

Tensile drawing behaviour of polyethylene terephthalate: Influence of molecular weight and pre-orientation

J. C. Engelaere, J. P. Cavrot and F. Rietsch

Laboratoire de Structure et Propriétés de l'Etat Solide, L.A. 234, Université des Sciences et Techniques de Lille, 59655 Villeneuve d'Ascq Cedex, France

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The drawing behaviour above the glass transition temperature has been studied for various viscosities of polyethylene terephthalate. The results suggest that the formation of a permanent physical network is very sensitive to the molecular weight. Consequently, the extension draw ratio achieved after cold drawing at room temperature has been found to be strongly affected by both degree of pre-orientation and molecular weight. The analysis of the two-stage deformation process shows that the pre-orientation birefringence is a relevant parameter in the description of natural draw ratio variation.

Keywords Tensile drawing; polyethylene terephthalate; molecular parameters; pre-orientation; natural draw ratio

INTRODUCTION

In a previous paper¹ the mechanical behaviour of amorphous polyethylene terephthalate (PET) was investigated for three different drawing procedures: homogeneous drawing ($T = 80^\circ\text{C}$), cold drawing at room temperature and two-stage drawing, namely homogeneous pre-orientation followed by cold drawing. For homogeneous drawing, the results showed good agreement with the Gaussian deformation model for draw ratios up to 2.5 and allowed us to consider the material as a physical network. However, the quantitative description of this network (particularly the determination of elastic chain number) was found to be in some disagreement with other studies^{2,3}. Moreover, in the two-stage deformation process, the pre-orientation stage led to a drastic increase in total draw ratio, inconsistent with a previous assumption that the maximum extensibility achieved after cold drawing has a constant value ($\lambda = 4$) independently of hot-drawing procedures^{3,4}.

So we find it interesting to obtain more precise information on these points by a systematic study of different intrinsic viscosity materials. The first part deals with the experimental measurements of shrinkage force and birefringence as a means of characterization of the degree of orientation achieved by stretching. The results presented in the second part of this paper emphasize the strong influence of molecular weight and are discussed in terms of polymer network formation.

EXPERIMENTAL

Deformation procedures

Dumb-bell shaped samples 5.15 mm in width and 20 mm in length were used from PET sheets of 200 μm in thickness, kindly supplied by Rhône-Poulenc Industries Laboratories. The initial birefringence of films was very low, 5×10^{-4} , and the degree of crystallinity, estimated from differential scanning calorimetry, was found to be

negligible. The study was conducted with samples of different intrinsic viscosities, i.e. 0.61, 0.69, 0.75, 0.78 as measured from films in *ortho*-chlorophenol at 23°C . The corresponding molecular weights, deduced from the Mark-Houwink relation, are given in *Table 1*.

For samples of each viscosity, three deformation processes have been performed:

(1) Homogeneous drawing at 80°C with various maximum draw ratios $\lambda_p = \frac{L}{L_0}$, from 1.05 to 7, where L and L_0 are the final and original length respectively.

(2) Cold drawing at room temperature. In that case the draw ratio is a specific quantity, called the natural draw ratio λ_N .

(3) Pre-orientation at 80°C to different values of λ_p , followed by cold drawing at 20°C . The final draw ratio λ_T after the two-stage drawing process is defined as the product $\lambda_p \lambda_N$.

An Instron deformation machine was used with a cross-head speed of 1 mm min^{-1} , which is low enough to approach isothermal drawing conditions³. All samples used for the series (1), (2) and (3) were first conditioned at 80°C for twenty minutes in a thermostatically controlled chamber, to erase any influence of the previous thermomechanical history of the initial sheet. The draw ratios were defined from the average distance between successive ink marks, initially disposed every millimetre on the sample surface, measured with a microscope.

Birefringence measurement

Birefringence was measured at room temperature on a Zeiss polarizing microscope with an Ehringhaus compensator. For the discussion of the results for series (1), we have used the Kuhn and Grün⁵ relation which refers to the uniaxial extension of a Gaussian network:

$$\Delta n = \frac{2\pi(\bar{n}^2 + 2)^2}{45\bar{n}} N(\alpha_1 - \alpha_2)(\lambda^2 - \lambda^{-1})$$

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766 POLYMER, 1982, Vol 23, May

Table 1 Characteristic parameters of rubber elasticity in the Gaussian behaviour region

Viscosities (ml g ⁻¹)	0.60 ¹	0.61	0.69	0.75	0.78
Molecular weight x10 ³ (kg mol ⁻¹)	18 800	19 000	22 000	25 000	26 000
Number of elastic chains per unit volume x 10 ⁻²⁶ (m ³)	1.48	2.88	2.93	3.29	4.24
Average molecular weight between consecutive entanglement points x10 ³ (kg mol ⁻¹)	5400	2800	2700	2400	1900
Stress-optical coefficient x10 ⁹ (m ² N ⁻¹)	4.95	7.63	6.73	6.62	6.52

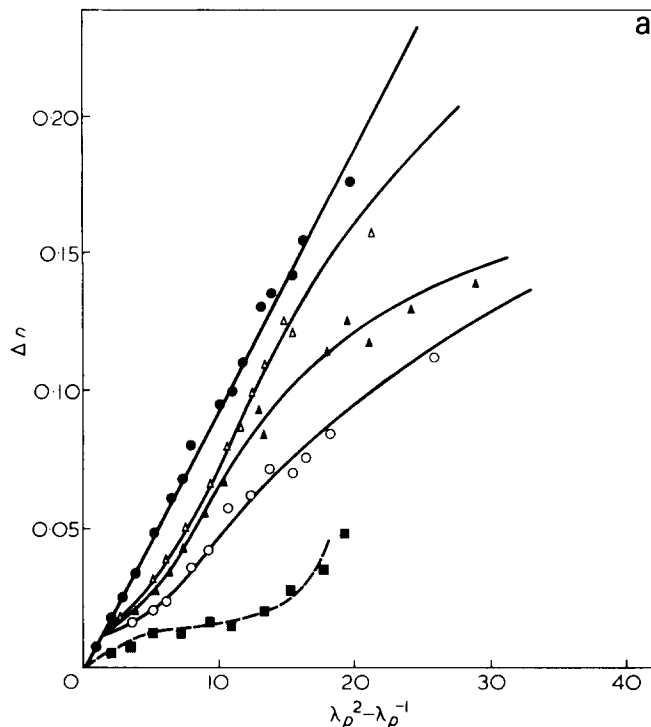


Figure 1 (a) Birefringence Δn versus the Gaussian parameter ($\lambda_p^2 - \lambda_p^{-1}$) plot for homogeneous drawing for specimens of different specific viscosities: ■, 0.60¹; ○, 0.61; ▲, 0.69; △, 0.75; ●, 0.78; the broken line corresponds to previous work¹

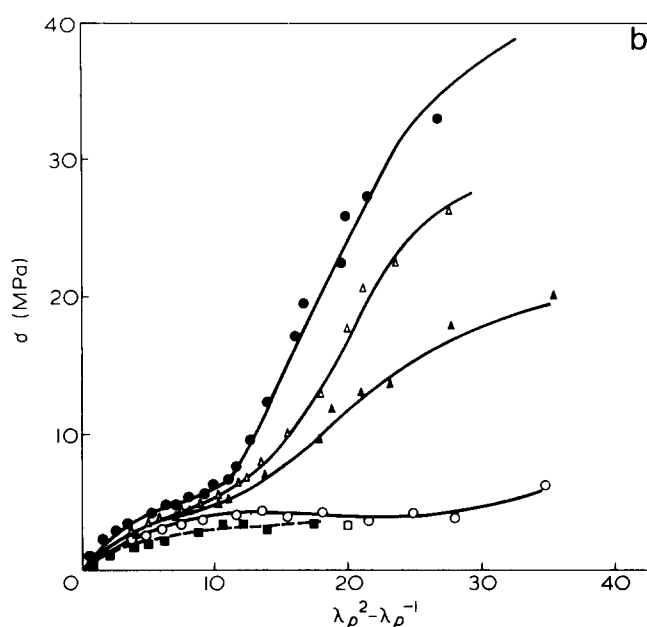


Figure 1 (b) Shrinkage stress σ versus the Gaussian parameter ($\lambda_p^2 - \lambda_p^{-1}$) plot for homogeneous drawing for specimens of different specific viscosities: ■, 0.60¹; ○, 0.61; ▲, 0.69; △, 0.75; ●, 0.78; the broken line corresponds to previous work¹

where \bar{n} is the mean refractive index of the polymer, $(\alpha_1 - \alpha_2)$ is the difference between the longitudinal and transverse polarizabilities associated with the random link, N is the number of elastically active chains per unit volume. In addition, the Gaussian model enables us to write the stress⁶ as: $\sigma = NkT(\lambda^2 - \lambda^{-1})$ and consequently derive the stress-optical coefficient $C = \frac{\Delta n}{\sigma}$.

Shrinkage stress measurement

When a deformation above the glass-transition temperature is frozen in by rapid cooling to the glassy state, the subsequent heating of the sample at constant length generates a shrinkage stress, which indicates the sample's potential recovery ability². The shape of the shrinkage stress *versus* time plot has already been discussed^{3,7,8}. Here, the shrinkage stress has been defined as the maximum stress recorded at a temperature just above the glass-transition temperature. The special equipment employed for the rapid heating is described elsewhere¹. The final temperature, 87°C, is reached in one minute.

RESULTS AND DISCUSSION

Homogeneous drawing: characterization of molecular parameters

Figures 1(a) and 1(b) show the birefringence Δn in the plane of the film, and the shrinkage stress (i.e. shrinkage force per unit cross-section) respectively, as a function of $\lambda_p^2 - \lambda_p^{-1}$, for the four viscosities studied. The measurements were conducted on samples quickly cooled previously under tension to room temperature to prevent any disorientation effect. We have also included on the same plots, the results obtained previously¹. Several comments can be made from these figures.

Firstly, the material previously studied and defined by a nominal viscosity of 0.85 has a surprising behaviour compared with the others. In fact, polymer processing for obtaining film can considerably alter the initial viscosity measured on pellets, which we call the nominal viscosity. Indeed, a measure on the film leads to a real viscosity of 0.60, more consistent with experimental results. Moreover, the classification in increasing viscosity order (Table 1) has been confirmed by glass-transition temperature measurements by differential scanning calorimetry at a constant heating rate. However this reflects the difficulty of quantitative comparison between sheets of different origins; in particular, some influence of molecular weight dispersity on mechanical response may be suspected.

Secondly, for the higher viscosities (0.75, 0.78) the birefringence Δn varies approximately linearly with the Gaussian parameter ($\lambda_p^2 - \lambda_p^{-1}$) which is very similar to the

behaviour of a physical network defined by permanent entanglement points. This has already been observed³ for a polymer of lower molecular weight, M_v of about 14 000. This difference is certainly connected with the difficulty of knowing precisely the real viscosity, as already noted in the previous section. For the lower viscosities some deviation from linearity appears at $\lambda_p=2$, which has been attributed to a possible progressive disentanglement, up to $\lambda_p=3.5$, followed by crystallization on stretching^{1,3}. Several papers^{2,9,10} have described the deformation of PET above the glass transition temperature as that of a rubber-like network. (In particular, a more refined investigation of the high-extension region¹⁰ has been performed with the assumption of a two-phase model, the birefringence being divided into amorphous and crystalline contributions. However, the study of the Gaussian behaviour region, $\lambda_p < 2$, leads simply to physical parameters characteristic of the assumed initial network structure. Our results (see Table 1) agree with a stress-optical coefficient approximately constant (independent of molecular weight) and the average molecular weight between consecutive entanglement points significantly decreases with increasing M_v . This latter observation is somewhat surprising far above the critical molecular weight¹¹, at least from a static configuration point of view. However, it can be noted that the variations with M_v are not quite regular, probably due in part to polydispersity effects, which implies that the qualitative interpretation only is valid here.

In the next part of this study, the material 'structure' achieved in the pre-orientation stage will be characterized essentially by the birefringence Δn_p .

Cold drawing: influence of the pre-orientation

Samples of various extension ratios λ_p (or variable birefringence Δn_p) were then deformed at room

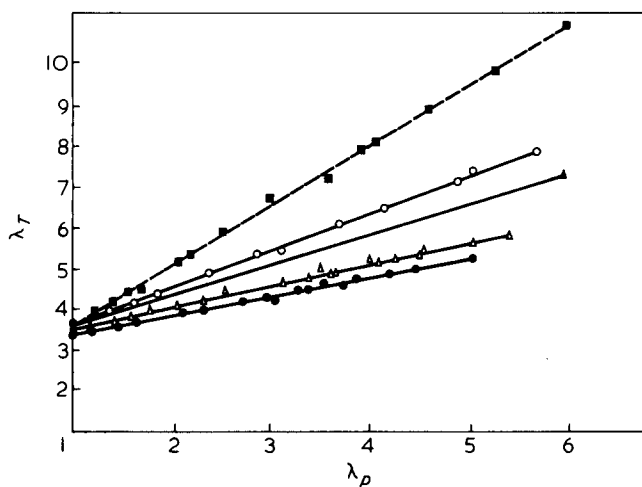


Figure 2 Total draw ratio λ_T , after the two-stage deformation process, as a function of pre-orientation draw ratio λ_p ; the broken line corresponds to previous work¹. ■, 0.60; ○, 0.61; ▲, 0.69; △, 0.75; ●, 0.78

temperature. After this second process the material is characterized by a total extension ratio λ_T given by $\lambda_T = \lambda_p \lambda_N$, and a total birefringence Δn . If we assume the additivity of hot and cold drawing birefringence contributions, Δn can be written as the sum of Δn_p and Δn_N respectively.

The influence of the pre-orientation has already been mentioned in several papers^{3,4,12}; the results led to an approximately constant maximum extensibility, which could be represented by the relation $\lambda_T = \lambda_p \lambda_N \approx 4$ for any value of λ_p . In that sense, the cold drawing of PET has been compared with the formation of a permanent network, the limiting behaviour of which is independent of the strain reached during the preceding hot drawing stage.

However, our results, which include larger values of λ_p , disagree with that assumption. From Figure 2, the variation of λ_T with λ_p can be fitted by an empirical linear relation of the form: $\lambda_T = a\lambda_p + b$, where a and b are constants for a defined viscosity. The natural draw ratio λ_N can then be described by $\lambda_N = a + \frac{b}{\lambda_p}$, the results of which are shown in Table 2. Independently of the mechanism which leads to rupture in the rubber-like deformation of PET, the existence of a limiting value for λ_p can be discussed from the numerical values of Table 2. As the lower value of λ_N which has a physical meaning is unity, this prescribes a finite limit for λ_p , except with the lower viscosity studied in a previous work¹. This fact is connected with the behaviour presented in the pre-orientation stage (Figure 1) where the occurrence of a permanent network is more evident when the molecular weight increases. Moreover,

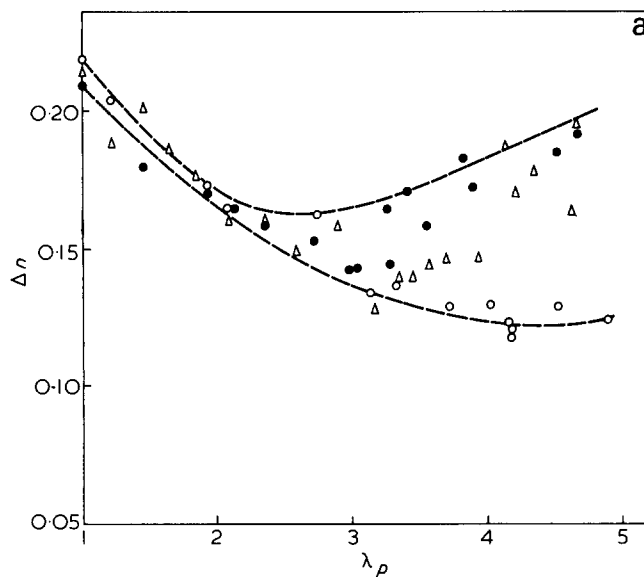


Figure 3 (a) Total birefringence Δn , after the two-stage deformation process, as a function of pre-orientation draw ratio λ_p . ○, 0.61; △, 0.75; ●, 0.78; the broken lines emphasize the differentiation in molecular weights for the higher pre-orientation draw ratios

Table 2 Natural draw ratio, λ_N , as a function of pre-orientation draw ratio λ_p : results computed from Figure 2

Viscosities (ml g ⁻¹)	0.60 ¹	0.61	0.69	0.75	0.78
λ_N	$1.5 + \frac{2}{\lambda_p}$	$0.9 + \frac{2.7}{\lambda_p}$	$0.75 + \frac{2.75}{\lambda_p}$	$0.53 + \frac{2.9}{\lambda_p}$	$0.47 + \frac{2.9}{\lambda_p}$

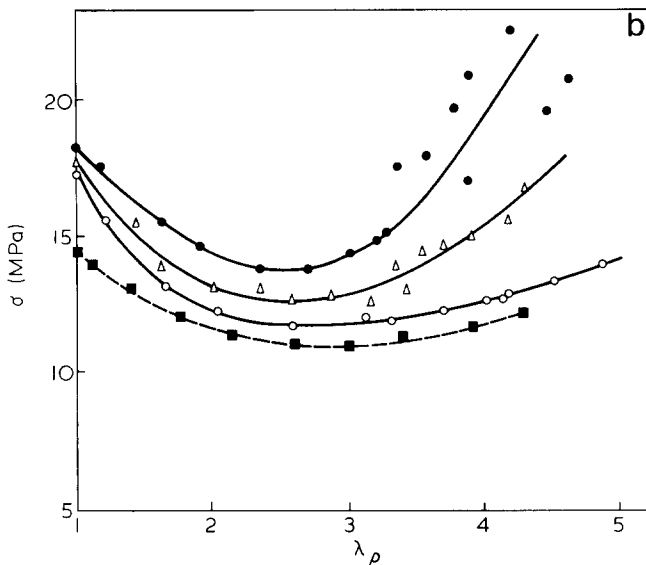


Figure 3 (b) Shrinkage stress σ , after the two stage deformation process, as a function of pre-orientation draw ratio λ_p . ■, 0.60¹; ○, 0.61; △, 0.75; ●, 0.78; the broken line corresponds to previous work¹

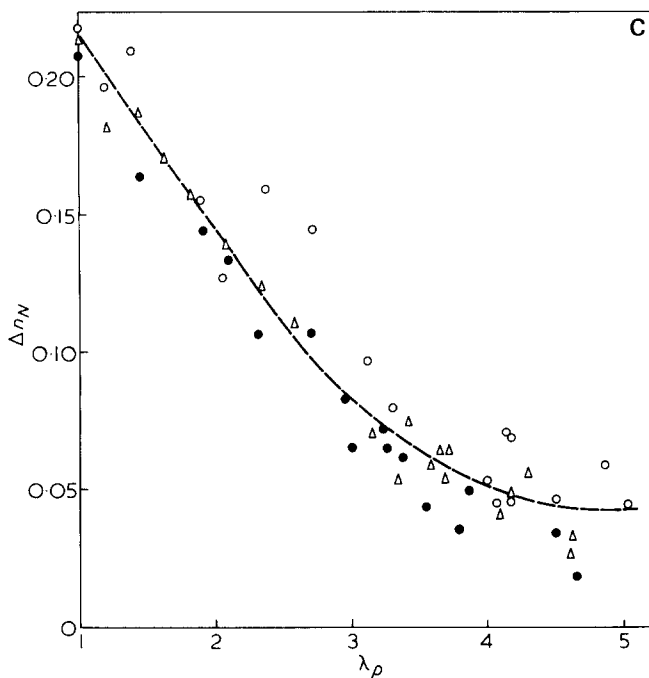


Figure 3 (c) Partial birefringence Δn_N , after the two stage deformation process, as a function of pre-orientation draw ratio λ_p . ○, 0.61; △, 0.75; ●, 0.78; the broken line marks the average variation

taking into account that the slope of the linear plot λ_T versus λ_p decreases with increasing M_v , it can be supposed that higher viscosity material should approach a constant maximum extensibility, corresponding to the hypothesis cited above (constant a equal to zero).

Figures 3(a) and 3(b) show that the total birefringence and shrinkage stress variations are essentially influenced by a first-stage process: above $\lambda_p = 2$, the curves are clearly differentiated with M_v . Consequently, the birefringence contribution Δn_N (Figure 3(c)), related to the cold-drawing stage, appears to be substantially insensitive to the molecular weight.

Since the macroscopic draw ratio, λ_p , can be achieved in several ways, an attempt to describe the deformation behaviour with a parameter more representative of molecular orientation is to use the birefringence Δn_p . The results (Figures 4(a), (b) and (c)) lead to average variations independent of M_v , drawn on the graphs as broken lines. Figure 4(d) represents the plot of the natural draw ratio λ_N versus birefringence Δn_p . This type of curve has been noted already for fibres of low orientation^{4,12,13}. Here, the validity of the relation is confirmed for higher degrees of orientation; the dependence on molecular weight appears only in the low pre-orientation region, because of the different upper limits of λ_N with M_v .

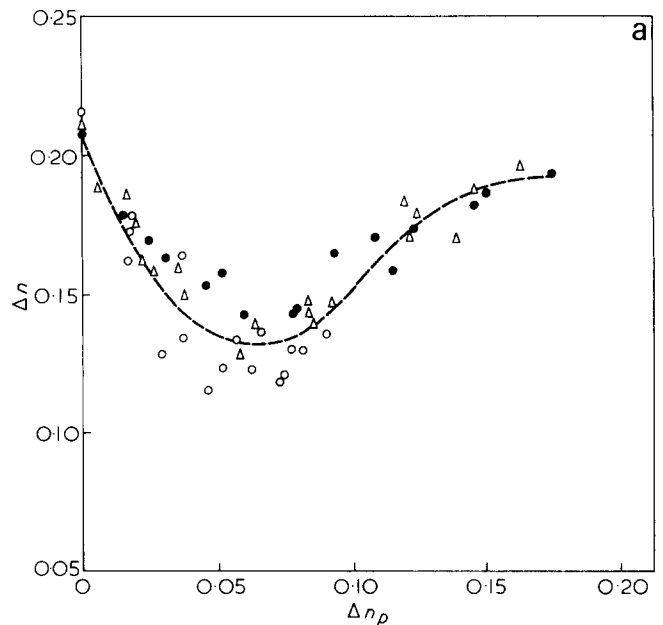


Figure 4 (a) Total birefringence Δn , after the two stage deformation process, as a function of pre-orientation birefringence Δn_p . ○, 0.61; △, 0.75; ●, 0.78; the broken line marks the average variation

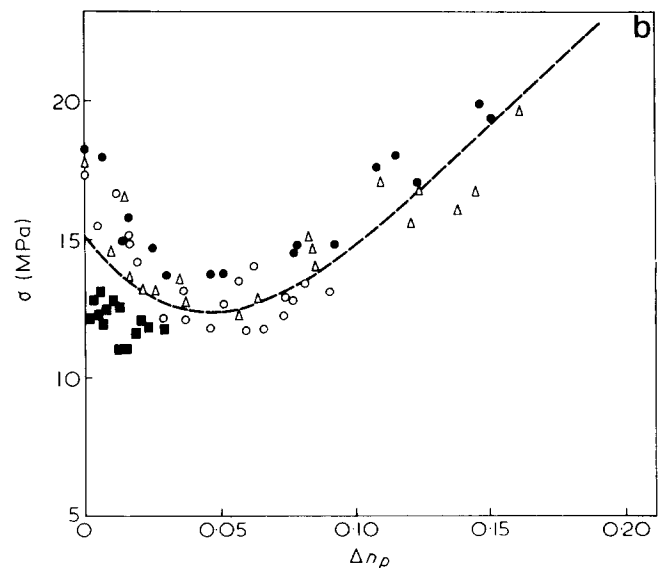


Figure 4 (b) Shrinkage stress σ , after the two stage deformation process, as a function of pre-orientation birefringence Δn_p . ■, 0.60¹; ○, 0.61; △, 0.75; ●, 0.78; the broken line marks the average variation

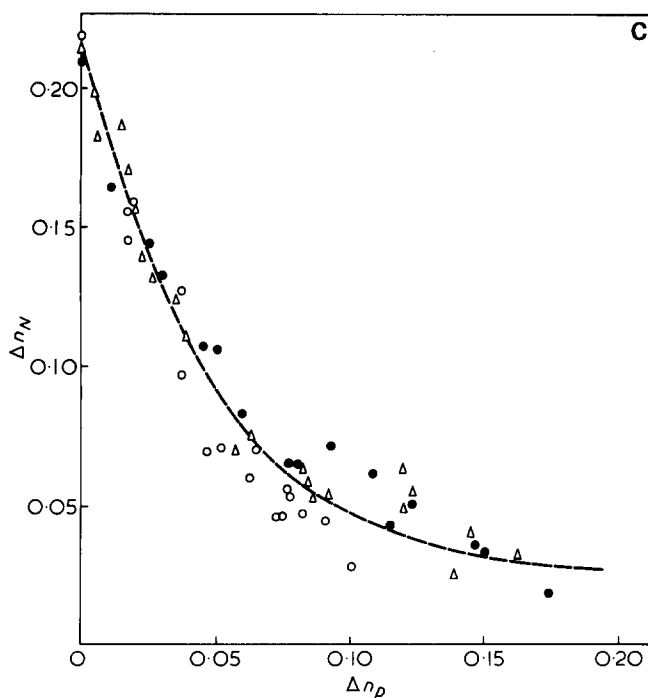


Figure 4 (c) Partial birefringence Δn_N , after the two stage deformation process, as a function of pre-orientation birefringence Δn_p . \circ , 0.61; \triangle , 0.75; \bullet , 0.78; the broken line marks the average variation

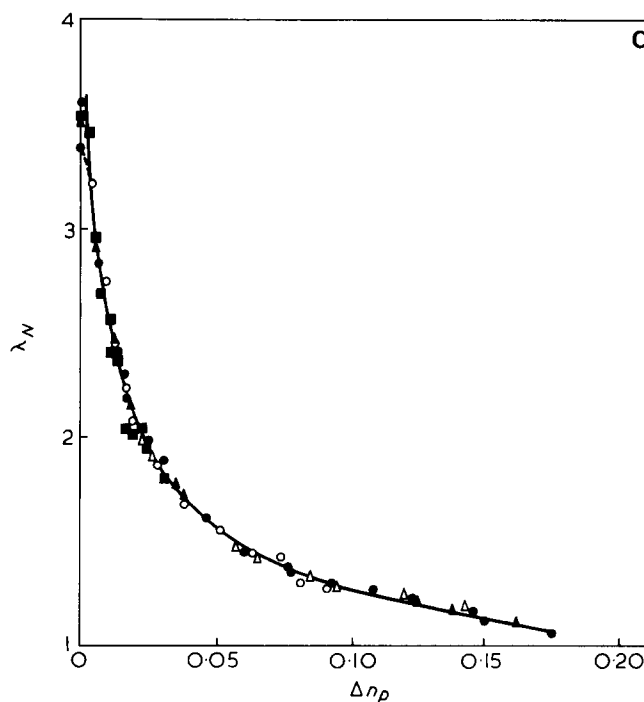


Figure 4 (d) Natural draw ratio λ_N , after the two stage deformation process, as a function of pre-orientation birefringence Δn_p . \blacksquare , 0.60; \circ , 0.61; \triangle , 0.75; \bullet , 0.78

Finally, the study of hot and cold drawing and their combination leads to principal conclusions summarized as follows:

(1) As already noted^{1,3,10}, the concept of a polymer network formed by entanglements of chains is consistent with the hot drawing of PET of various intrinsic viscosities, at least for moderate extensions.

(2) The natural draw ratio attainable in cold drawing can be modified by a pre-orientation, but, for low molecular weights the formation of a stable network is not obvious and the total extension increases linearly with the pre-orientation draw ratio.

(3) The birefringence achieved in hot drawing, instead of the deformation ratio λ_p , seems to be a good parameter to define the 'structure' of the pre-oriented material independently of the molecular weight. Concerning this final point, it would be interesting to confirm the existence of a unique relation between the natural draw ratio and the pre-orientation birefringence, for example by temperature and/or strain rate variations in hot stretching, to clarify the cold drawing mechanism and the

conditions of maximum extensibility variation for the occurrence of relatively high draw ratios.

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