Structural analysis of poly(ethylene terephthalate) reinforced with glass fibre: 1. A photoacoustic Fourier transform infra-red study

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Fourier transform infra-red spectroscopy coupled with photoacoustic detection (PA-*FT*i.r.) has proved to be a useful tool for finding out about quantitative structural changes in glass-fibre-reinforced poly(ethylene terephthalate) (PET) obtained by compression moulding and subsequently annealed. Analysis of the photoacoustic parameters indicates that the photoacoustic characteristics of the composite are very similar to those of the isolated matrix. It was demonstrated that glass-fibre-reinforced PET satisfies the same two-phase conformational model as the matrix. In contrast to the annealed matrix, the primary and secondary isomerizations cannot be detected in the composite. Therefore, the thermal treatment on the composite samples does not show further conformational changes. As a result, the manufacturing process seems to determine the composite microstructure, and its effect is quite similar to that observed in annealed matrix at the highest temperatures. Consequently, it can be considered that the *trans* isomer content in the amorphous phase is negligible in the composite.

(Keywords: poly(ethylene terephthalate); glass fibre; composite)

INTRODUCTION

Fibre-reinforced polymer composites offer a number of advantages, such as high modulus and specific strength, compared to traditional materials. The increased use of thermoplastics has brought about the need for a better understanding of the processing techniques used to manufacture these materials.

A critical issue in the manufacturing of semicrystalline thermoplastic composites is the microstructure or morphology of the matrix material whose features, such as apparent degree of crystallinity and layer structure, are greatly dependent on the processing. A detailed study on the influence of the industrial process of fabrication on poly(ethylene terephthalate) (PET) was carried out in a previous paper[1].

In composites, this situation is further complicated by the effect of the reinforcing fibres on the morphology of the matrix. It is well established that incorporation of reinforcements in thermoplastics leads to significant improvement of properties such as stiffness, tensile strength and heat distortion temperature. However, within the range of thermoplastic matrices the improvement in properties gained by adding reinforcement is an order of magnitude greater for semicrystalline polymers than for amorphous polymers. It has been proposed that this improvement is related to characteristics of the interfacial region[2–5].

Some fibres provide nucleating sites on their surfaces. Isolated spherulites may then be seen attached to the fibres; but where the nucleation density is sufficiently high along the fibre surface, the growth takes the form of a sheath surrounding the fibre and is then known as transcrystallinity. This columnar growth consists of embryonic spherulites which have been constrained to grow predominantly in a direction normal to the fibre surface, because they are prevented by their neighbours from spreading out sideways. However, it was confirmed that the transcrystalline structure is otherwise identical to that of normal spherulites[6].

Glass fibres are probably the most common of all reinforcing fibres for polymer matrix composites. Although, it is well known that glass fibre fails to promote transcrystalline regions in quiescent conditions or at low cooling rates[2,3,7], this interphase can be obtained by pulling out the fibre or by applying a sufficiently high cooling rate (higher than 50°C min^{-1})[3,7]. It is conceivable that external stresses due to the fabrication process or internal stresses induced at the fibre–matrix interface during cooling (e.g. from a mismatch in thermal expansion coefficients of fibre and matrix, which generates a large supercooling near the interface, consequently increasing the nucleation rate) are, at least partially, responsible for the phenomenon of transcrystallization[3].

In many cases, substantial quantities of fibres are added to the polymer matrix, which produces highly scattering or strongly absorbing samples for optical analysis. These samples are difficult to examine by conventional techniques; in such cases, the preparation of samples is complicated and time consuming. The use of Fourier transform infra-red spectroscopy coupled with photoacoustic detection (PA-*FT*i.r.) has already been used for the characterization of the isolated matrix[1], and study of

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the reinforced matrix by this technique appears quite promising, because a minimal, if any, sample preparation is required[8]. The general theory for the photoacoustic (PA) effect in condensed media was formulated by Rosencwaig and Gersho and is commonly referred to as the RG theory[9].

The purpose of this work is to determine the effect of fibre reinforcement, industrial process and subsequent annealing on the microstructure of PET. In order to characterize the evolution of conformers in PET composite as a function of annealing treatment, PA-*FT*i.r. measurements have been carried out.

EXPERIMENTAL

Materials

The sample used in this work was furnished by SNPE (France) as a 2 mm thick plate obtained by compression moulding.

The material chosen as the matrix was commercial PET (trade mark: PET 92T) and the glass-fibre reinforcements were Vetrotex R.o.99 2400 sizing 5175 (E-glass).

The impregnation process to manufacture unidirectional prepreg of continuous fibre-reinforced thermoplastics involves the passage of one or more bundles of reinforcement, electrostatically charged by friction on plastic rollers, through an aerosol of polymer. The aerosol is made of very fine divided polymer powder (particles of 60–100 μm) suspended in nitrogen gas. The powder is also electrostatically charged, attached to the reinforcement and then fixed by passing through an i.r. oven.

In the process of plate manufacture by compression moulding, five prepregs are joined by applying a pressure of 150–180 kN at a temperature of 280°C. The plates produced have dimensions of 200 mm × 100 mm × 2 mm.

The density of the composite (ρ_c) is 1.94 g cm^{-3} and the glass weight fraction (w_f) is 61.8%.

Samples of 3 mm × 2 mm × 2 mm were cut from the plates and introduced into a stabilized oven at different annealing temperatures (T_{ann}) ranging from 65 to 230°C, kept there for 1 h and then cooled to room temperature.

Photoacoustic Fourier transform infra-red measurements

PA–*FT*i.r. spectra of reinforced PET samples were obtained at room temperature on a Mattson Cygnus 100 *FT*i.r. spectrometer equipped with a MTEC 200 PA cell.

Two different sets of spectra were obtained, the first at 8 cm^{-1} resolution and averaged over 312 scans, and the second at 4 cm^{-1} resolution and averaged over 1120 scans. The best signal-to-noise ratio was obtained at a mirror speed of 0.12 cm s^{-1}.

Powdered carbon was used as a photoacoustically saturated (black) reference material.

RESULTS AND DISCUSSION

The vibrational behaviour of PET is well known (see, for example, refs 10–13) and we have carried out its photoacoustic characterization in a previous paper[1].

According to X-ray diffraction analysis, in the crystalline state the ethylene glycol fragment of PET can only adopt the *trans* conformation, whereas in the amorphous phase both *trans* and *gauche* conformations are present[11].

Photoacoustic characterization of the samples

The PA signal depends on optical, thermal and geometric parameters of the sample, and therefore different spectroscopic information can be obtained in relation to the values of these parameters[9]. The geometric parameter is given by the thickness of the sample ($l = 2$ mm).

Since the optical absorption coefficient (β) depends on the wavenumber of the radiation, it must be taken into account in order to calculate the optical parameters. In the experiments, quantitative measurements were only carried out over a frequency range[1,12] varying from 750 to 1000 cm^{-1}. Thus, β was calculated from the transmission *FT*i.r. spectrum for an unannealed prepreg at the most characteristic bands, i.e. at 793, 845, 876, 898 and 973 cm^{-1}, which gives β values ranging from 20 to 40 cm^{-1}. As a result, the optical absorption length ($l_\beta = \beta^{-1}$) ranges from 250 to 500 μm at these wavenumbers.

Finally, in order to obtain the value of the thermal diffusivity in the composite, the thermal conductivity and the specific heat were estimated by the following procedures.

Volume and weight fractions. The fibre content is one of the most important parameters in establishing the composite strength and stiffness characteristics. The relative proportions of matrix and fibre can be given as weight (W) or volume (V) fractions. From the rule of mixtures[14] and from matrix and fibre densities[15], values of $V_f = 48\%$ and $V_m = 52\%$ were obtained for the fibre and matrix, respectively, in our samples.

Thermal conductivity. Fibre orientation in the composite involves an important anisotropic behaviour, and longitudinal or transverse thermal conductivity can be distinguished.

Owing to the specific PA effect and the position of the sample in the cup, the transverse conductivity was preferential in our experiments and consequently the transverse transport coefficient (K_{ct}) was used in this work as the thermal coefficient. From the Halpin–Tsai equation[14] this coefficient can be computed as:

$$\frac{K_{ct}}{K_m} = \frac{1 + \zeta\eta V_f}{1 - \eta V_f} \tag{1}$$

where

$$\eta = \frac{\dfrac{K_f}{K_m} - 1}{\dfrac{K_f}{K_m} + \zeta} \tag{2}$$

$$\log \zeta = \sqrt{3} \log \frac{a}{b} \tag{3}$$

K_f, K_m are the thermal conductivity coefficients for fibre and matrix, and a, b are the dimensions of the cross-section of the fibre. For circular cross-sectional fibres, such as our case, the a/b ratio is one and therefore ξ also takes the value of one.

From equation (2) a value of $\eta = 0.851$ is obtained, taking $K_f = 4.45 \times 10^{-3}$ cal (s cm K)$^{-1}$ and $K_m = 3.59 \times 10^{-4}$ cal (s cm K)$^{-1}$ for thermal conductivities of fibre[16] and matrix[15]. Finally, from equation (1) the thermal conductivity of the composite was given by the value of $K_{ct} = 8.5 \times 10^{-4}$ cal (s cm K)$^{-1}$.

Specific heat. To estimate the specific heat of the composite (C_c), it was assumed to be an additive property, therefore the rule of mixtures for the fibre and matrix is suitable for describing it.

The specific heat of the matrix[15] is $C_{m(PET)} = 0.34$ cal g^{-1} K^{-1} and for the glass fibre, the specific heat of glass[15] $C_{f(glass)} = 0.186$ cal g^{-1} K^{-1} was used. Thus, the specific heat for the composite is obtained, $C_c = 0.27$ cal g^{-1} K^{-1}.

Thermal diffusivity coefficient. With the above values the thermal diffusivity coefficient for the composite, α_c (cm^2 s^{-1}), is given by:

$$\alpha_c = \frac{K}{\rho C} = 1.6 \times 10^{-3} \qquad (4)$$

Thermal diffusion length. According to the RG theory for the PA effect in solid materials, the thermal diffusion length (μ) is given by the average thickness from the sample surface, which contributes to the PA signal. The general definition of this parameter is[9]:

$$\mu = \left(\frac{2\alpha}{w}\right)^{1/2} \qquad (5)$$

where w is the angular modulation frequency (Hz) which can be calculated from the modulation frequency, f (Hz), with:

$$w = 2\pi f, f = v\nu \qquad (6)$$

where v is the optical velocity of the interferometer (cm s^{-1}) and ν is the wavenumber (cm^{-1}) of the i.r. radiation. In the Michelson design interferometer used in these experiments, v is twice the value of the mirror velocity.

In our particular case, the thermal diffusion length of the composite, μ_c (μm), is given by:

$$\mu_c = \frac{460}{\nu^{1/2}} \qquad (7)$$

In the experiments reported here, the spectral range analysed was 750–1000 cm^{-1} and consequently μ_c ranges from 15 to 16 μm, which is quite similar to the value obtained for the matrix (about 15 μm)[1].

From the above results, we conclude that $l \gg \beta^{-1}$ and $\mu_c < \beta^{-1}$; thus, the material to be analysed can be considered as an optically opaque and thermally thick solid. According to RG theory[9], only the light absorbed within the thermal diffusion length will contribute, in the case of our experiments, to the PA signal. Therefore, the structural information that will be presented below is characteristic of a surface depth of about 15 μm.

Vibrational spectra

In *Figure 1*, the general PA-*FT*i.r. spectra of unannealed and annealed composite at 90, 150 and 205°C are shown. Similarly to those obtained previously from the pure matrix[1], the bands situated at about 1730, 1275 and 1125 cm^{-1} show a strikingly different shape with regard to other bands. They cover very wide spectral ranges and have no well-defined maxima, but rather a wide plateau. In these areas, the sample is, according to RG theory, optically opaque and thermally thin; thus, there is PA 'opaqueness' as well as optical opaqueness, since the PA signal is independent of β and no structural information can be obtained from these bands[1,9].

In *Figure 2*, the spectral range 750–1000 cm^{-1} is shown; no new spectral band with regard to the matrix can be observed[1].

In *Figure 3*, the I_{973}/I_{793} and I_{898}/I_{793} intensity ratios for the matrix and composite *versus* annealing

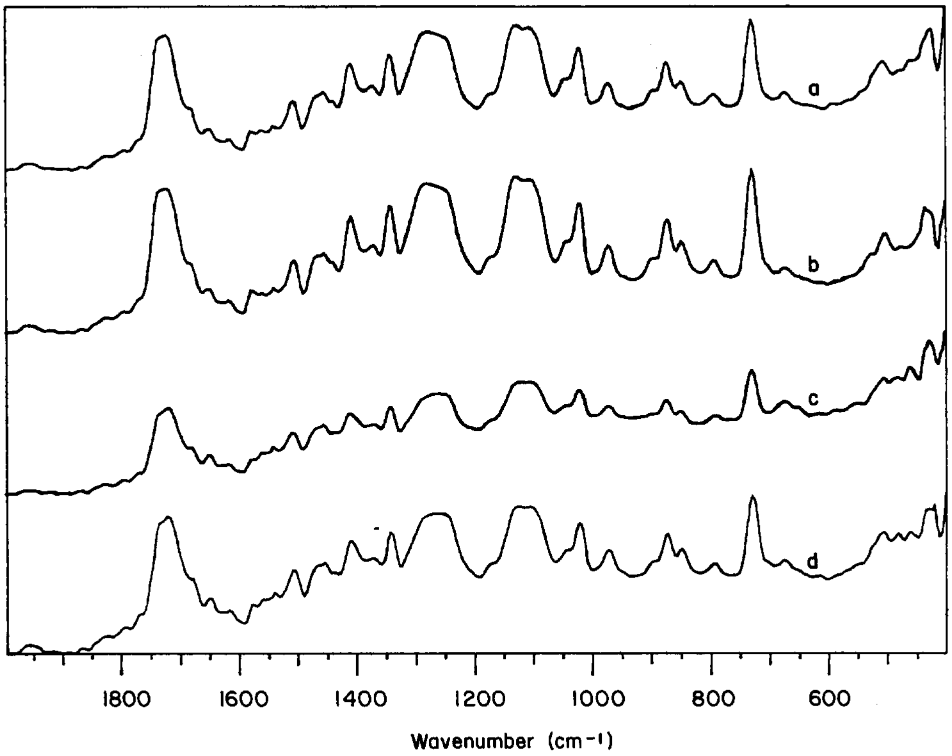

Figure 1 PA-*FT*i.r. spectra of glass-fibre-reinforced PET, (a) unannealed and annealed at (b) 90°C, (c) 150°C, and (d) 205°C, in the spectral range of 400–2000 cm^{-1} (8 cm^{-1} resolution)

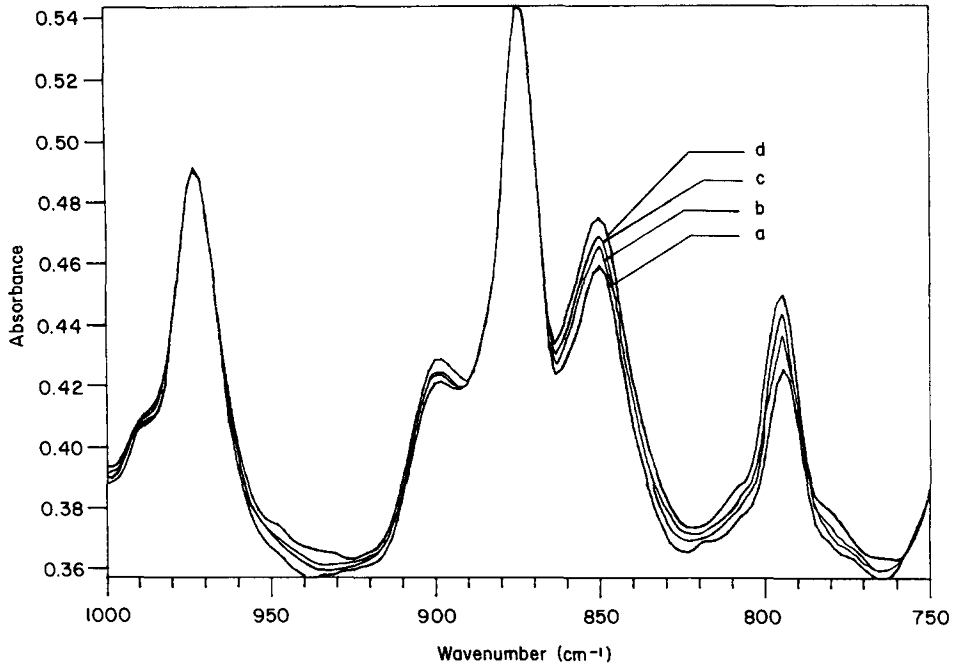

Figure 2 PA-*FT*i.r. spectra of glass-fibre-reinforced PET, (a) unannealed and annealed at (b) 90°C, (c) 150°C, and (d) 205°C, in the spectral range of 750–1000 cm^{-1} (4 cm^{-1} resolution)

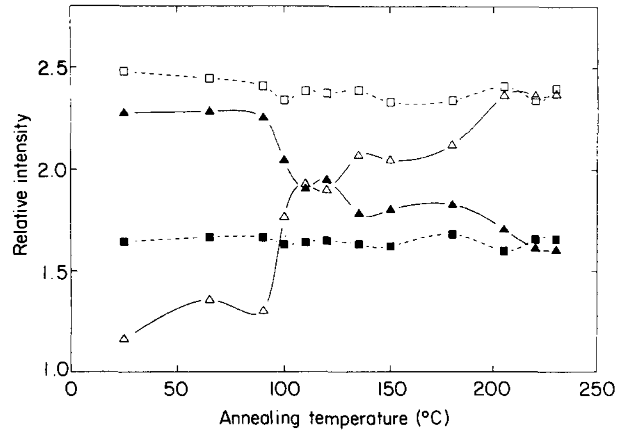

Figure 3 I_{973}/I_{793} and I_{898}/I_{793} *versus* annealing temperature for PET. △, ▲, matrix (from ref. 1); □, ■, composite

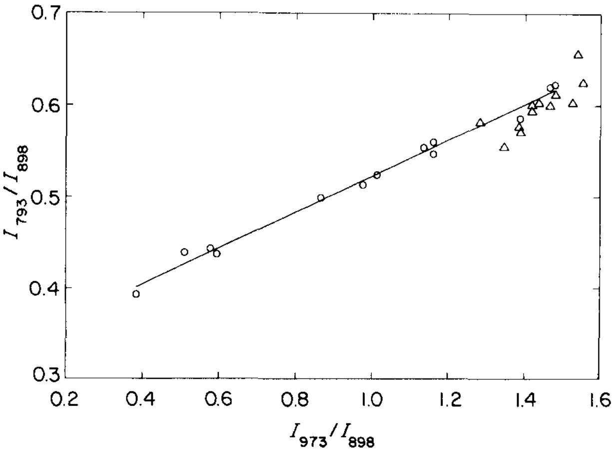

Figure 4 I_{793}/I_{898} *versus* I_{973}/I_{898}, providing verification of the two-phase conformational model in the composite. ○, ——, the model in the matrix (from ref. 1); △, experimental values of the composite

temperature are plotted (973 cm^{-1} band: *trans*, O–CH$_2$ stretching; 898 cm^{-1} band: *gauche*, CH$_2$ rocking; 793 cm^{-1} band: reference)[10–12]. A very important difference can be noted with regard to the matrix[1]: in the composite, no intensity variation with thermal treatment can be detected and the intensities tend towards those of the annealed matrix at the highest temperatures.

In a previous paper[1], it was demonstrated that PET satisfies a two-phase conformational model. Thus:

$$1 = p_1 \frac{I_{973}}{I_{793}} + p_2 \frac{I_{898}}{I_{793}} \qquad (8)$$

where p_1 and p_2 are the 973 and 898 cm^{-1} band-weights, which are related to the radiation–matter interaction. From this equation, we obtain:

$$\frac{I_{793}}{I_{898}} = p_1 \frac{I_{973}}{I_{898}} + p_2 \qquad (9)$$

In *Figure 4*, the straight line corresponds to this model in the matrix[1] and the experimental values for the composite have also been plotted. These experimental values fit on the straight line; therefore, it can be concluded that glass-fibre-reinforced PET satisfies the same two-phase conformational model as the matrix. Least-square curve fitting was carried out in order to obtain the p_1 and p_2 parameters.

The individual isomer distributions at different annealing temperatures:

$$p_1 \frac{I_{973}}{I_{793}},\ p_2 \frac{I_{898}}{I_{793}} \qquad (10)$$

for the matrix and composite are plotted in *Figure 5*. From this plot it can be noted that the conformational distribution of the composite tends towards values of the annealed matrix at the highest temperatures.

The sigmoidal evolution seen for the matrix at about $T_{ann} \approx 110$°C (primary isomerization) cannot be observed in the composite. Moreover, in contrast to the experiments in the isolated matrix, where the decrease in

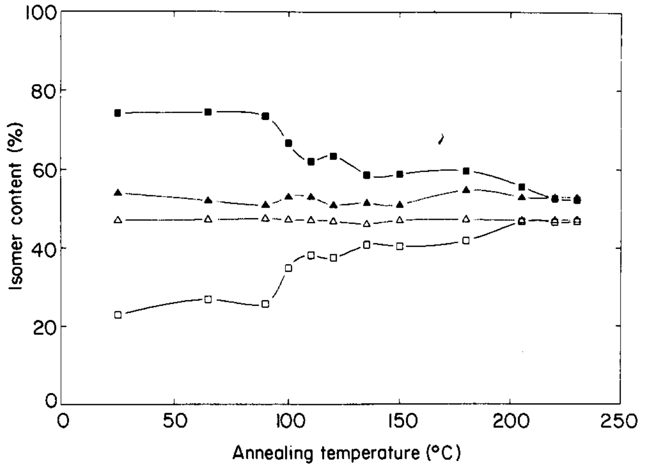

Figure 5 Distribution of rotational isomer contents for PET as a function of annealing temperature. Matrix: □, *trans*; ■, *gauche* (from ref. 1). Composite: △, *trans*; ▲, *gauche*

bandwidth of the band at 973 cm^{-1} (from 20.5 to 17.5 cm^{-1}) and the shift in frequency (from 876 to 873 cm^{-1}) were related to primary isomerization induced by annealing[1], no change in the bandwidth (17.5 cm^{-1}) or benzenoid mode (873 cm^{-1}) with thermal treatment on the composite was detected (see *Figure 2*). The approximately linear increase in *trans* isomer content, which appears in the matrix beyond 135°C (secondary isomerization), cannot be detected in the composite either.

It is also interesting to point out that the chain-folding band already appears at 988 cm^{-1} in the unannealed composite (*Figure 2*); however, in the matrix only the highest thermal treatments are supposed to remove crystal imperfections and improve chain packing at the amorphous–crystalline interphases[1].

Thus, it can be concluded from this spectroscopic analysis that the manufacturing process of the composite seems to determine its microstructure and the subsequent annealing does not result in further conformational changes.

Deconvolution and subtraction studies on the i.r. spectrum of PET have demonstrated that the band situated at 973 cm^{-1} and associated with the *trans* conformer can be resolved into two bands near 973 and 975 cm^{-1}. The latter has been associated with amorphous *trans* and the former with ordered *trans*[13]. However, it was proved in the matrix[1] that the conformational content of the amorphous *trans* isomer goes down, and eventually vanishes at the primary isomerization (about 110°C). Therefore, it can be assumed that the disordered *trans* isomer content is negligible in the composite.

At this stage of the study only spectroscopic information is available and nothing can be said about possible structural changes in the region around the fibre due to annealing treatment.

In order to obtain a more comprehensive interpretation for the composite and fibre–matrix interface, the correlation between PA-*FT*i.r. and d.s.c. will be discussed in a future paper.

CONCLUSIONS

This work shows that PA-*FT*i.r. is a useful tool for the study of PET morphology in glass-fibre-reinforced PET. It was demonstrated that the photoacoustic characteristics of the composite are very similar to those of the matrix: both are optically opaque and thermally thick in the spectral range 750–1000 cm^{-1}, and the thickness from the surface of the sample which contributes to the PA signal is about 15 μm.

From the composite experimental data, it was proved that glass-fibre-reinforced PET satisfies the same two-phase conformational model as the matrix. In contrast to the matrix, the annealing thermal treatment does not appear to affect the composite microstructure: the primary isomerization and the experimental effects related to it (bandwidth decrease and shift in frequency) cannot be observed; moreover, the secondary isomerization cannot be detected either. In conclusion, the thermal treatment on the composite samples does not show further conformational changes; the microstructure is determined mainly by the fabrication process and its effect is quite similar to that observed in the annealed matrix at the highest temperatures. Consequently, it can be considered that the disordered *trans* isomer content is negligible in the composite.

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