observed in PET.[15-17] The increased abundance of this species over other oligomers implies an ease of formation of three units into a tight turn. In addition, scission of a single bond of cyclic tris(ethylene terephthalate) essentially produces the proposed three-gauche-unit fold structure. The structural resemblance of the trimer and the fold of solution-crystallized PET suggests vibrational similarities. Figures 14 and 15 show the spectra of pertinent chemical species. The (A) spectra are of the "pure" gauche conformers from solution-crystallized samples and the (B) spectra are of cyclic trimer crystals dissolved in trifluoroacetic acid with the solvent subtracted out. Throughout most of the spectra a one-to-one correspondence exists between the "pure" gauche and the cyclic trimer samples when band shifts are taken into account. The similarities between the spectra are evidence for the occurrence of a fold structure composed of three gauche isomers.

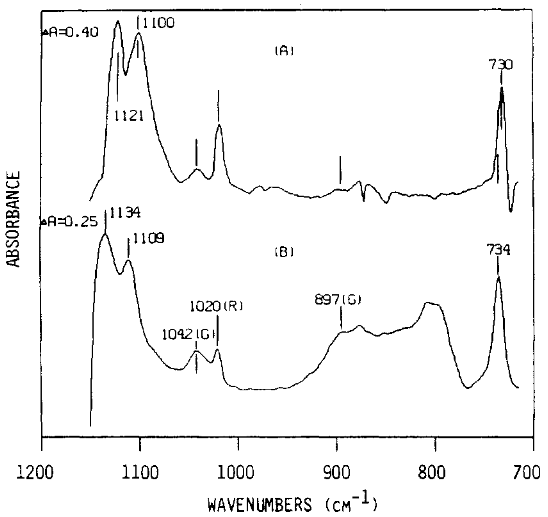

Figure 15. Same as Figure 14 in the 1200–700-cm^{-1} region.

Third, a thermodynamic treatment of the work of chain folding concurs with our results. This treatment has previously been applied to polyethylene.[18] Assuming a primary ethylenic rotation of the PET molecule, each gauche isomer increases the stored energy in the polymer backbone by 0.8 kcal/mol.[20] A fold surface free energy of 29 erg/cm^2 [19] leads to the number of gauche units per fold of 2.74.

Annealing treatments can reduce the number of fold gauche units as evidenced by the smaller values of n as seen for some samples in Figure 2. The effect is most obvious at high temperatures where the fold changes to a one-unit-gauche structure. In this case an increase in the lamellar thickness with annealing can conceivably occur by rotation of two of the gauche conformers into trans thus forming a tight fold of one gauche unit. This process will increase the lamellar thickness by up to 50%, enough to account for the presently reported change at high temperature. Note that reptation alone cannot explain an increse in trans units accompanied by a decrease in the number of gauche units in the fold. A combination of reptation and gauche-to-trans conversion of the fold units is proposed.

The correlation between lamellar thickness and relative conformer composition employed in this analysis makes no assumptions about the trans content in the amorphous phase. An increase in this species with annealing treatments will affect the presently reported results. If the trans in the amorphous phase increases with annealing, the conformers will be present in the folds or as tie molecules. Incorporation of trans molecules in the fold with annealing requires the formation of loose loop structures with annealing. Our data do not support the formation of such structures. An increase in the trans-amorphous species will, therefore, occur in conjunction with the formation of tie molecules. A similar conclusion was reached by other authors.[7] This process occurs by trans-esterification of fold units to adjacent lamellae. Small-angle X-ray patterns show that extensively annealed samples lose the discrete ring pattern characteristic of samples annealed for short times. The increased intensities at lower angles are indicative of the formation of larger structures. Therefore, the occurrence of trans-amorphous conformations in tie molecules is inferred.

The effect of the increased trans-amorphous content on the presently reported fold structure is now considered. Since the species cannot be spectroscopically distinguished from the crystalline trans conformation, the calculated number of crystalline stem segments is overestimated (eq 5). The total gauche will not be affected by the presence of trans conformers in the amorphous phase. It follows that the calculated number of gauche units in the chain fold is too low. This accounts for the small observed decrease in the number of gauche units in the fold of annealed samples. We therefore conclude that the annealing of solution-crystallized PET as a function of time and temperature does not significantly affect the fold structure. Note that this conclusion is not applicable to annealing temperatures which approach the melting point of the crystalline regions where the number of fold gauche units drops to one.

Conclusions

The relative trans content as measured by least-squares curve-fitting of digitized FTIR spectra increases asymptotically as the temperature of crystallization in dilute solution approaches the dissolution temperature. The trans content increases in a similar manner when dry samples are annealed close to the melt. Concurrent with the trans increases are asymptotic rises in the lamellar thickness as measured by SAXD. Linear changes in the trans content and the lamellar thickness are observed as a function of time of anneal. Correlation of FTIR and SAXD data establishes a fold structure of between two and three gauche units in solution-crystallized PET. At high temperatures of anneal, the number of gauche units is reduced to one. Time of anneal has no effect on the fold structure.

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Photoacoustic Infrared Spectroscopy of Doped and Undoped Poly(*p*-phenylene)

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ABSTRACT: The Fourier transform infrared photoacoustic spectra of poly(*p*-phenylene) (PPP) prepared by different means, perdeuterated PPP, and heavily doped PPP are examined. Upon doping, new spectral features appear similar to those observed in doped oligomers. The effect of dopant on polymer chain length is discussed. Also examined is PPP coordinatively doped by metal carbonyls.

Introduction

Its remarkable thermostable properties, in addition to access to electroconductivity, make poly(*p*-phenylene) (PPP), a unique polymer. Like many other extended π polymers, PPP may be oxidized or reduced with a concomitant increase in electroconductivity of over 12 orders of magnitude.[1] Also like other extended π polymers, PPP and its derivatives present a plethora of interesting experimental challenges due to insolubility, infusibility, opacity, varying and uncertain morphologies, and, in the

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