Structure of Uniaxially Drawn Poly(Ethylene Terephthalate) Films and Its Influence on Dye Sorption

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Synopsis

Drawing temperature, draw ratio, and tension during thermal treatments were varied to obtain poly(ethylene terephthalate) (PET) films with different structural modifications. These PET films were disperse dyed using a C.I. Disperse Blue 7 dye. Qualitative and quantitative characterization of molecular order and orientation was carried out using infrared spectroscopy and x-ray diffraction methods. Dye sorption was inferred from reflectance measurements using an optical spectrophotometer. It was observed that there was no unique dependence of dye uptake of poly(ethylene terephthalate) films on either orientation or crystallinity separately. Structural models have been proposed to explain the dye sorption behavior with special emphasis on the efficiency of chain packing, tortuosity, or compactness of the structure as an important criterion in governing the diffusion of dye molecules into the film matrix.

INTRODUCTION

Drawing and annealing can produce a range of structural modification in poly(ethylene terephthalate) films (PET). Because of their commercial importance, studies on the influence of drawing and thermal treatments on polymer structure and properties have been receiving considerable attention for many years.[1-27] Since dyeing is one of the most important steps in commercial wet-processing practices of plastics, films, and fabrics, innumerable attempts have been made to relate the diffusion behavior of disperse dyes to the morphology and structure.[28-41] However, many diverse approaches can be found in literature toward understanding the structural sensitivity of dye sorption. This is more evident from the publications on this subject by Warwicker,[32,34] Huismann and Heuvel,[36] and Yonetake et al.[41]

In an attempt to resolve this confusion, regarding the exact nature of the influence of structural modifications on dye sorption, systematic studies on structure–property relationship in PET were carried out in this laboratory. During these investigations some very interesting results were obtained which appeared to suggest the need for a modification in the existing concepts regarding the influence of structure on dye sorption. In this paper, studies on uniaxially drawn films are reported and subsequent papers will deal with similar studies on fibers also.

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EXPERIMENTAL

Materials

An amorphous film, as well as hot-stretched (at 85°C) PET films of different draw ratios (1 : 2, 1 : 3, and 1 : 4) were obtained through the courtesy of Du Pont, U.S.A.

Undrawn amorphous film was slowly drawn at 27°C room temperature (cold drawing) to 520% (i.e., the maximum drawing extension possible here) using a laboratory stretching device. Subsequently, heat setting was carried out at 230°C in an oven with an inert gas (N_2) atmosphere for 5 min. The samples were rapidly cooled back to room temperature after thermal treatment using acetone as quenching medium. Films which were set without allowing any dimensional change (shrinkage) are referred to as tension-set films and those set with allowance for shrinkage are referred to as slack-set films.

X-Ray Diffraction

Wide-angle x-ray diffraction patterns were recorded with the incident x-ray beam perpendicular to the draw axis and parallel to the thickness direction of films, using a cylindrical camera of radius 3 cm and Ni-filtered $CuK\alpha$ radiation at 35 kV and 18 mA.

Density

The flotation method was used to measure the sample density (ρ), using two different pairs of liquid, namely potassium iodine/water and CCl_4/n-heptane. Both pairs of liquid gave nearly the same results, which are reproducible with an accuracy of $+0.002$ g/cc.

Crystallinities were evaluated using the two-phase equation

$$X_d = \frac{(\rho - \rho_a)}{(\rho_c - \rho_a)} \times \frac{\rho_c}{\rho}$$

where ρ_c = density of 100% crystalline PET determined to be 1.456 g/cc from crystal structure, ρ_a = density of 100% amorphous PET (theoretically given as 1.335 g/cc).

Infrared Spectroscopy

Infrared (IR) spectra were recorded using a Perkin-Elmer Model 180 double-beam recording spectrophotometer. Polarized spectra were recorded using a silver bromide (AgBr) Polarizer. All precautions for minimizing the errors due to polarization of the monochromator were taken during spectra recording. The absorbances of the individual bands were determined using suitable base-line methods suggested in literature. Relative *trans/gauche* contents were computed by taking the ratio of the *trans/gauche* absorbances to the absorbances of a reference band at 1508 cm^{-1}, which is known to be sensitive to thickness (mass) but not to structure variations (internal thickness reference standard).

The dichroic ratios have been expressed as the ratio of absorbances in the parallel and perpendicular polarized transmission directions (A_{11}/A_1), respectively. For considerations best illustrated in Schmidt's paper,[42] absorption with a transition moment type T_1 were considered best suitable for measuring the axial orientation, while transition moments of type T_3 were considered suitable for planar orientation estimations.[42] Orientation functions were determined using Fraser's formula relating the dichroic ratios to the molecular organization functions. Transition moment angles were selected as 0° for both 1580 cm^{-1} and 1340 cm^{-1} bands as suggested from the configuration of PET molecular chains.

Dyeing

Dyeing experiments were carried out on all these films using a disperse (C.I. Disperse Blue-7) dye, without any carrier, at $90 \pm 2°$C for $1\frac{1}{2}$ h. All the films were dyed in the same dye bath and dyeing was repeated to verify the reproducibility of the results.

Optical Reflectance

Reflectance measurements were carried out using a "Pretema" optical spectrophotometer. For these measurements several layers of dyed films were prepared in order to make the sample sufficiently thick. These multilayered film samples were introduced into the "Pretema" spectrophotometer and the reflectances were obtained in the visible region between 400 to 700 nm. Reflectance curves were drawn using these data and K/S, which is a ratio of coefficients of absorption and scattering, respectively, were calculated using the Kubelka-Munk.

$$K/S = \frac{(1 - R)^2}{2R}$$

R is (%) percent reflectance at the absorption minima in the reflectance curve and is characteristic of the dye used.

In order to correct for the background reflectance, measurements were also carried out on the corresponding undyed films in each case and the true values of K/S were obtained using the following relationship:

$$(K/S)_{\text{true}} = (K/S)_{\text{dyed}} - (K/S)_{\text{undyed}}$$

RESULTS

X-Ray Diffraction

X-ray diffraction patterns recorded for cold-drawn and hot-stretched (at 85°C) films are reproduced in Figures 1 and 2, respectively. It is interesting to note that after thermal treatments the cold-drawn and hot-stretched highly oriented films show significant differences in their diffraction patterns. In cold-drawn film (Fig. 1), the x-ray patterns show all three prominent equatorial reflections with Miller indices 010, $\bar{1}$10, and 100 present on the equator,
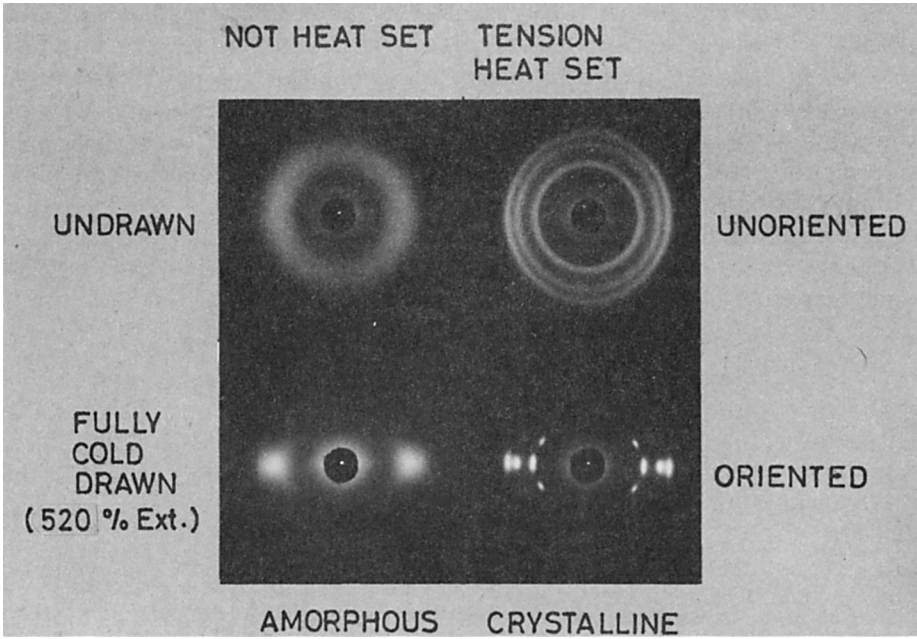
Fig. 1.   X-ray diffraction patterns of undrawn and cold-drawn films.
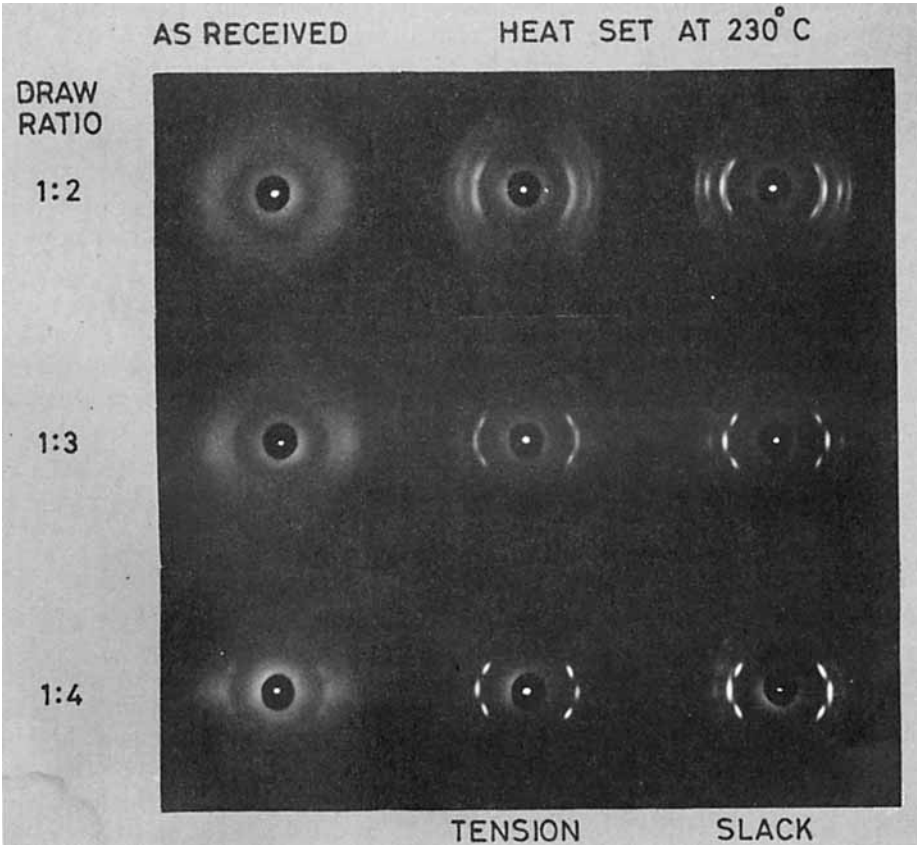

Fig. 2.   X-ray diffraction patterns of hot-stretched (85° C) films.

whereas in the x-ray patterns of hot-stretched commercial films (Fig. 2) reflection from the 1̄10 planes is reduced in intensity, while the 100 reflection is conspicuously absent. In other words, cold-drawn crystallized films exhibit a fiber-type diffraction pattern because they are first oriented and then crystallized, while the hot-stretched films commercially rolled gave different patterns because of their uniplane orientation introduced during the simultaneous drawing and crystallization that take place at the higher temperatures used during hot drawing and rolling. It is known[43] that when films are uniaxially commercially stretched, one particular crystallographic plane tends to become parallel to the film surface, that is, perpendicular to the thickness direction. In PET films this plane is represented by the Miller indices 100. As the uniplanar orientation increases, the plane normal becomes more and more parallel with the x-ray beam direction and the reflection from the 100 plane gradually disappears from the resulting x-ray diffraction patterns. Figure 2 shows that, in the case of hot-drawn commercial films, with increasing draw ratio a uniplanar and uniaxial orientation increased. This is more clearly brought out after thermal treatments. Two interesting observations were made from these x-ray diffraction patterns. The undrawn and hot-stretched 1:2 films both appear to be amorphous and poorly oriented initially. However, after the thermal treatments the undrawn film shows completely disoriented crystalline patterns and the 1:2 drawn film shows moderately oriented crystalline patterns. Secondly, the effect of tension during thermal treatments was
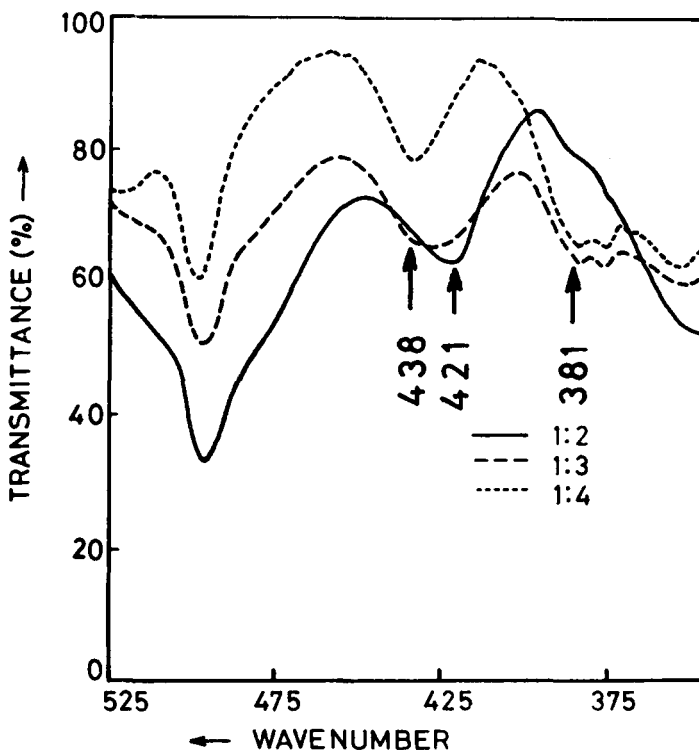

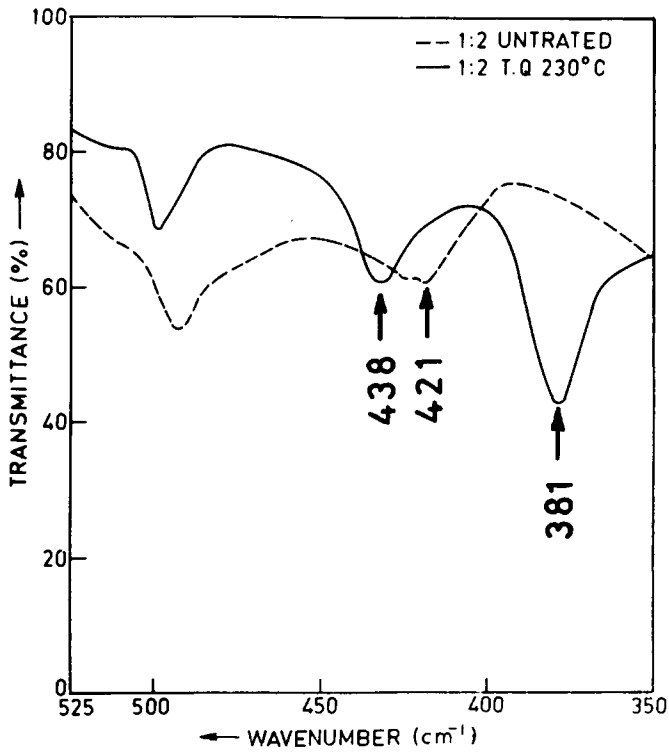Fig. 3.   Infrared spectra in the region 350–525 cm^{-1} for hot-stretched films.

Fig. 4.   Infrared spectra in the region 350–525 cm^{-1} for 1:2 drawn, as well as heat-set films.
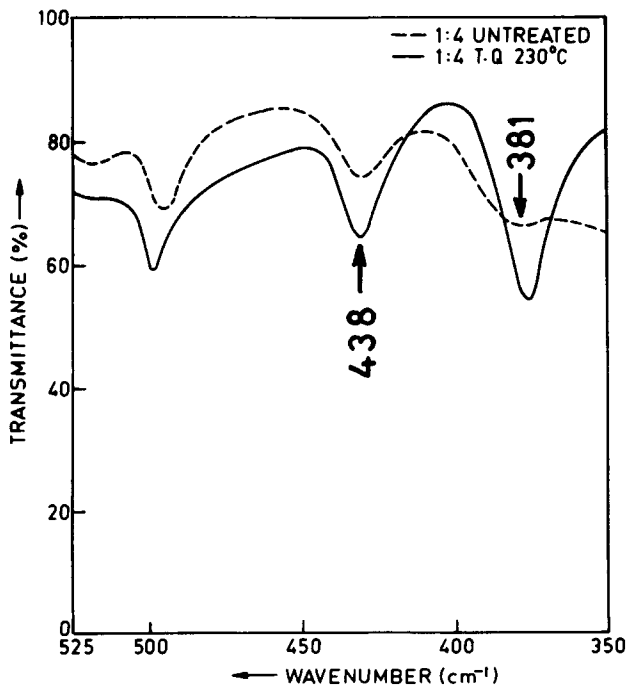

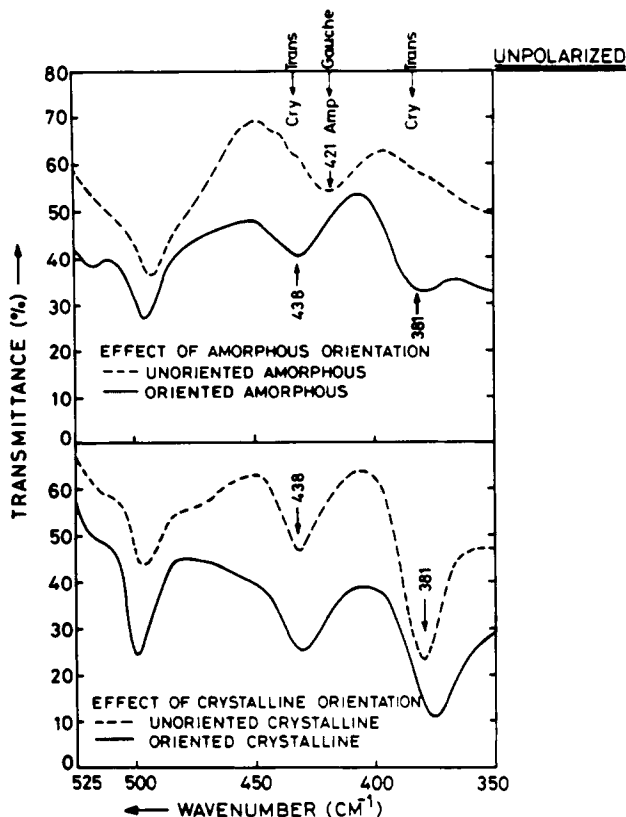Fig. 5.   Infrared spectra in the region 350–525 cm^{-1} for 1:4 drawn, as well as heat-set films.

Fig. 6.   Infrared spectra in the region 350–525 cm^{-1} for undrawn (-----) and cold-drawn (——)
520% (top), and corresponding heat-set films (bottom). Cry = crystalline, Amp = amorphous.

different in low ratio (1 : 2) and high draw ratio films (1 : 4). The 1 : 2 low draw
ratio tension-set films lower crystallite orientation and crystallinity than do
their corresponding slack-set films. In addition, a crystallographic tilt (100
maxima lying away from the equator) is indicated only in 1 : 2 tension-set
films x-ray patterns. In the high draw ratio (1 : 4) films the opposite trend to
the low draw film is observed for the slack and tension heat-setting treat-
ments.

Infrared Spectroscopy

Infrared spectra recorded in the region 350 cm^{-1} to 526 cm^{-1} which is
found in this work to be quite structure sensitive, are given in Figures 3 to 6.
In this spectral region (Fig. 3), the band at 421 cm^{-1} has been assigned to the
amorphous phase, while the bands at 438 cm^{-1} and 381 cm^{-1} are reported to
be more sensitive to the crystalline phase.[44,45] The presence of the 421 cm^{-1}
band and the absence of the bands at 438 cm^{-1} in the corresponding spectra
of undrawn (Fig. 6, top broken line) and 1 : 2 drawn films untreated (Fig. 4,
broken line) confirm the observation that they are totally amorphous. Ap-
pearance of absorption at 381 cm^{-1} and at 438 cm^{-1} in films with draw ratio
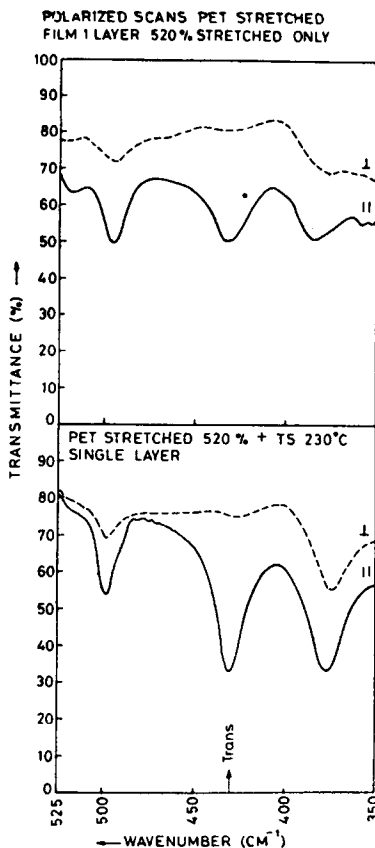1 : 3 and above (Fig. 3) indicate that partial order has been produced in them

Fig. 7. Polarized IR spectra in the region 350–525 cm^{-1} for cold-drawn and heat-set films.

on drawing. In all the thermally treated films, strong absorptions at 438 cm^{-1} 381 cm^{-1} are observed (Figs. 4–6) which indicated high crystalline order in them after thermal treatment (full line traces).

The polarized spectra for all these films in the same spectra regions are shown in Figures 7 and 8. All the absorption peaks in these regions (Fig. 7) are highly orientation sensitive and show high parallel dichroism (full lines). Figure 8 shows that low draw ratio (2 : 1) films do not possess any noticeable orientation before thermal treatments (top row), while after thermal treatment parallel dichroism is exhibited by all the bands, indicating that some orientation has accompanied crystallization. The effect of tension (middle row, Fig. 8) also showed opposite trends in orientation in low (2 : 1) and high draw ratio (4 : 1) films. These results are in agreement with the result of the x-ray diffraction differences.

To substantiate the observations regarding the influence of draw ratio and tension during thermal treatment on crystallinity and orientation changes in thermally treated films, quantitative estimates of orientation of the crystalline and amorphous regions were obtained. Determination of crystallite and amorphous orientation by infrared (IR) methods is difficult, because most orientation-sensitive absorption bands are due either to the "*trans*" or
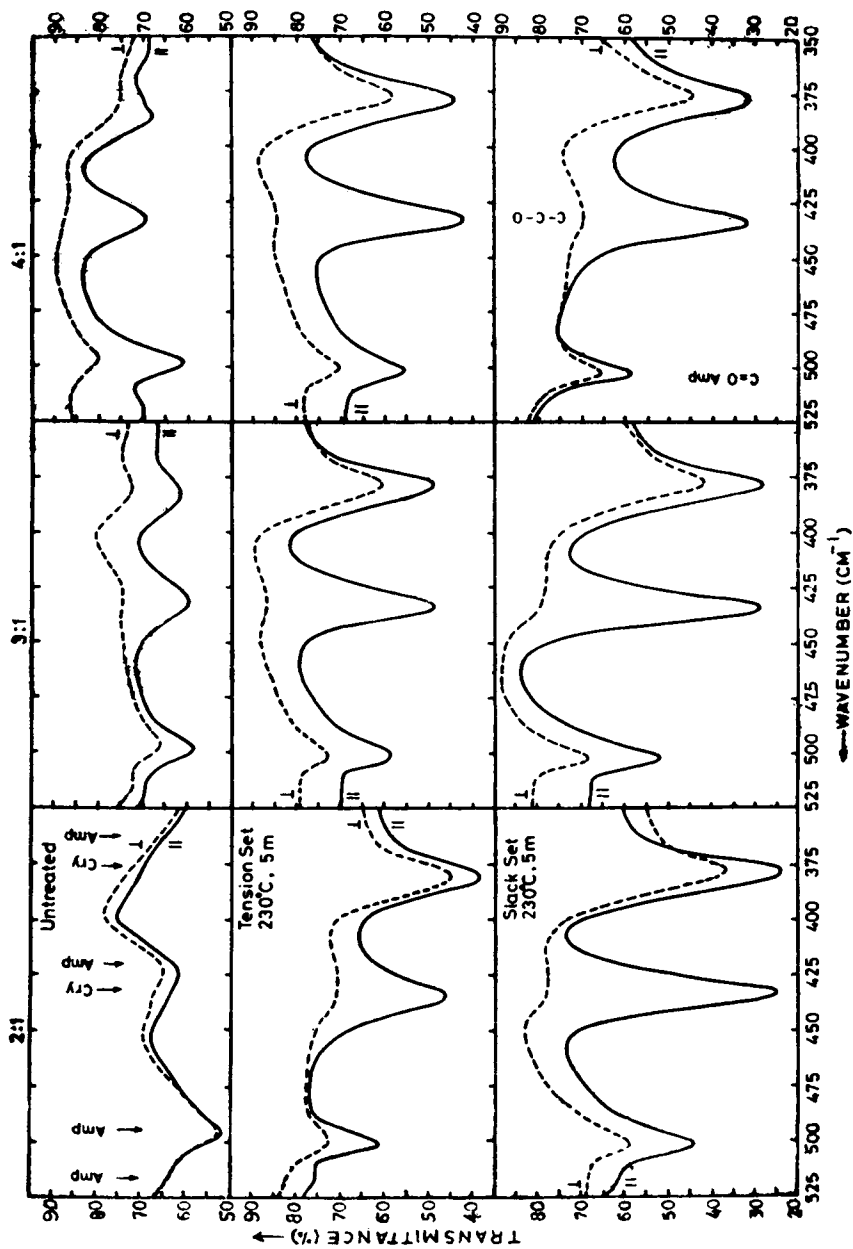
Fig. 8.   Polarized IR spectra in the region 350–525 cm^{-1} for hot-stretched and heat-set films. Cry = crystalline, Amp = amorphous.
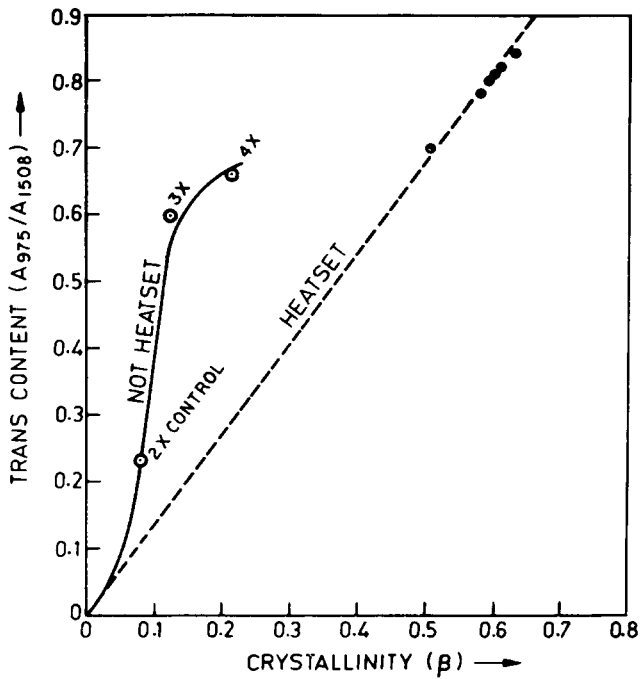
Fig. 9.   Relative *trans* contents (A_{975}/A_{1508}) as a function of density crystallinity.
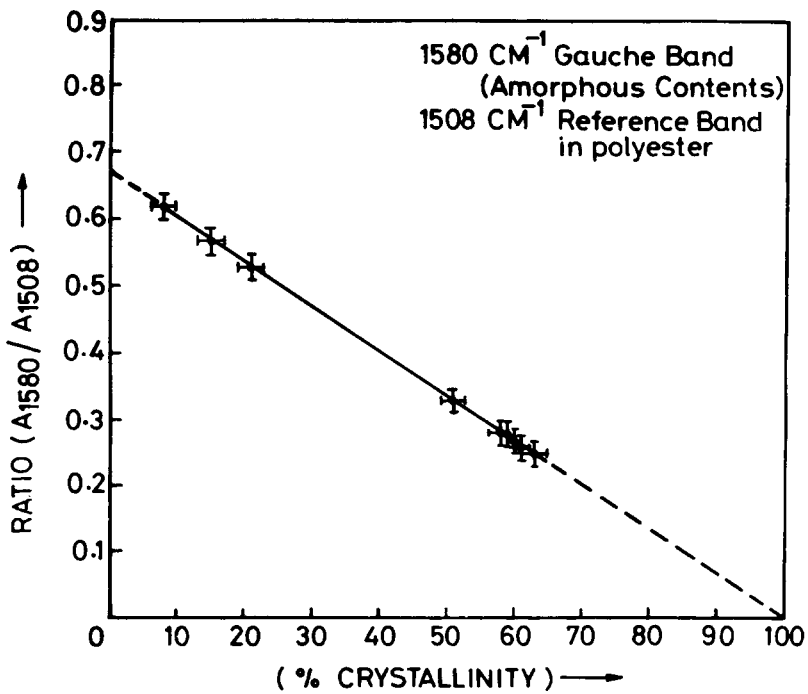

Fig. 10.   Relative absorbance at 1580 cm^{-1} (A_{1580}/A_{1580}) as a function of density crystallinity.

"*gauche*" configurations of the ethylene glycol molecule. Since the *trans* content is likely to be present both in the crystalline and amorphous regions,[42] the dichroism exhibited by these bands cannot be taken to estimate crystallite orientation. This is clearly suggested by examination of the relationship between density crystallinity and relative *trans* content as measured using the 975 cm^{-1} absorption band (Fig. 9). The drawn films with low density crystallinity show high *trans* content because of their highly oriented amorphous structure, while for drawn thermally treated films a linear relationship existed between crystallinity and *trans* contents. For this reason a different method is adopted here to get an indirect estimate of crystallite orientation. For measuring amorphous orientation, although any *gauche* band dichroic ratio can be chosen in order to minimize the errors in estimation due to the ambiguity in fixing the base line and due to overlapping by strong adjacent absorption bands, the 1580 cm^{-1} (amorphous ring mode) is chosen here to estimate amorphous orientation. This amorphous sensitive[46,47] absorption band is reported to provide a good estimation of amorphous orientation due to the absence of any base line and overlapping adjacent band problem. Its sensitivity to the amorphous phase is clearly indicated in Figure 10, where an inverse linear relationship of this band's relative intensity with density crystallinity is shown.

Orientation functions determined using the dichroic ratio of the 1580 cm^{-1} band has therefore, been chosen as representative of the amorphous orientation (f_a). Average axial molecular orientation is chosen to be represented by the orientation functions estimated using dichroic ratios of 1340 cm^{-1}. By substituting these two values (f_a and f_c...) and the density crystallinity (β) in the equation given below, an indirect estimation of crystallite orientation is obtained. In addition, for comparison, estimation of crystallite orientation directly from the dichroic ratio of the crystalline sensitive 438 cm^{-1} band as suggested by Novak[48] is also obtained.

$$f_{av} = \beta \cdot f_c + (1 - \beta)f_a$$

Where f_{av} = average molecular orientation, f_c, f_a = crystallite and amorphous orientation, respectively, and β = density crystallinity (fractional). The results are shown in Table I.

This data confirmed the trends observed from x-ray diffraction patterns regarding the effect of draw ratio and tension on the crystallite orientation of

TABLE I

Draw ratio	Slack-set films			Tension-set films		
	f_a	f_c1	f_c2	f_a	f_c1	f_c2
1 : 2	0.21	0.63	0.75	0.24	0.52	0.66
1 : 3	0.20	0.75	0.78	0.24	0.88	0.83
1 : 4	0.10	0.77	0.80	0.15	0.95	0.90

f_a = amorphous orientation.
f_c1 = crystallite orientation estimated by method suggested here.
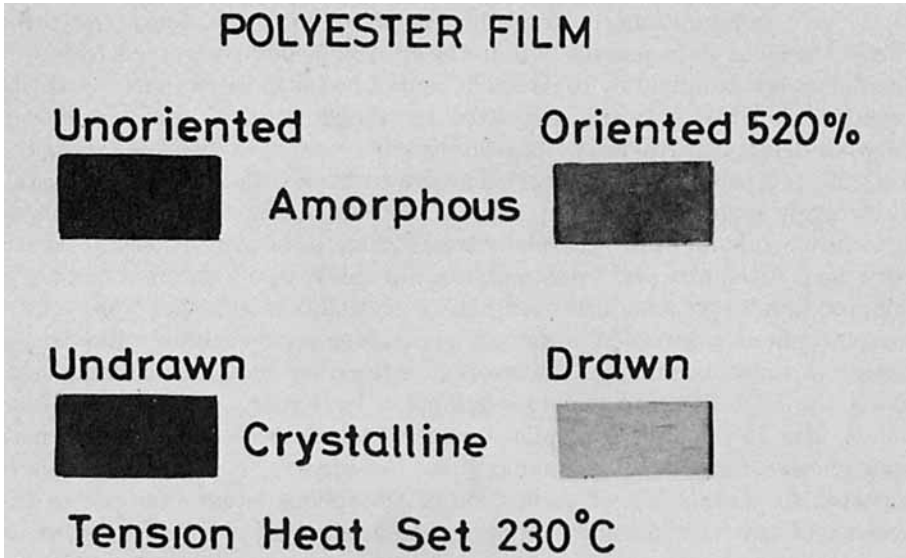f_c2 = crystallite orientation estimated using Novak's method.[48]

Fig. 11. Dyed films (cold-drawn series).

the subsequently thermally treated films. It is interesting to note that amorphous orientation is higher in the lower draw ratio (1:2) films than in high draw ratio (1:4) films. Tension during thermal treatments has always produced higher amorphous orientation. However, crystallite orientation is lower in tension-set films with a low draw ratio (1:2) than in corresponding slack-set films, while the opposite trend is exhibited in films with high draw ratio (1:4).
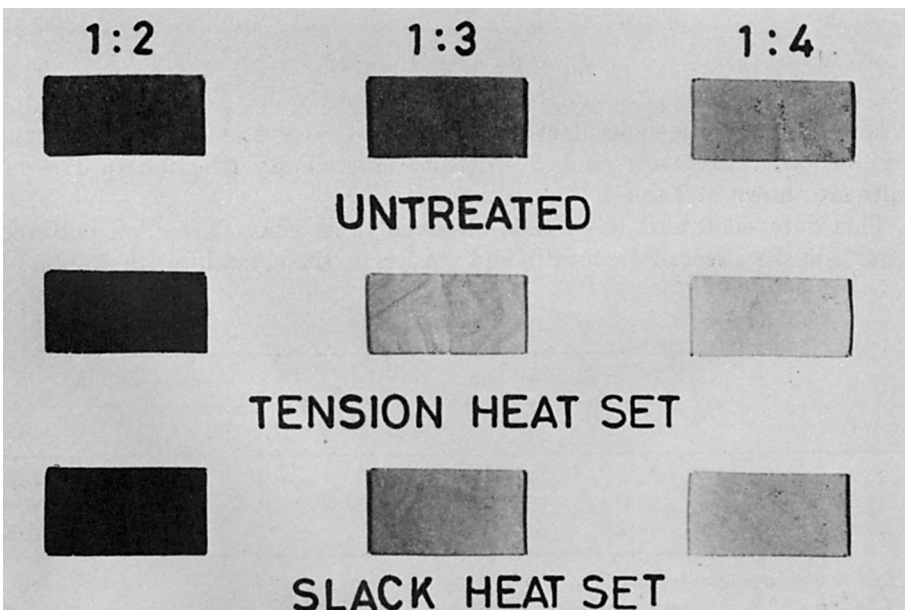

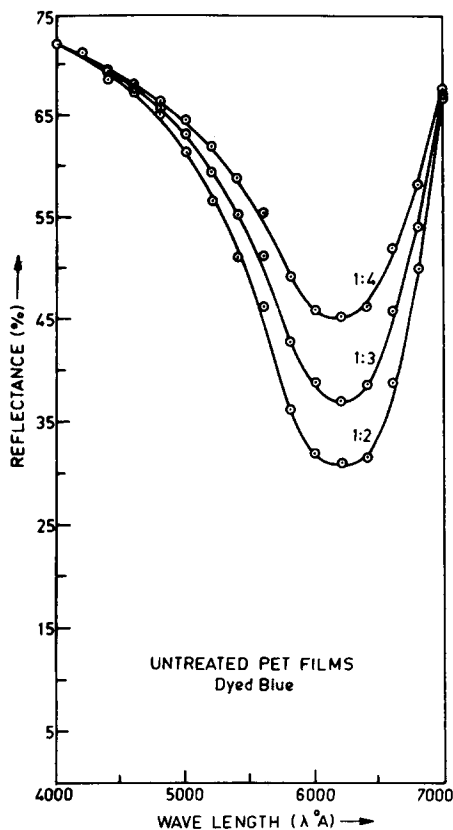Fig. 12. Dyed-films (hot-drawn series).

Fig. 13. Optical reflectance curves for dyed films of different draw ratios.

Dye Sorption

Figures 11 and 12 show the photographic reproductions of dyed films. A quick qualitative assessment of these photographs indicated that dye sorption was reduced greatly due to orientation alone as a large decrease in dye sorption is observed in highly drawn (cold, as well as hot stretched) films without any thermal treatments. Thermally treated low draw ratio and undrawn films, still showed considerably higher dye sorption than the untreated and thermally treated highly drawn films.

Figures 13, 14, and 15 show the corresponding optical reflectance curves for films of different draw ratios, low draw ratio (1 : 2) heat-set films and high draw ratio (1 : 4) heat-set films, respectively. The opposite effect of tension during thermal treatments of low and high draw ratio films on their dye sorption behavior is evident from Figures 14 and 15. (TQ, tension-quenched, and SQ, slack-quenched curves are on opposite sides of the unheated controls for low 1 : 2 and high 1 : 4 draw ratios.)

Dye sorption behavior observed here, tends to be more dependent on crystallite and molecular orientation, than on total crystallinity. Further confirmation of this comes from an examination of the relationship, between K/S (measured from the reflectance curves) and crystallinity as measured from density as shown in Figure 16. Initially, within a small range of densities,
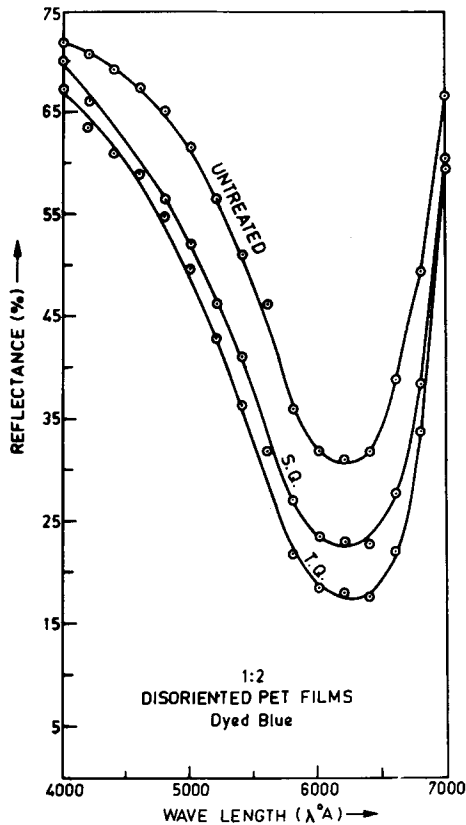
Fig. 14. Optical reflectance curves for dyed low draw ratio (1 : 2) and heat-set films.

a rapid decrease in dye sorption is observed, and at higher densities only a small variation in K/S values can be noticed.

Since the films in which a rapid decrease in K/S value with only a small increase in density was noticed are only drawn but not thermally treated, the decrease in dye sorption can only be attributed to increasing molecular orientation rather than to any change in total crystallinity. Besides, the 1 : 2 slack- and tension-set films showed an exceptional trend in that they showed high dye sorption even when their density crystallinities were fairly high. Hence, crystallinity alone does not seem to affect the dye sorption significantly. On the other hand, orientation effects appeared to have a dominant role. The predominant influence of orientation on dye sorption is also evident from Figure 17 where the relative *trans* content is plotted, because in all oriented crystalline materials the *trans* segment represents an extended chain configuration and therefore any increase in *trans* content represents an increase in orientation. An exceptional trend shown by low draw ratio films might be due to their lower orientation despite high crystallinity.

DISCUSSION

Poly(ethylene terephthalate) molecule is composed of aliphatic segments (ethylene glycol) which are flexible, and of aromatic segments (terephthalic acid) which are rigid.
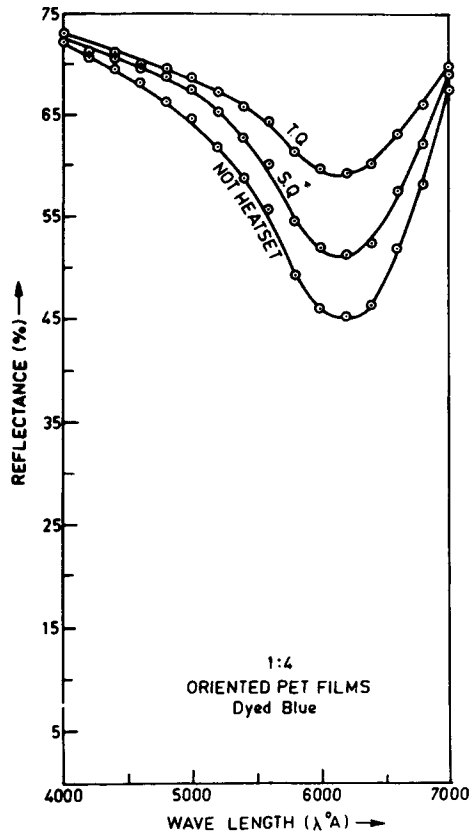
Fig. 15.   Optical reflectance curves for dyed high draw ratio (1 : 4) and heat-set films.
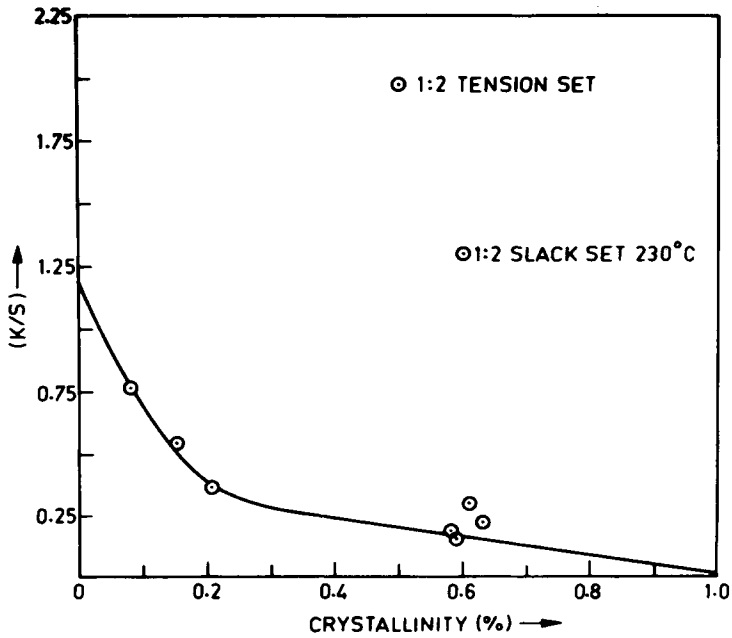

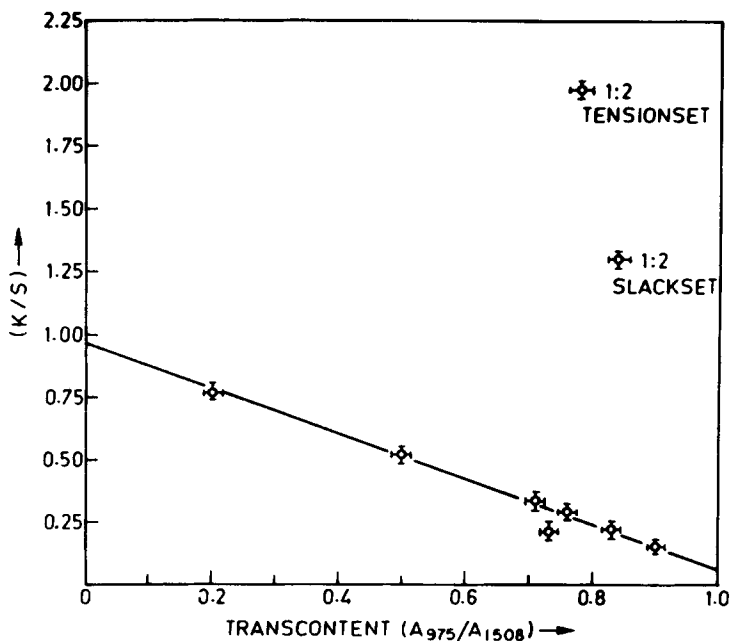Fig. 16. K/S as a function of density crystallinity.

Fig. 17.   K/S as a function of relative *trans* contents.

A planar molecule ensures better lateral register, and therefore increases the chances of crystals to grow perpendicular to the drawing, or orientation, axis. This planarity is facilitated by rotation of the aromatic segments (benzene ring) in PET molecule, which is known to occur only at temperatures above 120°C. As drawing temperatures were much below this value (≤ 80°C), drawing mainly leads to orientation of molecular chains in the draw direction without any substantial improvement in lateral order (perpendicular to the draw axis). Hence, the highly drawn film may possess a high uniaxially oriented structure but still does not have any substantial order. This is inferred from the result that the *trans* content is very high while density and x-ray crystallinities showed no significant presence of order in these films. Hence, on the drawn films one can speak of a so-called oriented noncrystalline or mesophase. However, in order to explain the curious result that thermal treatment led to crystallization in an oriented state of the initially unoriented amorphous (1 : 2) films, one must assume that there already existed some short-range ordered regions in a predominantly noncrystalline matrix of an undrawn film. These short-range ordered regions probably acted as nuclei for crystal growth which occurs on thermal treatment. One can visualize the undrawn film to possess a network structure with a chance association of a few parallel chain segments forming the short-range ordered region, randomly distributed throughout the film. On drawing, an affine deformation occurs and then these tiny crystallite nuclei quickly try to align along the draw direction. The sizes of these nuclei are so small that the polarized IR scan does not detect any dichroic effects, and neither does x-ray diffraction show any discrete reflections or any anisotropy of intensity distribution, even when

many of these nuclei are appreciably aligned along the draw direction. In undrawn films these nuclei are randomly oriented, and subsequent thermal treatment leads only to an unoriented crystalline structure. As a result of even a small amount of drawing these small short-range ordered regions align appreciably along the draw direction and act as nuclei for crystal growth, which occurs by rotation, conformational change, and alignment of the molecular chain segments along these nuclei. On exposure to thermal energy, these nuclei grow into larger crystals thus producing an oriented crystalline structure.

Different effects of tension during thermal treatment on low and high draw ratio films can be explained by their different structural features. The low draw ratio films may still retain the network-type structure as in the case of initially undrawn films with the difference that in the former the network is highly strained with large internal stresses frozen-in. Highly drawn films may possess a fibriller structure due to almost complete alignment of molecular chains along the draw direction and partial or paracrystalline order development in the lateral direction. Hence, the molecular relaxation forces accompanying crystallization are very large in less oriented or low draw ratio films. When such films are heat set under tension, since no dimensional changes are allowed, the high relaxation stresses generated are relieved by the tilting of crystal nuclei in a direction perpendicular to the draw direction, resulting in a crystallographic c axis tilt (see Fig. 2, 1 : 2 tension-set film) and also low crystallite orientation, as well as low crystallinity.

In high draw ratio films, crystallization rates are faster and almost all the crystal nuclei are aligned along the draw direction. Thus, crystallization in the oriented state precedes the relaxation process, and therefore tension during thermal treatments leads to greater orientation in them.

Keeping in mind these structural differences, the dye sorption differences in these films are not difficult to explain. From the reflectance curves it can be observed that low draw ratio tension-set films picked up less dye than the slack-set films. The opposite trend is shown by highdraw ratio films. From structural studies it was noted that crystallite orientation is lowest in 1 : 2 tension-set films and is higher in 1 : 4 tension-set films. K/S values of these two films show large differences, while their density crystallinity values exhibit only marginal differences. Similar trends are also noticeable in 1 : 2 and 1 : 4 slack-set films. In the cold-draw series, unoriented crystalline films picked up much less dye than the oriented noncrystalline (520% drawn) and oriented highly crystalline (520% drawn and tension set) films.

Thus, crystallinity alone does not seem to significantly influence the dye sorption behavior in PET, while orientation does appear to have an important role.

This greater sensitivity of dye sorption to orientation, rather than to total crystallinity alone, cannot be explained on the basis of the conventional models, which assume dye diffusion to be mainly controlled by chain segmental mobility. Differential scanning colorimetry (DSC) studies[48] showed that low draw ratio films do not show any distinct glass transition in their thermograms after thermal treatments, which made them indistinguishable from those obtained for high draw ratio heat-set films. Thus, after thermal treatments, both in high and low draw ratio films, the glass transition
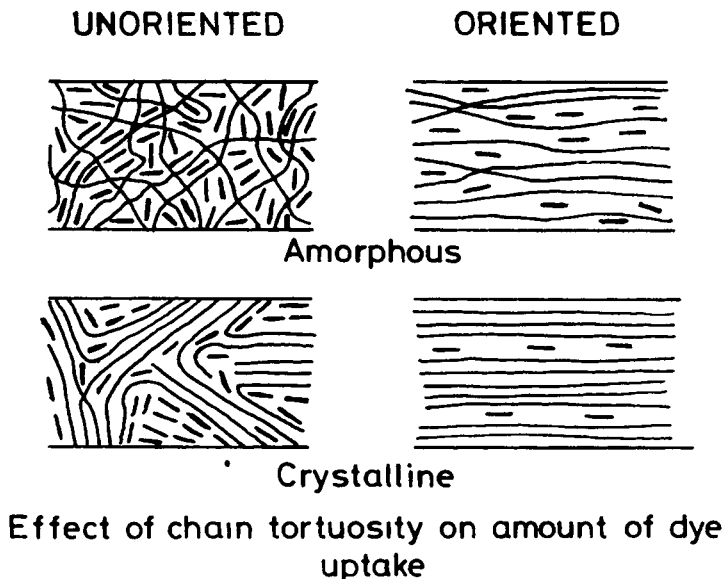
Fig. 18. Network models, schematic representation of the effect of orientation on compactness of structure and dye diffusion, (long lines are PET molecular chains, short rods are dye molecules).

temperature shifts to higher temperatures, much above the temperature at which they were dyed (at $90 \pm 2°C$).

It is logical to expect that orientation of structural elements should affect the efficiency of packing of these structural elements in the sample matrix. In a given volume, if structural elements are highly disoriented with respect to each other, less efficient compactness of structure results leaving large amounts of void or empty spaces between them. On the other hand, within the same volume, if all the structure elements are more or less uniformly oriented much more efficient packing and compactness is achieved leaving very little void or empty space between the structural elements. In addition to affecting the compactness of structure, chain orientation also affects the tortuosity[32-34] of the diffusion channels (empty or void spaces). The dye molecule shape used in this study can be assumed to be rod, or platelet type.[32] The diffusion of this disperse dye molecule into the film matrix must be affected by the length and width of the diffusion channels which are much more controlled by orientation than any other structural parameter. Such a situation is schematically represented in Figure 18 which shows a network model which explains the dye pickups in the unoriented, oriented amorphous (cold-drawn) and heat crystalline fibers.

It is suggested that the relative arrangement of the structural elements with respect to each other, the compactness of the structure, as well as the tortuosity of the diffusion channels (empty spaces surrounding the structural elements) are more important than the individual effects of orientation or crystallinity alone in controlling the dye sorption behavior in polyester films. The studies of polyester filaments[49] and small-angle x-ray scattering results[50] obtained in this laboratory have provided supporting evidence for these concepts.

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