

Effect of Diethylene Glycol Content and Annealing Temperature on the Structure and Properties of Poly(ethylene Terephthalate)*

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Synopsis

The effect of 2,2'-oxydiethanol (diethylene glycol, DEG) content (ranging from 2 to 15 mol %) and of the annealing temperature (in the range from 100 to 260°C) on the density, calorimetric, dynamic- and static-mechanical and small angle X-ray scattering (SAXS) behavior of undrawn and drawn samples (granules, films, and bristles) of poly(ethylene terephthalate) (PET) has been studied. The known dependences on the annealing temperature are confirmed. Some discrepancies with earlier investigations of the dependences on the DEG content are established: constant values for the SAXS intensity and long spacing, for the lamellar thickness and for the volume fraction crystallinity α_c . These discrepancies are explained by the variation of the glass transition temperature (T_g) and melting temperature (T_m) of the materials with different DEG contents. The previous hypothesis of the segregation of the comonomer (DEG) units into the amorphous regions is confirmed.

INTRODUCTION

By reason of the unavoidable formation of diethylene glycol (2,2'-oxydiethanol, DEG) under the conditions of industrial synthesis of poly(ethylene terephthalate) (PET) and the incorporation of the DEG in the chain,^{1,2} commercial PET almost always represents a random copolymer, containing diethylene-glycolterephthalate (DEGT) units. This is the reason for the large number of investigations of the mechanism of DEG formation²⁻⁶ and the influence of DEG on many important properties of PET.⁷⁻¹⁰ The extent of this influence is directly related to the concentrations of DEGT units incorporated into the PET chain.

Recently, Frank and Zachmann¹¹ have investigated samples with different DEG contents (up to 15 mol %) and established large differences in the crystallization halftimes at temperatures near the glass transition (T_g) and melting (T_m) temperatures. They explained these differences as being associated with the decrease of T_g and T_m with increasing DEG content.

The investigation in two previous papers^{12,13} of samples similar to those used here confirmed the decrease of T_m with DEG concentration and established a decrease of the density, not only for the partially crystalline state,¹¹ but also for the fully amorphous material. The latter information

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proved to be very important in calculating the crystallinity index α_c from density measurements. At the same time, it was found that the unit cell parameters are unaffected by the DEG content and that the chemical degradation of partially crystalline PET proceeds by a two-stage process. The product of the degradation from the initial stage contains almost the entire quantity of the chemical bonded DEG. It was established also that there is a large increase with increasing DEGT concentration of both the intensity and the long spacing of small angle X-ray scattering (SAXS), for samples annealed at 240°C. On the basis of these data, a model was proposed, according to which the DEGT units are predominantly concentrated in the amorphous regions of the partially crystalline copolymer.

The present paper is intended to furnish additional information on the behavior of EGT/DEGT copolymers, using a broader range of specimen and processing conditions and further methods of characterization.

EXPERIMENTAL

Samples

Commercial poly(ethylene terephthalate) (PET) with $\bar{M}_v = 13,000$ and with different amounts (1.83, 3.09, 3.60, 4.27, and 14.9 mol %) of bonded diethylene glycol (2, 2'-oxydiethanol, DEG) (supplied by BASF, West Germany) was used to obtain samples in the form of thin films and bristles.

Films of thickness 0.07–0.08 mm were prepared by slow evaporation of the solvent from solution of the polymer in CF_3COOH . It has been established in separate GPC experiments that PET is inert to this solvent. Bristles of diameter 0.7–0.9 mm were prepared by extruding the polymer melt from a metal syringe into an ice-water bath.

Films and bristles so prepared were drawn by an Instron machine at a rate of 0.02 cm/min in a temperature chamber at temperatures near the glass transition temperature of the corresponding polymer, according to Ref. 11. The drawing proceeded until all material passed through a neck, corresponding to a draw ratio of about 4:1 and a final film thickness of 0.01–0.03 mm and a bristle diameter of 0.4–0.6 mm.

The undrawn and the drawn samples were isothermally annealed, the former with free ends, and the latter both with free ends and with fixed ends. The annealing took place for 6 h in a vacuum oven with temperature constant within ± 2 –3°C. The annealing temperatures T_a were: 100, 150, 200, 220, 230, 240, and 260°C. All samples were air-quenched after annealing.

Methods

Density

The densities of undrawn and drawn samples were measured by means of a gradient column, using a mixture of carbon tetrachloride and hexane. The volume fraction crystallinity α_c was calculated from the density data, using the equation:

$$\alpha_c = (\rho - \rho_a)/(\rho_c - \rho_a) \quad (1)$$

where ρ is the experimentally measured density and ρ_a and ρ_c are the densities of 100% amorphous and fully crystalline PET. Experimentally determined values for the fully amorphous granules with corresponding DEG content were used for ρ_a . A value of 1.515 g/cm^3 ¹² was used for ρ_c .

Differential Scanning Calorimetry (DSC)

Calorimetry measurements were done on the films and granules only. A Perkin-Elmer Model 2 DSC apparatus was used for all calorimetry work. The instrument was calibrated daily using indium as a reference. All scans were conducted under a nitrogen atmosphere at a range of 5 mcals and heating rate of $20^\circ\text{C}/\text{min}$. The weight of the samples was measured using a Cahn Gram Electrobalance; most sample weights were approximately 4.0 mg. The heat of fusion was determined by comparing the endotherm area to that of a known weight of the reference material (indium).

Dynamic Mechanical Measurements

Dynamic mechanical measurements were performed on the films only. A Rheovibron Direct Reading Viscoelastometer, Model DDV-II-B, was used. All measurements were carried out at a frequency of 11 cps. The heating rate was maintained at $1\text{--}2^\circ\text{C}/\text{min}$, and a slow purge of dry nitrogen was passed through the sample chamber.

Static Mechanical Measurements

Static mechanical measurements were performed with the bristles on an Instron Model 1185 testing machine, at room temperature, with a crosshead displacement rate of $2\text{--}10 \text{ mm}/\text{min}$. The sample length was approximately 25 mm.

Small-Angle X-Ray Scattering (SAXS)

SAXS measurements were carried out with the bristles, using the Oak Ridge National Laboratory 10-m SAXS Instrument.¹⁴ This instrument utilizes "pinhole"-collimated radiation from a rotating anode source and a two-dimensional position-sensitive detector. The incident beam is 1 mm^2 . A 4 m specimen-to-detector distance was used.

RESULTS

Density Measurements (Granules, Films, and Bristles)

In Figures 1(a) and 1(b) are shown the dependences of the density, for all samples (granules, films, and bristles), on the bonded DEG content. In agreement with the earlier results,^{12,13} the density visibly decreases with increasing DEG content, irrespective of the specimen's form and preliminary thermal or mechanical treatment.

In Figures 2(a) and 2(b), the same density values are shown plotted against the annealing temperature T_a . One observes the well-known¹⁵ increase of the density with increasing T_a , irrespective of sample's form and DEG content. It can be seen also that the unannealed bristles and those annealed

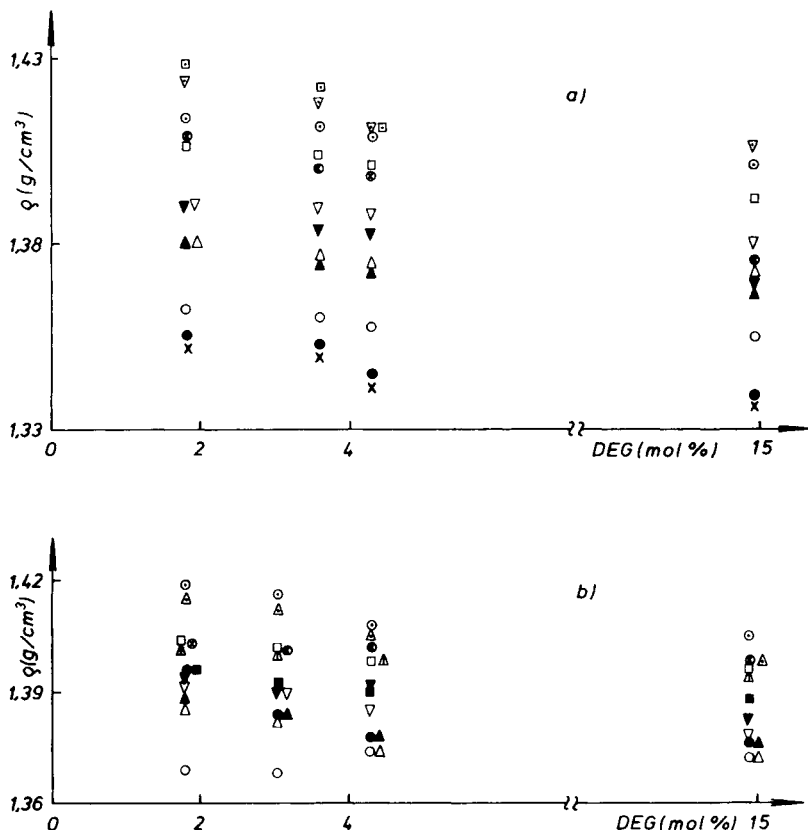


Fig. 1. Dependence of the density on the DEG content: (a) bristles; (b) films; (○) unannealed samples. Annealing temperatures ($^{\circ}\text{C}$): (\triangle) 100; (∇) 150; (\square) 200; (\odot , \otimes) 220; ($\triangle\triangle$) 230; ($\nabla\nabla$) 240; (\square) 260. (○, \triangle , ∇ , \square , \odot , \triangle , ∇ , \square) Drawn samples; (\bullet , \blacktriangle , \blacktriangledown , \blacksquare , \otimes , \triangle) undrawn samples.

at lower T_a (up to 150°C) have lower density values than those of the films. The density values of the drawn bristles are higher in comparison to those of the undrawn bristles at all T_a . For the films, on the contrary, one observes, for T_a 's up to 150°C , higher density values for the undrawn samples. This behavior is known from a previous investigation on PET.¹⁶ It was suggested in this previous investigation that the lower density value of the bristles at lower temperatures could be explained by voids formed during the process of extrusion from the melt.

The density of the granules is given in Table I and is compared there with the density values of the same samples measured 8 years ago.¹² One observes a significant increase of the density (0.008 – 0.012 g/cm^3) for all DEG contents. As can be seen from the wide-angle X-ray patterns in Figure 3, the samples are still fully amorphous. This means that the increase of the density observed (Table I) is due to alteration processes occurring in the amorphous phase during the long storage. Such physical aging has been shown to be associated with a crosslinking of the PET chains.¹⁷ These processes change the density, but do not change the order, of the amorphous phase.

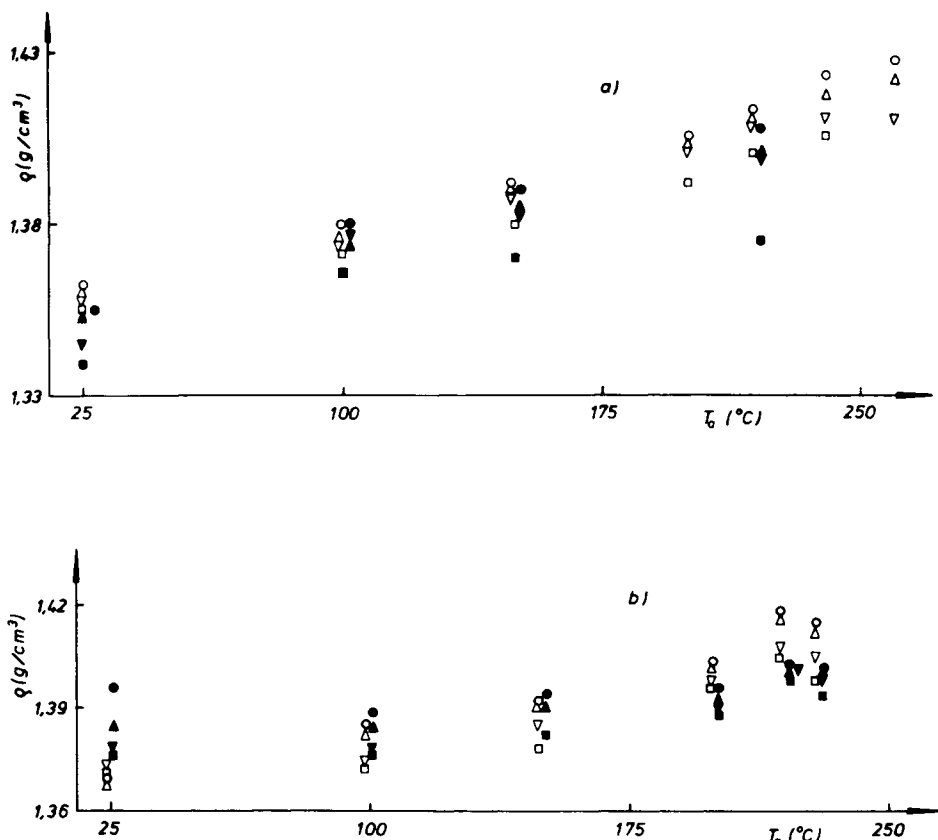


Fig. 2. Dependence of the density on the annealing temperature T_a : (a) bristles; (b) films. $T_a = 25$ unannealed samples; (○, △, ▽, □) drawn samples; (●, ▲, ▼, ■) undrawn samples. DEG content (mol %): (○●) 1.83; (△▲) 3.09 (films), 3.60 (bristles); (▽▼) 4.27; (□■) 14.9.

The density change of the fully amorphous samples upon the storage time infers that the value of amorphous density obtained by extrapolation of the current density values must differ from the values reported in Ref. 12. From these density results it can be concluded that the increased content of the chemically bonded DEG in PET chain leads to (1) a decrease of the density of the fully amorphous phase and (2) lower values of the crystallinity index, calculated according to eq. (1), at each annealing temperature. The latter phenomenon could result from the lower density of the amorphous phase or from a simultaneous decrease of the density of the two phases in the

TABLE I
Density of Amorphous, Isotropic (According to X-Ray Examination) PET Samples
with Various DEG Contents

DEG (mol %)	1.83	3.6	4.27	14.9
ρ_a (g cm ⁻³)				
This paper	1.352	1.350	1.342	1.336
According to Ref. 12	1.341	1.338	1.334	1.328

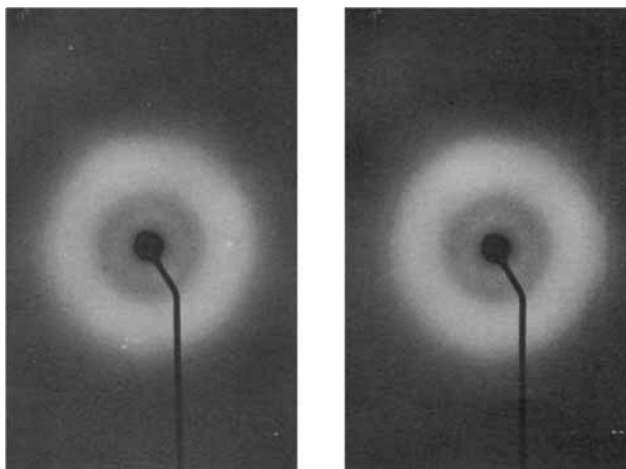


Fig. 3. Wide angle X-ray scattering patterns of granules containing DEG (mol %): (a) 1.83 and (b) 14.9.

partial crystalline state. The second possibility was checked by calculating the crystallinity index α_c for bristles and films, using the measured ρ_a and constant ρ_c . These results are shown in Figures 4(a) and 4(b). In contrast to the results in Ref. 12, α_c does not visibly change up to $T_a = 200^\circ\text{C}$. Only at the highest T_a (220, 230, 240, and 260°C) could the effect observed there be seen: a clearly expressed decrease of α_c with increasing DEG content. Exceptional are the samples containing 14.9 mol % DEG; their α_c values are the same or even higher than those for 4.27 mol % DEG.

The general constancy of α_c with DEG content for each T_a is evidence that the primary influence on the density decrease with DEG content is the changing amorphous density.

Calorimetry (Granules and Films)

In Figure 5 are represented parts of the DSC curves of the granules, illustrating how the glass transition temperature T_g , crystallization temperature T_{cr} , melting temperature T_m , and the area taken into account when calculating the heat of fusion ΔH_f were determined.

In all DSC curves from the films, even those from undrawn and unannealed films, there is no clearly expressed peak of crystallization and inflexion point for the glass transition. Determination of T_g and T_{cr} for these samples would be very difficult and unsure. For this reason only T_m and ΔH were determined for the films. Two melting peaks are observed only for the films annealed at T_a above 200°C ($T_a = 200$ and 230°C).

Figure 6 represents the dependence of T_g and T_{cr} of the amorphous granules on the DEG content. T_g decreases with increasing DEG content in the PET chain. The value of the T_g decrease (7°C) is almost the same as that measured in Ref. 11— 8°C . Within experimental error, there is no significant change in T_{cr} .

In Figure 7 is shown the dependence of T_m on the DEG content for undrawn films, unannealed and annealed at the various T_a , as well as for

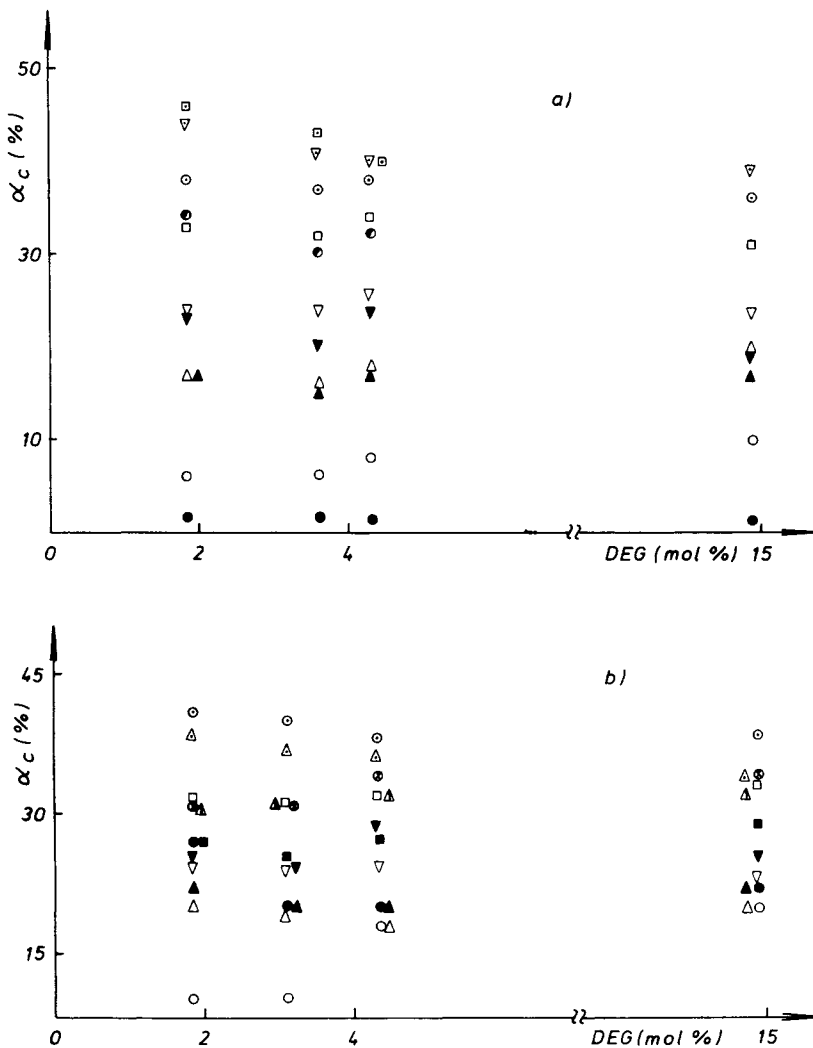


Fig. 4. Dependence of the volume fraction crystallinity α_c on the DEG content: (a) bristles; (b) films; (○, △, ▽, □, ⊙, ▽, ⊠) drawn samples; (●, ▲, ▼, ■, ⊙, ⊗, △) drawn samples; (○, ●) unannealed samples. Annealing temperatures (°C): (△△) 100; (▽▽) 150; (□□) 200; (⊙⊙—bristles, ⊙⊙—films) 220; (△△—films) 230; (▽—bristles) 240; (□—bristles) 260.

the amorphous granules. T_m , for all T_a , is very sensitive to the amount of the comonomer DEG in PET: T_m decreases by about 30°C when the DEG content is increased from 1.83 to 14.9 mol %. This T_m decrease is the same as that observed in Refs. 12 and 13. An influence of T_a on the T_m values could not be seen; for samples with equal DEG content, T_m is almost constant. The temperatures of the lower melting (1st) peak, observed only for the samples annealed at 220 and 230°C, are also sensitive to the DEG content; they decrease by about 20°C. The well-known¹⁸ dependence of T_m on the crystallization temperature can be seen here: The temperature position of the lower melting peak increases with increasing T_a for samples with equal DEG content.

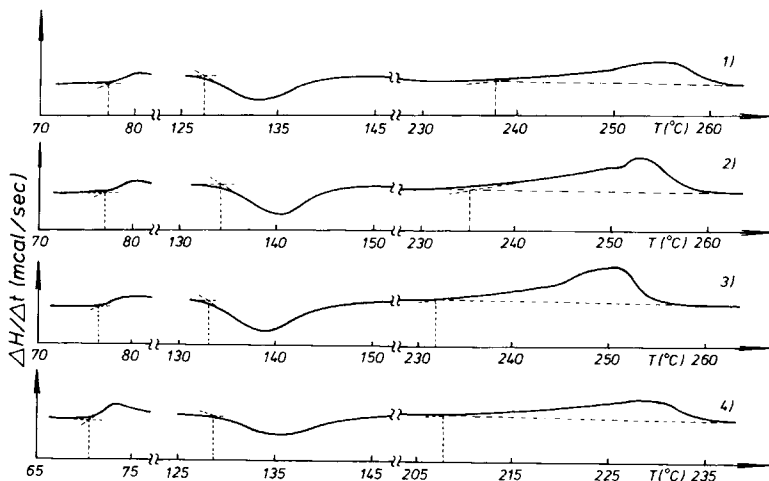


Fig. 5. Parts of the DSC curves of the granules. DEG Content (mol %): (1) 1.83; (2) 3.09; (3) 4.27; (4) 14.9.

The measured T_m values are low in comparison to those observed earlier,^{11,12} for samples with equal DEG content. This difference is likely the result of different methods used for the determination of T_m .

For the drawn films, annealed with either fixed or free ends, the dependence of T_m on the DEG content is identical to that shown in Figure 7, for samples with equal DEG content and T_a . Obviously the form of the samples, the method of their annealing, and the annealing temperature do not influence the value of calorimetrically determined T_m for samples of equal DEG content.

In Figure 8 is shown the dependence of the crystallinity index W_c , calculated from the area of the second peak only on the DEG content in the undrawn films. In contrast to α_c , calculated from the density ρ (Figs. 4), calorimetry measurements provide W_c values which decrease with increasing DEG content, for all annealing temperatures. An influence of T_a for samples with equal DEG content is clearly expressed only at $T_a \geq 200^\circ\text{C}$; samples annealed at higher T_a exhibit higher W_c values. Annealing at $T_a \leq 200^\circ\text{C}$ provides W_c values which are close to each other. Even the W_c values of the amorphous granule are close to those for samples annealed up to 200°C at the same DEG content. For the lower annealing temperatures

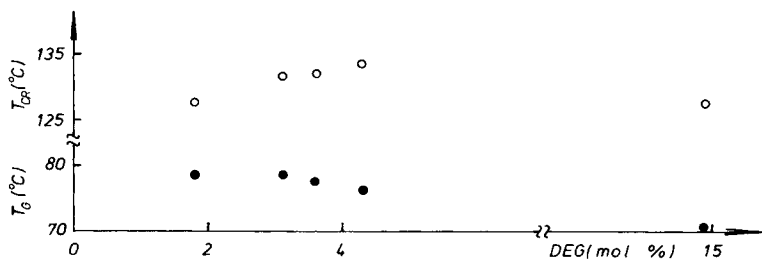


Fig. 6. Dependence of T_g (●) and T_{cr} (○) (calorimetry measurements) of the amorphous granules on the amount of bonded DEG.

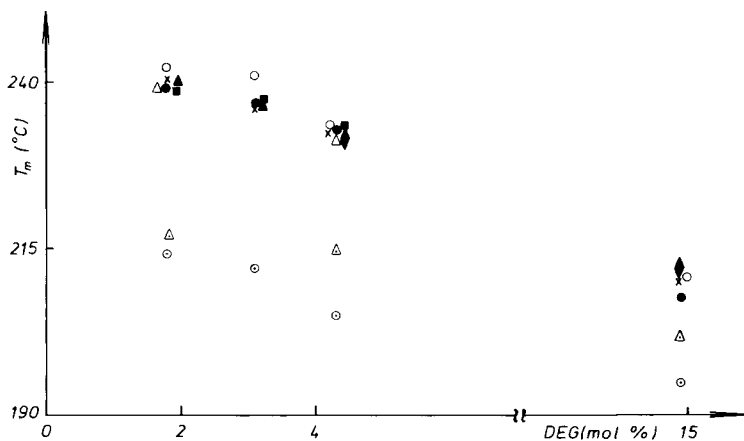


Fig. 7. Dependence of T_m (calorimetry measurements) of undrawn films on the DEG content: (x) commercial amorphous granules; (●) unannealed films. Annealing temperatures (°C): (▲) 100; (▼) 150; (■) 200; (○)—1st peak, (○)—2nd peak) 220; (△—1st peak, △—2nd peak) 230.

($T_a \leq 200^\circ\text{C}$), recrystallization¹⁹⁻²¹ occurs during heating, as evidenced by the lower temperature endotherm. This recrystallization appears to put all such samples into the same thermodynamic state, as evidenced by the invariance of W_c from the melting peak (second endotherm).

Dynamic Mechanical Measurements (Films)

The variation of the loss tangent ($\tan \delta$) with temperature for films which had been previously annealed at 100°C is shown in Figure 9. The temperature dependence of the complex tensile modulus E^* , calculated from $\tan \delta$, is given in Figure 10. The course of the dependences of the storage modulus E' and the loss modulus E'' on temperature are similar to those

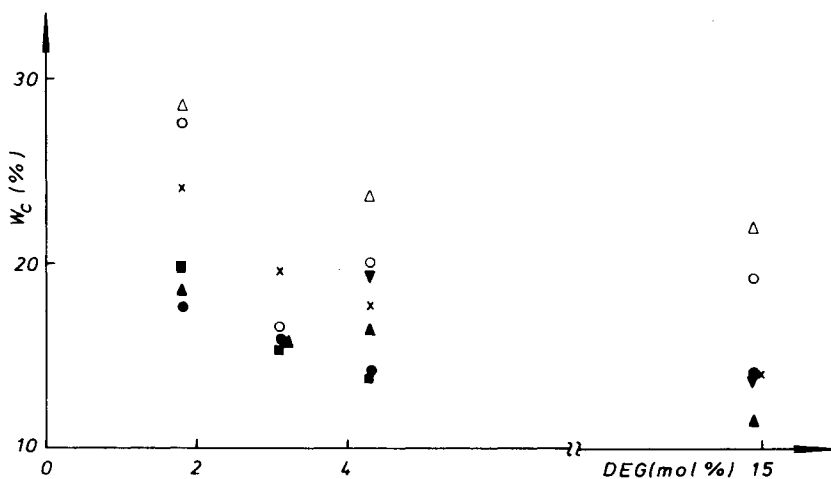


Fig. 8. Dependence of crystallinity index W_c (calorimetry measurements) for undrawn films on the DEG content: (x) commercial amorphous granules; (●) unannealed films. Annealing temperatures (°C): (▲) 100; (▼) 150; (■) 200; (○) 220; (△) 230.

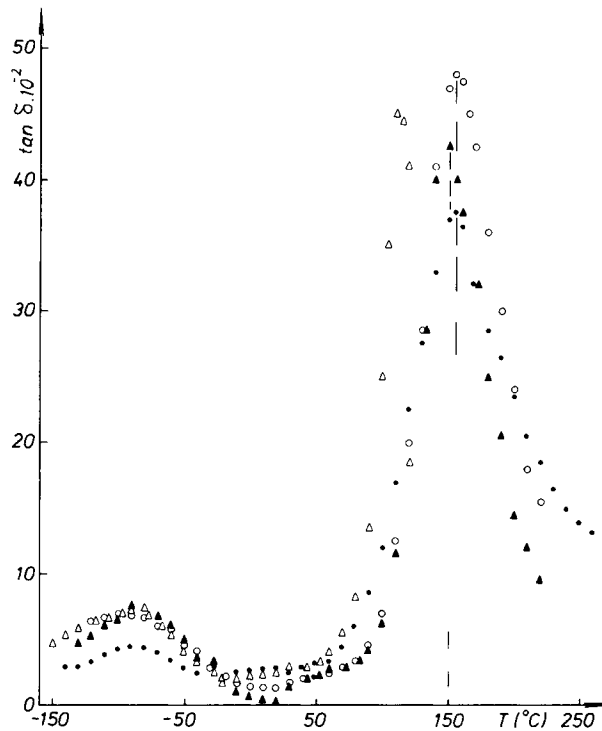


Fig. 9. Dependence of the loss tangent ($\tan \delta$) on temperature for drawn samples with different DEG content, annealed 6 h at 100°C. DEG content (mol %): (●) 1.83; (○) 3.09; (▲) 4.27; (△) 14.9.

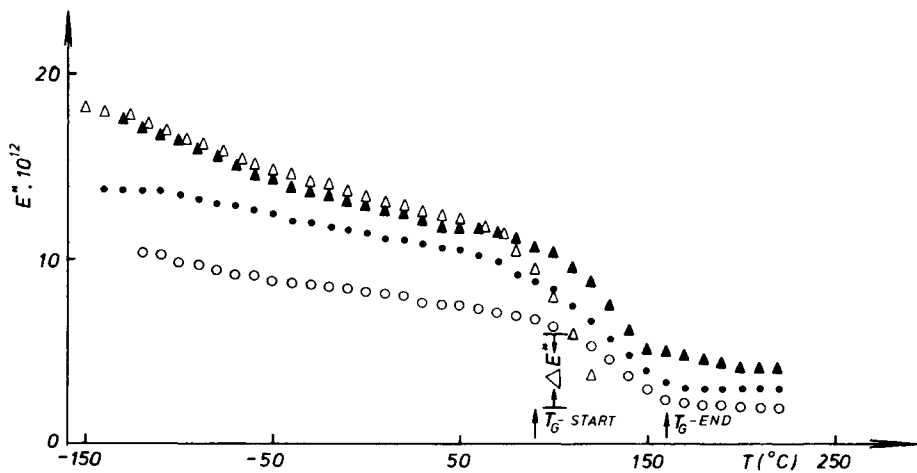


Fig. 10. Dependence of the complex tensile modulus E^* on temperature for drawn samples with different DEG content, annealed 6 h at 100°C. DEG content (mol %): (●) 1.83; (○) 3.09; (▲) 4.27; (△) 14.9.

for E^* and $\tan \delta$, with a corresponding shift of the α peak to lower temperatures.

The temperature dependence of these quantities ($\tan \delta$, E^* , E' , E'') for films annealed at other temperatures T_a is similar to that for $T_a = 100^\circ\text{C}$. For the undrawn and unannealed films, the $\tan \delta$ plot is interrupted at its steepest slope at about 90°C , in the α peak, because of plastic flow of the films.

In Figure 9 two clearly expressed relaxation processes are observed: The sharp, intense α process (α peak) at higher temperatures and the broad maximum of the β process at lower temperature. Under the conditions of our measurements, the β peak appears at almost the same temperature (about -90°C) and approximately equal intensity for all films (drawn and undrawn, annealed and unannealed). There is no definite dependence on drawing or annealing. Further, there is no regularity of the location or intensity of the β peak with DEG content. According to Ref. 22, the β peak is attributed to the motion of methylene and/or carboxyl groups in irregular folds—i.e., to the appearance or disappearance of the irregular folded structure. According to Ref. 23, such changes are connected with the predominance of one of the two competitive processes acting during the annealing of drawn samples: crystallization and disorientation. T_g was determined as the peak maximum of the α process in Figure 9. The beginning and end (marked T_g -start and T_g -end in Fig. 10) of the step in plots of E^* and E' vs. T were used to define a "modulus step height," ΔE^* or ΔE . The dependence of T_g on the DEG content is shown in Figures 11(a) and 11(b).

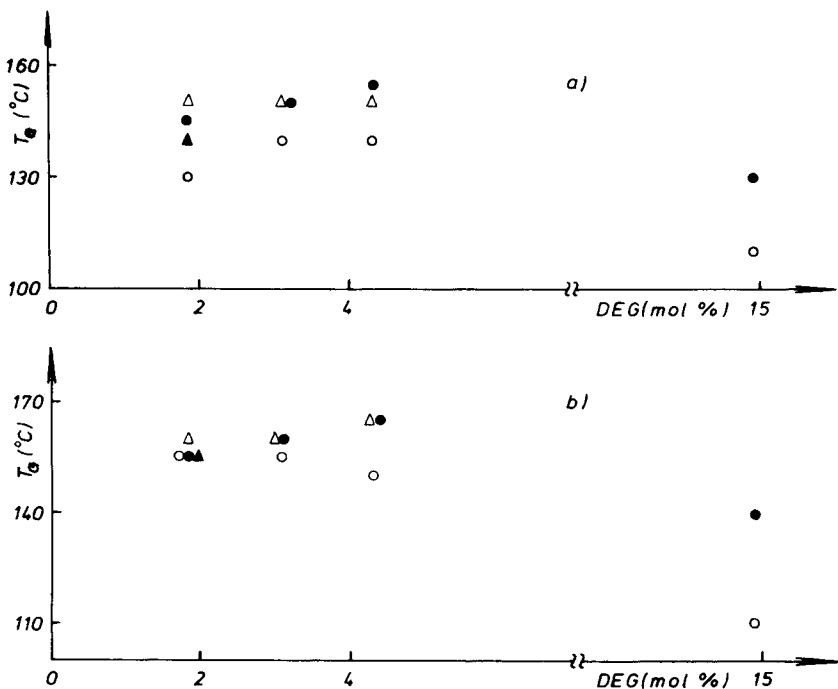


Fig. 11. Dependence of T_g on the DEG content: (a) from E' and (b) from $\tan \delta$, for drawn films, annealed ($^\circ\text{C}$) at: (○) 100; (●) 150; (△) 200; (▲) 230.

The dependence of T_g on the annealing temperature is shown in Figures 12(a) and 12(b). T_g values determined from E'' are located at lower temperatures. At low DEG contents (up to 4.27 mol %), there is a slight increase of T_g with increasing DEG content, as seen in Figures 11(a) and 11(b). At the highest DEG content (14.9 mol %), a pronounced decrease of T_g (about 25–30°C) is observed. These shifts in T_g are much greater than those determined by calorimetry for the amorphous granules (Fig. 6). With increasing annealing temperature, T_g passes through a maximum value, located between $T_a = 150$ and $T_a = 200^\circ\text{C}$, in agreement with Ref. 23.

The values for the step height (ΔE^* , $\Delta E'$), determined from E^* and E' , are demonstrated in Figure 13(a) as a function of the DEG content, and, in Figure 13(b), as a function of the annealing temperature T_a . A significant increase in the step height (4×10^{12}) is observed only for the highest DEG content [Fig. 13(a)]. With increasing annealing temperature, ΔE^* and $\Delta E'$ pass through a maximum value of about 200°C. In Ref. 23 this maximum appears at 240°C.

Figure 14 shows that the temperature of the start of the α process (T_g start) of the drawn films, determined from E^* and E' , does not depend on the DEG content and is constant (90°C) with increasing annealing temperature T_a . For the unannealed, drawn and undrawn films, this process begins at a lower temperature (60°C).

The end of this process (T_g -end) is also independent of the DEG content, but it is very sensitive to the annealing temperature. It increases from 160 to 200°C in the annealing temperature range 100–230°C.

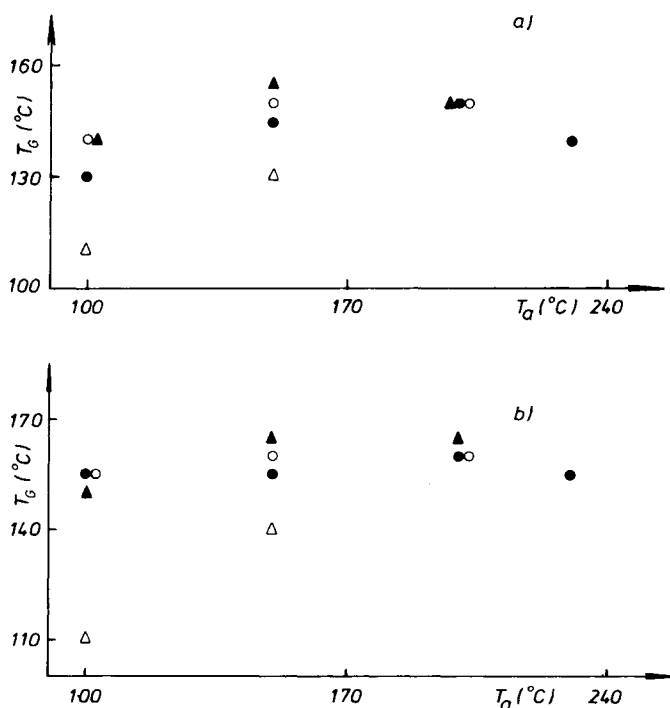


Fig. 12. Dependence of T_g on the annealing temperature: (a) from E'' and (b) from $\tan \delta$, for drawn films with DEG content (mol %): (○) 1.83; (○) 3.09; (▲) 4.27; (△) 14.9.

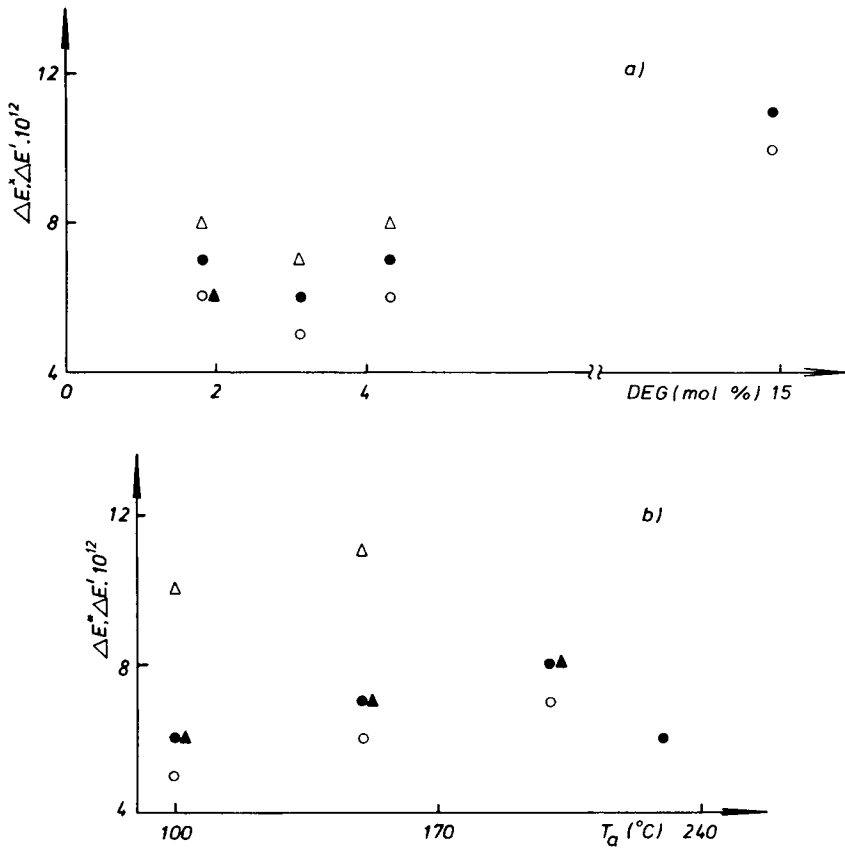


Fig. 13. Dependence of the step height ΔE^* and $\Delta E'$, determined, respectively, from E^* and E' on: (a) the amount of the bonded DEG; (b) the annealing temperature T_a . (a) Annealing temperatures (○) 100; (●) 150; (△) 200; (▲) 230. (b) DEG content (mol %): (●) 1.83; (○) 3.09; (▲) 4.27; (△) 14.9.

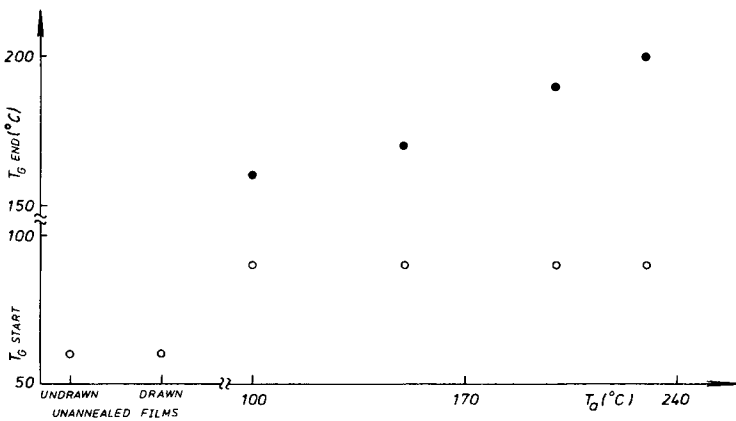


Fig. 14. Dependence of $T_{g\text{-start}}$ (○) and $T_{g\text{-end}}$ (●), determined from E^* and E' , on the annealing temperature.

Static Mechanical Measurements (Bristles)

The stress-strain curves for drawn bristles containing 14.9 mol % DEG, which have been annealed at different temperatures, are shown in Figure 15. Characteristic of all the curves is the absence of a maximum, corresponding to neck formation. Only the unannealed bristles show a very weak trend to neck building. As in Ref. 23, this can be explained by the fact that all samples are preoriented.

The tensile modulus E , identified with the maximum slope of the stress-strain curve, and the tensile strength σ_t , associated with the maximum stress, are plotted in Figures 16 (a) and 16 (b) as a function of the annealing temperature and in Figures 17(a) and 17(b) as a function of the DEG content. The trend of the dependence on T_a [Figs. 16(a) and 16(b)] is in agreement with the data reported in Ref. 23: E decreases and σ_t passes through a maximum with increasing T_a for all amounts of DEG in the PET chain. The only exception is for 14.9 mol % DEG; for this copolymer E is constant and even increases at the highest T_a and the maximum for σ_t is weakly expressed. In the dependence of E on T_a , the minimum observed in Ref. 23 is absent; E for the annealed bristles decreases monotonically with increasing T_a , presumably following a reduction in orientation with increasing temperature.

E and σ_t decrease with increasing DEG content [Figs. 17(a) and 17(b)] for unannealed and annealed bristles up to $T_a = 200^\circ\text{C}$. For the bristles annealed at higher T_a (220 and 240°C), such a decrease of E and σ_t with DEG content up to 4.27 mol % is observed. At the highest DEG content there is an increase of E and σ_t for these two T_a .

Small-Angle X-Ray Scattering (SAXS of Bristles)

Strongly oriented SAXS patterns are observed for drawn bristles which have been annealed at temperatures above 100°C . A typical pattern is shown

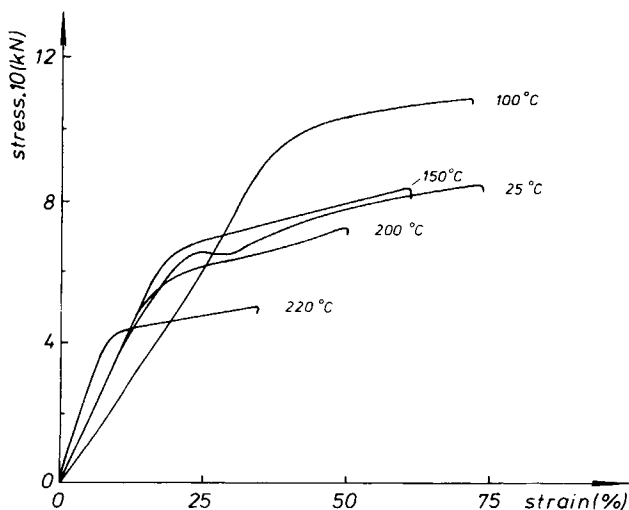


Fig. 15. Stress-strain curves of drawn bristles, annealed for 6 h at the indicated temperatures. DEG content 14.9 mol %.

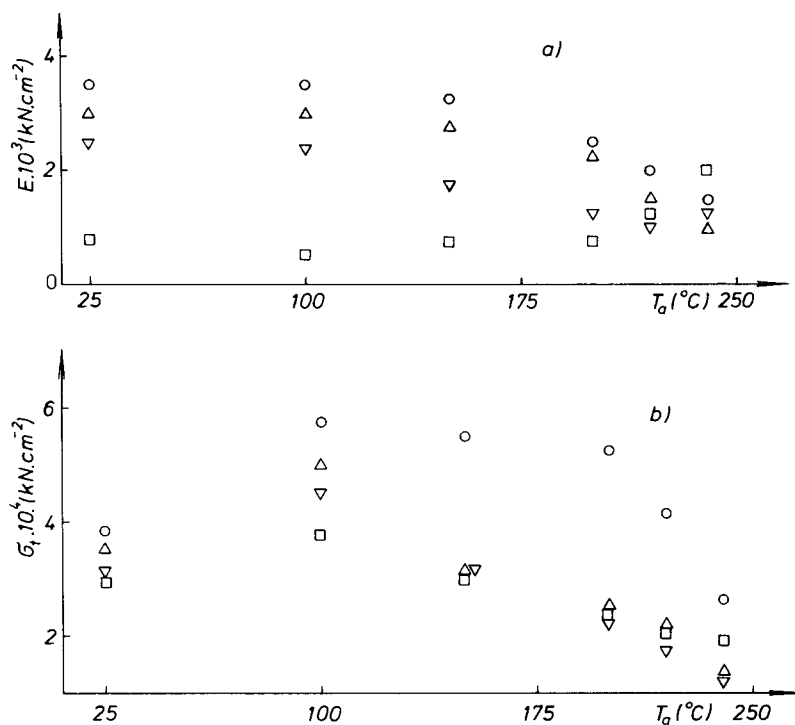


Fig. 16. Dependence of (a) the modulus of elasticity E and (b) the tensile strength σ_t on the annealing temperature T_a . DEG content (mol %): (○) 1.83; (△) 3.6; (▽) 4.27; (□) 14.9.

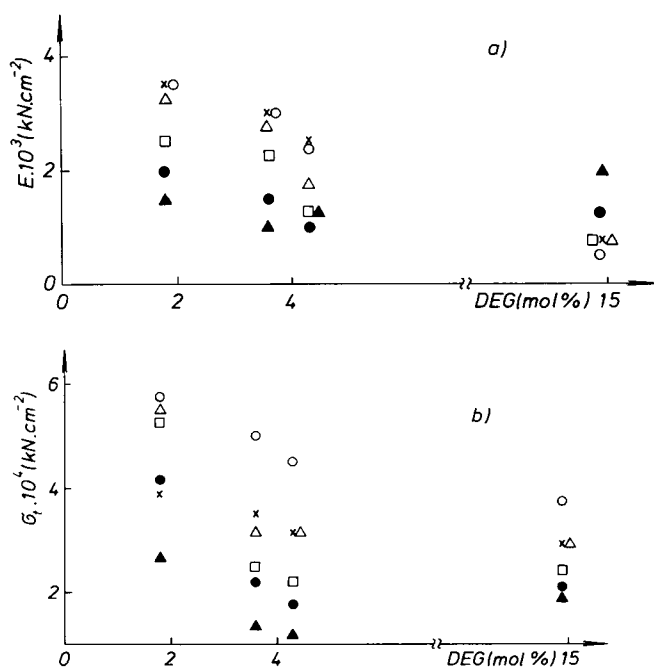


Fig. 17. Dependence of (a) the modulus of elasticity E and (b) the tensile strength σ_t on the DEG content. Annealing temperatures ($^{\circ}\text{C}$): (○) 100; (△) 150; (□) 200; (●) 220; (▲) 240; (X) unannealed.

in Figure 18. Two SAXS Bragg lobes appear. The lobes are highly elongated normal to the draw direction—evidence of a fibrillar morphology.

The dependence of the long spacing L and the intensity I (in arbitrary units) of the Bragg lobe on the annealing temperatures are shown in Figures 19(a) and 19(b). The dependence of these quantities on the DEG content is shown in Figures 20(a) and 20(b). One observes the well known increase of long spacing values with increasing annealing temperature²⁴ [Fig. 19(a)]. In contrast to the results in Ref. 12, L remains constant as the DEG content increases [Fig. 20(a)], for all T_a lower than $T_a = 240^\circ\text{C}$. Only for the samples annealed at the highest T_a 's (240 and 260°C) can an increase of L with increasing DEG content be seen.

In spite of the great dispersion of the experimental points, the intensity I of the SAXS lobe varies in the same manner [Figs. 19(b) and 20(b)] as the long spacing; it increases with increasing T_a and remains constant when the DEG content is increased. The exceptions are again the samples annealed at the highest T_a ; for them I increases with DEG content. As can be seen from the figures, the annealing method—with fixed or with free ends—does not significantly influence the values of L and I .

In Figure 21 is presented the dependence of the lamellar thickness $L \cdot \alpha_c$ on the DEG content for specimens annealed at the different temperatures. $L \cdot \alpha_c$ values are obtained using the α_c values from Figure 4(a) and L values from Figure 20(a). In contrast to the results in Ref. 12, the lamellar thickness remains constant with the increasing DEG content for samples annealed at 110, 200, and 220°C . Only for samples annealed at the highest T_a (240°C) does $L \cdot \alpha_c$ decrease with increasing DEG content, but only up to 4.27 mol % DEG. For the sample containing 14.9 mol % DEG $L \cdot \alpha_c$ increases again.

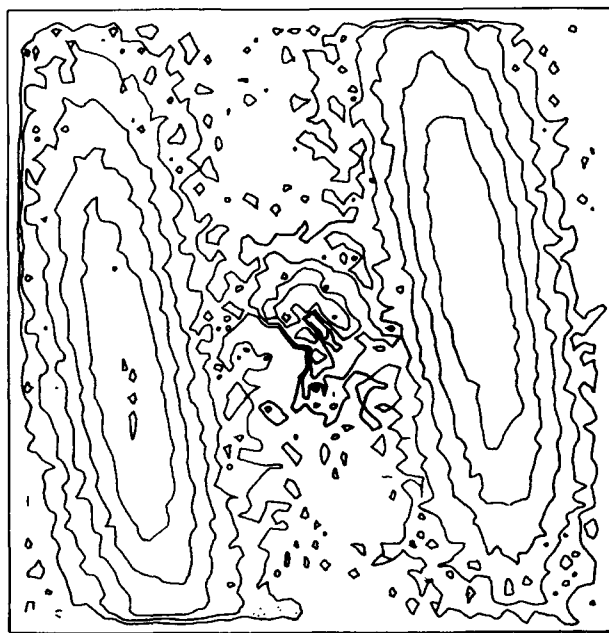


Fig. 18. Typical SAXS contour plot. Contour levels differ by a factor of 2. The plot shown is for a drawn bristle containing 4.27 mol % DEG, annealed 6 h at 220°C .

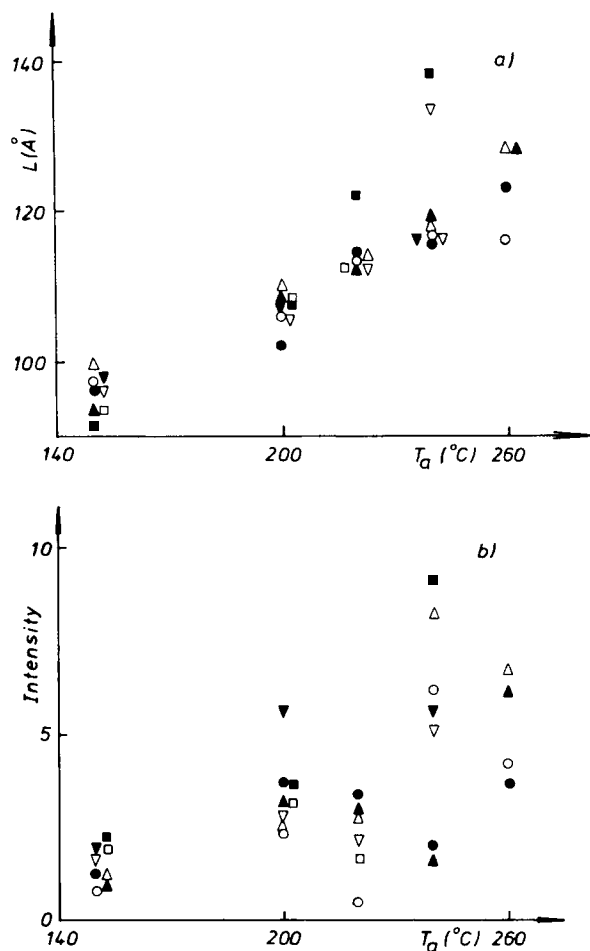


Fig. 19. Dependence of (a) the long spacing L and (b) the peak intensity I (arbitrary units) on the annealing temperature T_g . DEG content (mol %): (○●)1.83; (△▲) 3.6; (▽▼) 4.27; (□■) 14.9. (○,△,▽□) bristles annealed with fixed ends; (●,▲,▼,■) bristles annealed with one free end.

DISCUSSION AND CONCLUSIONS

Part of the results of these investigations confirm the experimental data and conclusions made in our previous^{12,13,25} and in other reports¹¹ on the influence on the concentration of chemically bonded DEG in the PET chain and on the behavior of PET itself.²³ Density ρ , melting temperature T_m and glass transition temperature T_g , and crystallinity index W_c determined by other methods, decrease with increasing DEG content (Figs. 1, 6, 7, 8, and 11), irrespective of the sample form (granules, films, bristles), temperature, and manner of annealing.^{11,12} On the other hand, the tensile modulus E decreases, while the long spacing L and SAXS intensity I increase, the tensile strength σ_t , the step height ΔE^* and $\Delta E'$ and the temperature position of the maximum of the α process pass through a maximum [Figs. 13(b), 16, and 19] with increasing annealing temperature T .^{11,12,23}

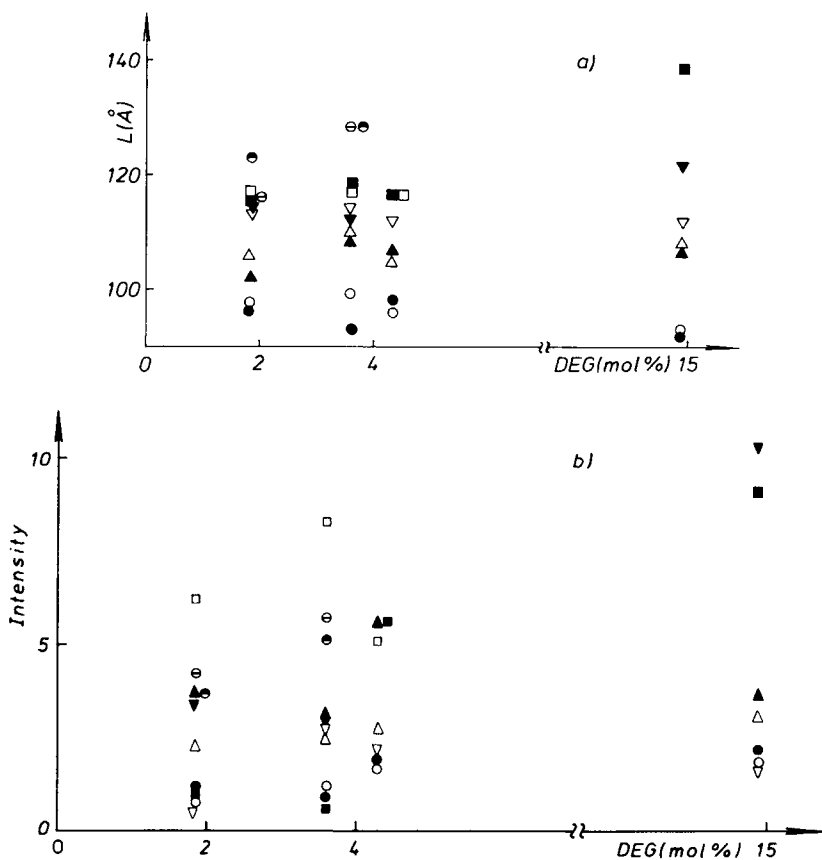


Fig. 20. Dependence of (a) long spacing L and (b) intensity (arbitrary units) on the DEG content. Annealing temperatures ($^{\circ}\text{C}$): (\circ , \bullet) 150; (\triangle , \blacktriangle) 200; (∇ , \blacktriangledown) 220; (\square , \blacksquare) 240; (\odot , \odot) 260. (\circ , \triangle , ∇ , \square , \odot) Bristles annealed with fixed ends; (\bullet , \blacktriangle , \blacktriangledown , \blacksquare , \odot) bristles annealed with one free end.

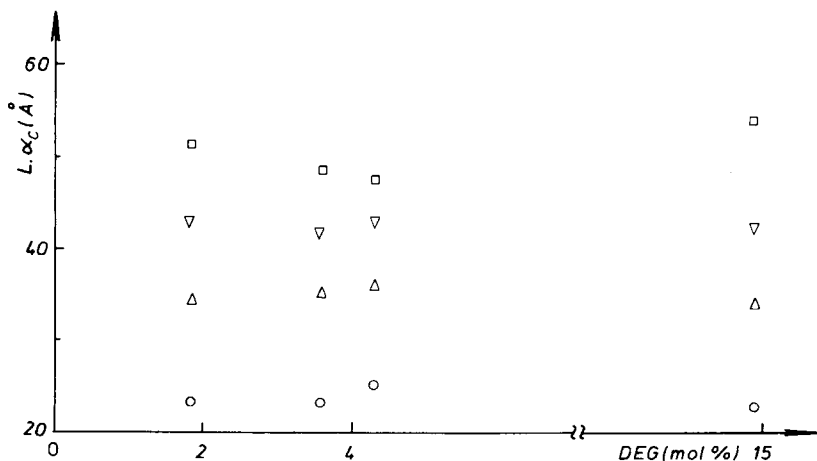


Fig. 21. Dependence of the lamellar thickness $L \cdot \alpha_c$ on the DEG content. The data are obtained using L values from Figure 20(a) and α_c values from Figure 4(a). Annealing temperatures ($^{\circ}\text{C}$): (\circ) 150; (\triangle) 200; (∇) 200; (\square) 240.

At the same time, there are some essential discrepancies with the previous work. In the first place, there is the higher density of the amorphous granules with equal DEG content after the long storage (Table I). The values of α_c , calculated according to eq. (1) and the values of L , I , and $L \cdot \alpha$ (Figs. 4, 20, and 21) are independent of the DEG content for annealing temperatures up to 200 or 220°C. Up to $T_a = 200^\circ\text{C}$ it is quite difficult to discover any influence of the annealing temperature on the calorimetrically measured W_c . Only above this temperature is such an influence clearly expressed (Fig. 8). α_c , determined by means of density, decreases with increasing DEG content, for samples annealed above $T_a = 200^\circ\text{C}$ (Fig. 4). Above this same annealing temperature, changes in the trends of the dependence of E and σ_t (Fig. 17) and $L \cdot \alpha_c$ (Fig. 21) on the DEG content for the samples containing 14.9 mol % DEG are also observed: an increase of the respective quantities can be seen. In the same temperature range, there is also an increase of the long spacing L with increasing DEG content [Fig. 20(a)].

The problems will be easier to tackle if they are separated into two categories: (1) the influence of the annealing temperature T_a on the measured quantities for the samples with equal DEG content and (2) the influence of the amount of chemically bonded DEG on the same quantities at a given annealing temperature T_a .

At all DEGT concentrations, one observes the well-known dependence of the considered quantities on the annealing temperature T_a ^{15,24}: increase of the density ρ (and therefore of the crystallinity α_c or W_c), of the SAXS long spacing L and intensity I , and of the lamellar thickness $L \cdot \alpha_c$; decrease of the modulus of elasticity E ; and the observation of a maximum in plots of tensile strength σ_t vs. increasing annealing temperature.

Deviations from former investigations are observed in the dependences of the same quantities on the amount of bonded DEG: α_c , L , I , and $L \cdot \alpha_c$ do not decrease with increasing DEG content, they remain constant. Only at $T_a > 200^\circ\text{C}$ do these quantities again follow the known dependence¹²; their values decrease with increasing DEG content. But even at these temperatures of preliminary annealing, samples containing 14.9 mol % DEG deviate from the known dependence; there is again an increase of the values of the above quantities.

The explanation of the observed behavior should be based on processes occurring in all samples oriented before annealing: crystallization and disorientation. The explanation must also account for the results which follow the trends of the previous investigations^{11,12}: a decrease of T_g and T_m with increasing DEG content. This decrease is a result of the greater mobility of the chain determined by the ether bond. This behavior has already been shown by Zachmann¹¹ and is confirmed in Ref. 12 and in these investigations.

The decrease of T_g and T_m with increasing DEG content leads to a reduction of the temperatures of the maximum crystal nucleation and growth rates. This reduction is confirmed by Zachmann's pioneering investigations of the influence of DEG content on the half-times of the crystallization process.¹¹

If parameters characteristic of the DEG level are to be found, so that specimens may be meaningfully compared, it is necessary that the trans-

formation at T_g go to completion within the annealing time used. This requires that the annealing temperature lie far from both T_g and T_m . For temperatures nearer T_g or T_m , the transformation cannot proceed to completion in the allotted time.

From the half-times of the crystallization process (Ref. 11, Figs. 4 and 6), one can conclude that the temperature range over which the transformation should be complete for all specimens is between 100–105°C and 200–210°C. In the same temperature range the structural parameters, measured in this work—long spacing L , SAXS intensity I , lamellar thickness $L \cdot \alpha_c$, and crystallinity α_c —are insensitive to the DEG content. At annealing temperatures higher than 200–210°C, the structure formation processes in the samples with different DEG content are interrupted at different stages of their completion within the chosen annealing time of 6 h. In this way, and since the crystallization rate decreases with DEG content, the observed increase of L and I , and decrease of α_c and $L \cdot \alpha_c$ with increasing DEG content can be explained.

This incompleteness of the microstructure formation processes at $T_a > 200^\circ\text{C}$ also explains the discrepancies in the DEG-content dependence of α_c and W_c (Figs. 4 and 8) below this temperature. In that range, α_c determined by ρ remains constant, while W_c measured from DSC curves continuously decreases with increasing DEG content. In the former, the density of the structure formed at the temperature of the preliminary annealing is measured. In the latter, this microstructure undergoes additional changes at the heating rate used. These changes (partial melting and recrystallization) proceed almost to the final melting temperature of the sample.¹⁵ The rate of these changes and their degree of completion will depend on the temperature of the preliminary annealing, as well as on the DEG content, i.e., on the half-times of the crystallization process at temperatures close to the final melting temperature. These half-times of crystallization, as Zachmann has shown,¹¹ increase strongly with increasing DEG content. At the same high annealing temperatures above $T_a = 200\text{--}210^\circ\text{C}$, samples containing 14.9 mol % DEG are quite close or in the range of the final melting temperature (Fig. 8). Their structure will be formed from the melt or from the partially molten state. And this explains the higher values of L , I , $L \cdot \alpha_c$, E , σ , and ΔE^* for such samples at these annealing temperatures.

The discussion to this point attempts to explain the course of most of the dependences investigated in this work. But it also leaves some open questions. Guzman and Fatou²⁶ have established that the pure homopolyetherester based on terephthalic acid and diethylene glycol does not crystallize. Thus it is clear that comonomer DEGT sequences must be excluded from the copolymer crystals. It was found in Ref. 12 that the DEG content indeed does not influence the unit cell parameters. In the present investigation, it was shown that $L \cdot \alpha_c$ is not influenced by DEG level. This is another strong indication the the comonomer does not influence the crystalline phase; the DEGT units remain in the amorphous phase. The question is, then, why does the DEGT comonomer not influence the crystal thickness, the degree of crystallinity, and the SAXS intensity? If the comonomer cannot enter the crystal, one would *a priori* expect that the distribution of DEGT comonomer units would reduce the crystallizable sequence lengths

to such an extent that only very thin crystals can form, thereby reducing $L \cdot \alpha_c$ below the value found for pure PET and consequently also reducing the degree of crystallinity. According to calculations made in Ref. 12 the segment length free of DEGT units depends strongly on the DEG concentration: At 14.9 mol % DEG, the mean distance between two DEGT units is about 70 Å. The value is higher than the highest lamellar thickness value (54 Å) measured here (Fig. 21). Therefore, the limiting value for the lamellar thickness, determined by the DEG content (70 Å) at 14.9 mol % DEG is still not achieved. Thus, in order to see the influence of the DEG content on the value of the lamellar thickness, one needs DEG concentrations higher than 14.9 mol %. The values of the lamellar thickness in Figure 21, calculated from the values of the long spacing L and these of the volume fraction crystallinity α_c , were also tested via a Guinier SAXS plot for the sample with 14.9 mol % DEG, annealed at 240°C. The value for the lamellar thickness from this plot is approximately 50 Å. This is close to the value (54 Å) determined by $L \cdot \alpha_c$ for the same sample.

It should be pointed out that the present result, using naturally aged material, differs from the previous results,¹² when fresh material was used, in that (a) the absolute level of crystallinity is lower than previously and (b) with fresh material, an increase in the amorphous layer thickness $(1 - \alpha_c)L$ with DEG level was noted, but was not seen in the present work. It is suggested that both effects in the present work are due to elastomeric strains acting to inhibit crystallization, a degree of crosslinking having occurred during room-temperature aging of the material.¹⁷ In this manner, the spacing between crystallites is controlled more by long-range inhibiting strains than by the segregation of DEG units. The confirmation of the other suggestions made in Refs. 12 and 13 concerning the exact distribution of the DEGT units between the crystalline and the amorphous phase needs additional investigation of single crystals and deuterated samples of PET with different DEG content.

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