Microstructure of Amorphous and Crystalline Poly(ethylene terephthalate)

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ABSTRACT: The microstructures of amorphous and crystalline poly(ethylene terephthalate) (PET) homopolymers have been determined in terms of their *trans* and *gauche* conformational isomer contents by using a combination of infrared and density characterization techniques. The effects of isothermal crystallization (from the glassy state between 105–150°C), as well as the effects of different monomer units in the polymerization process, have been investigated. Results indicate that samples, polymerized from different monomer and catalyst systems, show different microstructures in terms of *trans* and *gauche* isomers. These variations result in significant differences in PET optical properties. Further investigations find that these dissimilar behaviors accompany conformational isomer variations in the amorphous phase, suggesting different transformation mechanisms of *trans* and *gauche* isomers at early stages of crystallization. These unlike microstructural transformation processes give rise to further changes, which are evident in terms of the intensity of Vv light scattering, haze values, thermal properties, and FTIR spectral results. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1965–1976, 1998

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INTRODUCTION

In poly(ethylene terephthalate) (PET), the ethylene glycol linkages can exist in two rotational conformations; a *trans* or extended form, and a *gauche* or relaxed form.[1–3] These isomers can be transformed from one conformation to the other by partial rotation about C—C bonds. Because only two conformational isomers are possible in PET samples, PET can be considered to satisfy a two-phase conformational model.[4,5] The conformation in the crystalline phase of PET must be *trans*, whereas the amorphous phase consists of both *trans* and *gauche* isomers. Fourier transform infrared spectroscopy (FTIR) has been widely used to study PET conformational changes during

the crystallization of PET as a result of orientation and/or annealing.[5,6–11] Schmidt,[12] as well as Lin and Koenig,[13] have quantitatively determined conformational isomeric compositions in PET by using combinations of infrared and density measurements.

The macroscopic properties of PET depend on its specific internal morphologies and microstructural arrangement. A variety of microstructures can be developed in PET by various processing and preparation techniques. The natures of these microstructures significantly influence thermal, mechanical, optical, and permeation properties; however, the relationships among microstructures, polymerization processes and final properties of PET are not completely understood. In this research, the microstructures of amorphous and crystalline PET homopolymers have been determined in terms of the *gauche* and *trans* conformational isomer components by using polarized in-

ternal reflectance infrared spectroscopy (IRS). The effects of thermal crystallization have been investigated in relationship to differences in-monomer units and polymerization processes. Optical properties have been evaluated in terms of haze measurements, and correlations between these properties and PET microstructures have been developed.

EXPERIMENTAL

Materials

Amorphous sheets of poly(ethylene terephthalate) (PET) homopolymers, with thicknesses between 10–15 mils (0.25–0.38 mm), were used for this work. They were prepared under different manufacturing conditions and have been designated as polymers A and B. Polymer A was prepared from dimethyl terephthalate (DMT) monomer and has an intrinsic viscosity (I.V.) of 0.80, which is equivalent to a weight average ($\bar{M}_w$) molecular weight of about 57,000. Polymer B was prepared from terephthalic acid (TPA) monomer and has an I.V. of 0.81, which is equivalent to a $\bar{M}_w$ of about 58,000.

Thermal Crystallization

Prior to crystallization, the amorphous PET sheet samples were annealed at 85°C for 15 min to remove residual stresses. Isothermal crystallization of the samples was performed in a thermal chamber under unconstrained conditions at 105, 110, 120, 130, and 150°C for times from 5 min to 4 h.

Compression Molding

A limited number of samples were prepared by compression molding to ensure measured property changes did not result from processing conditions experienced by sheets as prepared by their manufacturer. Amorphous sheets of PET A were vacuum dried overnight at 120°C before being placed in a Carver press that had been preheated to 275°C. The two parts of the press were brought together (without pressure) on the sample sandwiched between two Teflon® covered metal plates. The PET was then permitted to melt in order to destroy all previous stress and crystallinity. Pressure on the sample was then gradually increased to 5000 lbs., held for about 30 s, and released. Amorphous compression molded samples were

obtained by quickly removing and quenching the remelted sheets in cold water.

Density

Sample densities were measured at 25°C in a gradient column made from aqueous calcium nitrate solution and calibrated by suspending glass beads with known densities according to ASTM procedure (D 1505–85). Accuracy was within ± 0.0003 g/cm^3.

Fourier Transform Infrared Spectroscopy

Infrared spectra were obtained with a Perkin-Elmer model 1600 FTIR spectrophotometer. Polarized internal reflectance spectroscopy (IRS) techniques were used to characterize the internal structure of PET. The samples were cut in rectangles 10×48 mm. For each sample condition, two pairs of samples were cut. One pair was cut with the machine direction (MD) parallel to the extrusion direction of the sheet. The other pair was cut perpendicular to the first pair, which is the transverse direction (TD) of the sheet. Each pair of cut samples was positioned on both side of a $50 \times 20 \times 2$ mm thallium bromide-iodide (KRS-5), 45° reflectance element, mounted in a Harrick internal reflectance accessory. The accessory was placed in a Harrick TMP-V twin parallel mirror reflectance attachment. Spectra were obtained from 256 scans and recorded for each sample direction with respect to the polarized radiation (0 or 90° to the electric vector with respect to the entrance slit). All spectra were recorded with 4 cm^{-1} resolution.[10]

Small-Angle Light Scattering

Light scattering patterns were obtained with a small-angle photographic light scattering apparatus. A Spectra-Physics model 155 helium-neon gas laser ($\lambda_0 = 6358$ A^0) was used as a light source. Exposure times were regulated with a camera-type shutter, and patterns were recorded on Type 57 (4×5 in.) Polaroid Land Film.[14] Both Vv and Hv modes of scattering were utilized. In the Vv mode, both polarizer and analyzer are in parallel directions, while in the Hv mode they are perpendicular to each other.

Haze Measurement

A Gardener Pivotable-Sphere Hazemeter (model HG 1204) and a Gardner Digital Photometric

Figure 1. Modified structural factor (A'_0) values for gauche (□) and *trans* (△) isomers plotted as functions of density for A PET.

Unit (model PG 5500) were used to measure percent haze according to the ASTM D 1003–61 procedure. Haze measured by this procedure is defined as the percentage of transmitted light which, in passing through the specimen, deviates from the incident collimated beams by forward scattering at an angle greater than 2.5°.

Thermal Characterization

A Perkin-Elmer differential scanning calorimeter (DSC-7) was used to characterize PET crystallization behavior. Samples of about 10 mg were weighed in aluminum sample pans. Thermal measurements were performed with a stream of dry nitrogen flowing over the samples to prevent oxidative degradation. Isothermal scans were recorded as functions of time after samples had been rapidly heated to the desired crystallization temperature. For A-materials, crystallization temperatures were 107, 110, and 112°C. Those for B-materials were 103, 105, and 107°C. Crystallization conditions were maintained until thermal equilibrium had been achieved. The fractional crystallinity as a function of time was calculated using standard Perkin-Elmer software.

RESULTS AND DISCUSSION

Fourier Transform Infrared (FTIR)

Infrared spectral changes examined in this work are associated with the rotational isomers of the PET ethylene glycol residue. Specific band intensities at 1340 cm^{-1} and 1370 cm^{-1}, which are assigned as *trans* and *gauche*, respectively, were measured. These band intensities were normalized with that of the 1410 cm^{-1} band, which results from phenylene ring vibrations and is not sensitive to changes in sample orientation and conformation. Peak heights were taken using standard Perkin-Elmer software. The modified structural factor A'_0 was calculated for *gauche* and *trans* rotational isomers according to the method developed by Lofgren and Jabarin.[10] Values for the modified structural factor (A'_0) are obtained from the averaged spatial attenuation indices measured in the machine, transverse, and thickness directions, and are proportional to overall levels of *trans* and *gauche* molecular conformations without respect to material orientation or direction.

Modified structural factors for both *gauche* and *trans* isomers are plotted as functions of density in Figs. 1 and 2 for A and B homopolymers. From the figures, it can be seen that A samples (made from DMT), exhibit obvious differences in development of *trans* isomer, at given density values, in comparison to B samples (prepared from TPA). B samples show behavior consistent with a linear correlation between the modified structural factor of *trans* and *gauche* conformational bands and density, as described in most available references.[10,12,13] The A PET samples, however, show nonlinear relationships at low densities and linear relationships at higher densities for both *trans* and *gauche* values. No published article could be found illustrating these nonlinear relationships.

Figure 2. Modified structural factor (A'_0) values for *gauche* (□) and *trans* (△) isomers plotted as functions of density for B PET.

Figure 3. Spherulite size plotted as a function of density for A PET samples crystallized at 110°C (○) and 120°C (△).

To prove that the nonlinear behavior of A samples did not result from differences in sheet preparation processes, additional samples were melted and compression molded from the A material. These remelted, amorphous sheets were then thermally crystallized and subjected to the previously described analyses. Changes in *trans* and *gauche* contents, with respect to densities, were nonlinear and virtually identical to those shown in Fig. 1. Because results obtained for A samples, made by compression molding, are equivalent to those recorded for the original sheets, it appears that nonlinear *gauche* and *trans* correlations with density result from material differences rather than method of amorphous sheet preparation.

Small-Angle Light Scattering (SALS)

The spherulitic radii for samples A and B were measured with small-angle light scattering (SALS) in the Hv mode. Light scattering patterns were similar to those observed by Jabarin[14] with the size of the pattern decreasing with increasing crystallization time. Spherulite size is inversely proportional to size of the scattering pattern according to eq. (1)[14] where

$$U_{max} = \frac{4\pi R}{\lambda} \sin \frac{\theta_{max}}{2} = 4.1 \qquad (1)$$

and λ is the wavelength of light in the scattering medium, R is the spherilite radius, and θ_{max} is the scattering angle where the intensity is maximum.

Decreasing pattern size; therefore, indicates increasing spherulite size. Figures 3 and 4 show spherulite sizes plotted as functions of density for materials A and B. From these figures, it can be seen that A material has much larger spherulite sizes than B material at low densities and also has much larger maximum spherulite size than B material before impingement. When the density of B material is lower than 1.36 g/cm³, the spherulites are too small to be measured by the small-angle light scattering method. The spherulites of A material, however, can be measured even when the density is as low as 1.335 g/cm³.

The above phenomena can be explained as follows. In B PET samples, there may be some solid substance, impurity, or residual catalyst originating from synthesis and processing, acting as nucleation centers. B materials appear to have generated many more active centers during the nucleation process. If spherulite size is reduced due to increased nucleation by the presence of a nucleating agent,[15] the spherulite radii could be too small to be measured by SALS, but the numbers of the spherulites would be much larger, and finally they would impinge with each other much sooner. Because this impingement retards further growth of the spherulites, the maximum sizes of B spherulites are smaller than those of A spherulites.

Haze Measurement

The variations of the percent haze with time, at various crystallization temperatures, for A and B samples are shown in Figures 5 and 6. At each

Figure 4. Spherulite size plotted as a function of density for B PET samples crystallized at 110°C (○), 120°C (△), and 130°C (×).

Figure 5. Variations in percent haze with time for A PET samples crystallized at 110°C (○), 120°C (△), and 130°C (×).

Figure 7. Variation of percent haze in relationship to density of A PET samples crystallized at 110°C (○), 120°C (△), and 130°C (×).

temperature, the haze values for A samples rise sharply to reach a maximum. For B samples, at low temperatures, the haze gradually increases to the maximum value. Comparing these two kinds of samples, B samples have smaller haze values than A samples at each temperature.

The variation of the percent haze was also related to density at various crystallization temperatures for A and B samples, as shown in Figures 7 and 8. In the case of A PET, a sharp increase in haze occurs while the density is still quite low (1.341 g/cm^3). In the case of the B PET, however, the haze increases very slowly up to the maxi-

mum value at fairly high density. The maximum haze values of the A samples are higher than those of the B samples.

Percent haze has been related to spherulite radii in Figures 9 and 10 for A and B materials, respectively. It can be seen from the plots, that even at the same radius, the haze values of A samples are much higher than those measured for B samples. These results as well as the non-linear changes in *trans* and *gauche* values, exhibited by Sample A, will be further analyzed and discussed in the Correlations and Conclusions sections.

Figure 6. Variations in percent haze with time for B PET samples crystallized at 105°C (□), 110°C (○), 120°C (△), and 130°C (x).

Figure 8. Variation of percent haze in relationship to density of B PET samples crystallized at 105°C (□), 110°C (○), 120°C (△), and 130°C (×).

Figure 9. Relationship of percent haze to spherulite radius for A PET samples crystallized at 110°C (○) and 120°C (△).

Isothermal Crystallization Kinetic Study

Differntial scanning calorimetry (DSC) was used to obtain isothermal crystallization scans of A and B samples. Data recorded in these scans were then used to construct typical sigmoidally shaped isotherms at each temperature. B samples crystallized at lower temperatures and within much shorter times than A samples. It should be noted that the highest crystallization temperature (107°C) that could be measured for B PET is the lowest crystallization temperature used for A PET. This is because B material crystallization was too fast to characterize, when the crystallization process was carried out above 107°C.

The crystallization kinetics of polymers can be studied using the classical theory of Avrami for phase transformation:[16]

$$\theta_a = e^{-kt^n} \qquad (2)$$

where k is the kinetic rate constant, which is a function of nucleation and the growth processes, n is the Avrami exponent describing the mechanism of crystallization, θ_a is the fraction of untransformed material, and t is the crystallization time.

The activation energy of crystallization E_A can then be calculated according to the Arrhenius equation:[17]

$$k = Ae^{(-E_A/RT)} \qquad (3)$$

where, k is the kinetic rate constant, A the pre-exponential constant, E_A is the activation energy of crystallization, T is the temperature, °K, and R is the universal gas content.

The Avrami exponents, the kinetic rate constants, as well as the activation energies of crystallization obtained for A and B samples, are given in the Table I. As can be seen, the activation energy of A PET is higher than that of B material. The lower the activation energy, the lower potential energy that a polymer molecule needs to transform from the amorphous phase to the crystalline phase. This, therefore, enhances the rate of crystallization and lowers the temperature required for the activation of crystallization. Consistent with this explanation, SALS results as well as those from DSC have indicated higher rates of crystallization and lower crystallization activation temperatures for B than for A materials.

CORRELATIONS

To correlate results obtained for density, FTIR, SALS, haze, and DSC, the transformation behavior of conformational isomers in different phases, during the crystallization process, must be understood. The microstructure of PET, therefore, was further investigated by calculation of conformational isomer contents in the amorphous and crystalline phases.

Figure 10. Relationship of percent haze to spherulite radius for B PET samples crystallized at 110°C (○), 120°C (△), and 130°C (×).

Table I   Values Describing Isothermal Crystallization Kinetics of A and B PET

Sample	Crystallization Temperature (°C)	Avrami Exponent (n)	Kinetic Rate Constant (k)	Activation Energy, E_A	
				(kJ/mol)	(kcal/mol)
A	107	4.1	3.45e–15 s^{-4}	231	(55.3)
	110	3.6	1.68e–12 s^{-4}		
	112	3.3	4.30e–11 s^{-3}		
B	103	5.3	1.17e–19 s^{-5}	190	(45.4)
	105	5.3	2.99e–18 s^{-5}		
	107	5.1	6.99e–17 s^{-5}		

Calculation of Conformational Isomer Contents

The results of factor analysis, as well as spectroscopic comparisons, have confirmed that only *trans* and *gauche* isomers are spectroscopically distinguishable within the frequency regions concerned.[13] The following relationship can, therefore, be obtained in the infrared measurement:

$$T_a + T_c + G = 1 \qquad (4)$$

where, T_a is the fraction of *trans* isomer in the amorphous regions, T_c is the fraction of *trans* isomer in the crystalline phase, and G is the fraction of *gauche* isomer.

Lin and Koenig[13] used extrapolation methods and the combined measurement of density and infrared to determine the conformational isomer contents of PET in the amorphous and crystalline regions. They assumed the densities of *trans* and *gauche* in different regions are constant during the crystallization process. Because the morphologies and structures are changed during crystallization, the densities in the different regions must change with the change of structure. Results obtained by using this approach with our data were, therefore, not reasonable. Schmidt[12] also used the combined measurement of density and infrared, but introduced a different data analysis method. Schmidt's method was adapted in this study. Calculations for the isomer contents in different regions of PET proceed through the following steps: (1) extrapolate the data shown in Figures 1 and 2, of modified structural factor vs. density for *trans* isomer, to 1.455 g/cm^3 (100% crystalline PET) to obtain the maximum amount of *trans* structure for each kind of sample. (2) Calculate the *gauche* content (G) by subtracting the actual *trans* content, which is directly obtained from FTIR spectra from the maximum

trans content. (3) Calculate the crystalline *trans* content (T_c) from density results. (4) Calculate the amorphous *trans* content (T_a) according to eq. (4).

Results of these data analyses are shown in Figures 11 and 12 for A and B samples, respectively. It can be seen that for A PET, the amorphous *trans* isomer content increases sharply around a density of 1.341 g/cm^3, and then decreases and finally approaches zero. Changes in *gauche* content are also not linear with respect to density. Behavior of A PET samples is, therefore, not consistent with the published literature,[13] in which the amorphous *trans* and *gauche* contents both linearly decrease with density. In the case of B PET samples, results, as shown in Figure 12, are consistent with the published literature.[13]

Figure 11.   Crystalline *trans* (T_c), amorphorus *trans* (T_a), and *gauche* (G) conformational isomer concentrations as functions of density for A PET.

Figure 12. Crystalline *trans* (T_c), amorphous *trans* (T_a), and *gauche* (G) conformational isomer concentrations as functions of density for B PET.

Correlation between FTIR Results and Isomer Content Calculations

The nonlinear behavior of A PET samples can be explained in terms of the levels of conformational isomers in different regions. From the conformational isomer content analyses of A samples in Figure 11 it can be seen that changes in amorphous *trans* contents do not give a linear relationship with density. Crystalline *trans* contents, calculated from density measurements, are linearly related to destiny. The combined amorphous and crystalline *trans* values yield the total *trans*, with the nonlinearity contributed by the amorphous *trans* contant. *Gauche* behavior for A PET samples can be explained in the same manner. In the case of B PET samples (Fig. 12), the linear trends for *trans* isomers in the amorphous and crystalline phases lead to the total *trans* contents exhibiting linear relationships with density in a manner that is consistent with the published literature.[10,12,13] *Gauche* contents of B samples also decrease linearly with increased density values.

Lin and Koenig[18] studied *gauche-trans* isomerization of PET. They pointed out that isothermal crystallization can be deemed as a structural transformation that includes three phenomena: (1) reorganization of amorphous regions; (2) crystallization of amorphous chain segments; and (3) reorganization of crystalline regions. *Gauche-trans* isomerization occurs above T_g and is the predominant mechanism in the primary transformation stage of the crystallization process. Rodriguez-Cabello et al.[5] and

Jabarin[19] also pointed out that in the amorphous phase, the majority of amorphous *trans* isomers are associated with partial uncoiling of polymer chains, which are extended chain units making up the interlamellar links. Those partially extended units raise the local state of order (short-range order) in the amorphous phase.[5,13,19] Levels of amorphous *trans* depend on the tautness of the structure,[12] which could be considered as taut or extended tie chains between the lamellae.

Comparing A and B PET samples, it can be seen that the trends for amorphous *trans* and *gauche* content variations with density are different. For B PET samples, as a result of annealing, the *gauche* and amorphous *trans* contents decrease linearly as the crystalline *trans* content increases. The decrease of the amorphous *trans* content corresponds to a decrease in the number of extended tie chains in the amorphous regions, and thus an increase of the lamellae thickness in the crystalline regions. Therefore, during crystallization, as the PET crystallinity or density increases, amorphous trans confirmations change into crystalline *trans* by changing short-range ordered extended tie chains into long-range ordered lamella. *Gauche* forms are also changed into *trans* forms in the crystalline region, by long-range ordering of the coiled polymer chains. At high crystallinity, levels of amorphous *trans* approach zero, and the tie chains will be lost while the lamellar thickness increases. In the case of A PET samples, at low crystallinity, amorphous *trans* contents increase first and then decrease as crystallinity increases. This could be explained as follows. Because the crystallization activation energy for A PET samples is relatively higher than that for B PET samples, at the early stage of crystallization, the thermal energy is not enough to surpass the long-range ordering conformational barrier. *Gauche* isomers (which are randomly coiled chain units) only partially rotate to extended forms (which are amorphous *trans*) by gaining energy from thermal crystallization. Therefore, at low crystallinity, some of the *gauche* content is transformed to amorphous *trans* by short-range ordering, while lower levels of the *gauche* and amorphous *trans* contents are transformed to crystalline *trans* by long-range ordering.

From the above discussion, we can conclude that the different microstructures observed for A PET vs. B PET samples result from different transformation behaviors of *gauche* and amor-

phous *trans* isomers during thermal crystallization. Because properties of PET depend on its microstructure, the different microstructures will now be correlated with optical properties.

Correlation between SALS and Haze Measurement

When amorphous or nonoriented PET is heated to above its Tg, it crystallizes rapidly, forming an opaque material exhibiting spherulitic superstructures. Changes in the optical properties of PET are often characterized by haze, which is a combination measurement of surface and bulk effects. Haze in crystalline polymers results from the scattering of light, which is due to optical heterogeneities such as spherulites. The small-angle light scattering method, which is used to study the fluctuations of such heterogeneities, can be used to interpret the haze behavior variations in polymer films. The equations for light scattered intensities of the Hv and Vv modes are shown below:[20]

$$I_{HV} = A \cos^2 \rho_2 V^2 (3/U^3)^2 \{(\alpha_t - \alpha_r)[\cos^2(\theta/2)/\cos \theta]$$
$$\times \sin \mu \cos \mu (4 \sin U - U \cos U - 3SiU)\}^2 \quad (5)$$

$$I_{Vv} = A \cos^2 \rho_1 V^2 (3/U^3)^2 \{(\alpha_t - \alpha_s)$$
$$\times (2 \sin U - U \cos U - SiU) + (\alpha_r - \alpha_s)$$
$$\times (SiU - \sin U) - (\alpha_t - \alpha_r)[\cos^2(\theta/2)/\cos \theta]\cos^2 \mu$$
$$*(4 \sin U - U \cos U - 3SiU)\}^2 \quad (6)$$

where the terms are defined as follows:

A = constant of proportionality
V = volume of the spherulite
R = radius of the spherulite
θ = scattering angle in the scattering medium
μ = azimuthal angle
α_t = tangential polarizability of the spherulite
α_r = radial polarizability of the spherulite
α_s = polarizability of the surroundings
$\cos \rho_1 = \cos\theta/(\cos^2\theta + \sin^2\theta \cos^2\mu)^{1/2}$
$\cos \rho_2 = \cos\theta/(\cos^2\theta + \sin^2\theta \sin^2\mu)^{1/2}$
$U = (4\pi R/\lambda)\sin(\theta/2)$
$SiU = \int_0^\mu (\sin x/x)dx$

From the above equations, it can be seen that intensities of both the Vv and Hv mode are pro-

portional to V^2, which means they are proportional to the sixth power of the spherulites' radii. This can be used to explain the lower haze value of B than A PET at the same densities. Because B material has smaller spherulite sizes than A material, the intensity of the scattering is lower, resulting in lower haze values.

A comparison of the equations for light-scattering intensity shows that the term $(\alpha_t - \alpha_r)$ exists in the case of both I_{Hv} and I_{Vv}. The equation for I_{Vv} has two additional terms $(\alpha_t - \alpha_s)$ and $(\alpha_r - \alpha_s)$. Jabarin[14] has pointed out that these two terms are dominate factors in the I_{Vv} equation at the early stage of crystallization. Because Vv scattering is the major contributor to the haze behavior at the early stage of crystallization, these two terms are considered the most important factors controlling haze behavior at this stage. Considering α_s (which is the polarizability of the surroundings) as polarizability of the amorphous phase, the two terms $(\alpha_t - \alpha_s)$ and $(\alpha_r - \alpha_s)$ then represent polarizability differences between the spherulites and their surrounding amorphous phase. Therefore, the morphology or microstructure of the amorphous phase is a very important factor for haze behavior at the early stages of crystallization.

Correlation between Haze and IR Measurement

Changes of the conformational isomer contents in the amorphous phases of A and B samples can be used to interpretate their different haze behaviors. From Figure 11 it can be seen that for A PET, amorphous *trans* content increases at a density of around 1.341 g/cm^3 and then decreases, finally approaching zero at high density. These changes could be used to explain the haze values increasing sharply to a maximum around a density of 1.341 g/cm^3, as shown in Figure 7. While for B-homo, Figure 8 shows that the haze values just gradually increase to the maximum value, and correspondingly, Figure 12 shows that the amorphous *trans* and *gauche* both linearly decrease with increased density. Comparing the results for A and B samples, their amorphous phases appear to be different, especially at densities around 1.341 g/cm^3. These differences may be responsible for the differences in haze behaviors observed between these two samples.

It can, therefore, be concluded that the microstructure or morphology of the amorphous phase is the most important factor for the haze response at early stages of crystallization. Be-

35 min. @ 110°C

40 min. @ 110°C

60 min. @ 110°C

100 min. @ 110°C

3 hr. @ 110°C

20.5 hr. @ 110°C

Figure 13. Vv small-angle light scattering patterns recorded for A PET, during various stages of spherultic growth at 110°C. (Exposure times, filters, and other photographic conditions were held constant.)

cause the structures of the amorphous phase are different, α_s, which represents the polarizability of the surrounding amorphous phase, is different. This leads to different values of $(\alpha_t - \alpha_s)$ and $(\alpha_r - \alpha_s)$, which represent the polarizability difference between the spherulites and their surrounding amorphous phase. The inten-

sities of Vv scattering are then different, resulting in obvious different haze behaviors between A and B samples. A series of photographs from SALS, Vv scattering for A and B samples, are shown in Figures 13 and 14, respectively. These photographs were taken with the same filters and the same exposure times, and can therefore

30 min. @ 110°C   35 min. @ 110°C

40 min. @ 110°C   60 min. @ 110°C

105 min. @ 110°C   3 hr. @ 110°C

Figure 14. Vv small-angle light scattering patterns recorded for B PET, during various stages of spherulitic growth at 110°C. (Exposure times, filters, and other photographic conditions were held constant.)

be used to further illustrate that B PET gives less Vv scattering intensity than A PET, leading to lower haze values at early stages of crystallization.

CONCLUSIONS

Poly(ethylene terephthalate) (PET) samples, polymerized from different monomer and cata-

lyst systems, were found to develop different microstructures after exposure to equivalent crystallization conditions. These microstructural differences were monitored in terms of crystallization behavior and property changes using differential scanning calorimetry (DSC), density, infrared (IR), small-angle light scattering (SALS), and haze measurements. Major conclusions resulting from interpreting the in-

terrelationships and implications of these studies are as follows: (1) During the initial stages of lower temperature crystallization, A and B polymers behave differently. Crystallization of the B material gives larger Avrami exponents, lower activation energy, and faster rates of crystallization. (2) Modified structural factor (A_0') *trans* values of B materials increase linearly with increasing density, while corresponding *gauche* values decrease linearly. Within a range of lower density or crystallinity values, A materials exhibit nonlinear behavior, unlike that previously described in the published literature. (3) Amorphous *trans* as well as crystalline *trans* and *gauche* values, obtained from combined measurements of density and infrared spectroscopy, indicate the expected linear relationships with density for B materials. Consistent with published literature, amorphous *trans* and *gauche* contents approach zero at high levels of crystallinity or density. In the case of A samples, amorphous *trans* contents increase sharply at very low densities, then begin to decrease, and finally approach zero at higher crystallinity. *Gauche* values show corresponding sharp decreases at very low densities, level off at moderate densities, and continued decreases with increasing crystallinity. (4) At equivalent densities, B polymers contain larger numbers of smaller spherulites than A polymers. (5) Samples with increased amorphous *trans* contents exhibit correspondingly higher haze values than samples of equivalent density but lower amorphous trans values. Results obtained with small-angle light scattering (Vv mode) indicate that in addition to the number and volume of spherulites, haze is affected by differences in the polarizability of noncrystalline (amorphous *trans* and *gauche*) materials surrounding the spherulites.

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