Molecular mobility phenomena in oriented semicrystalline polymers. Electron paramagnetic resonance and mechanical analyses

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The drawing of semicrystalline polymers induces a wide structural rearrangement that affects the organization of the crystalline component and the properties of the amorphous phase. In particular, drawing strongly reduces mobility in the amorphous phase, and this is expected to play a role in the glass transition that is directly connected with mobility in the amorphous component. In agreement with this picture, the elastic modulus data and the electron paramagnetic resonance spectra indicate indirectly that T_g increases on increasing the degree of drawing. This effect depends quantitatively on differences in the degree of drawability of the various samples.

(Keywords: fibres; modulus; molecular mobility; glass transition)

INTRODUCTION

It is well known that molecular mobility in a bulk polymer depends not only on chain flexibility but also on supramolecular organization. In semicrystalline systems, segments of polymeric chains are frozen in the ordered phase, thus also reducing the mobility in the amorphous component. The reduced molecular mobility affects the physical properties that are related to it, among which is the glass transition temperature. Indeed, an increase in the crystalline content increases the glass transition temperature T_g and results in a broader transition range[1,2]. However, while the influence of crystallinity has been described, not much is known about the connection between T_g and system morphology. This connection is expected to be present as a consequence of the effects that different morphologies have on the amorphous phase.

Unidirectional cold drawing of a semicrystalline polymeric film is a typical case which has shown how different morphologies can affect the microstructure and thermodynamic state of the amorphous component[3,4]. Cold drawing changes the initial spherulitic morphology into the final microfibrillar morphology of the drawn sample; in such a process the free volume and mobility of the chains in the amorphous phase are drastically reduced. This effect is quite evident when the fibres are compared with undrawn samples using an experimental approach based on the analysis of the transport parameters. The results obtained are clearly indicative of reduced molecular mobility, at least at the room temperature at which the analysis was carried out[5-8].

On this basis we extended the study to a wide temperature range in order to obtain a wider picture of the relationships between drawing and molecular mobility. Our purpose was also to obtain experimental evidence, even if not directly, on the influence that cold drawing has on T_g. The systems investigated were low-density polyethylene (LDPE), high-density polyethylene (HDPE) and isotactic polypropylene (iPP), which were studied using the transport parameters as analytical tool[5-8]. For each system a wide deformation range was analysed. The experimental techniques were chosen after remembering that (in LDPE, HDPE and iPP) analysis of the glass transition requires thermal scanning in a range that excludes techniques such as analysis of the transport properties.

In particular, electron paramagnetic resonance (e.p.r.) spectra were detected on samples in which a stable radical probe was previously introduced. This analysis is a method for investigating how molecular mobility changes as a function of temperature, if different e.p.r. spectra are detected at different temperatures. Moreover, the e.p.r. data were compared with the mechanical behaviour analysed by detecting the elastic modulus as a function of temperature in the same temperature and drawing range.

The results obtained are discussed in light of the influence that cold drawing has on molecular mobility and morphology.

MATERIALS

LDPE, HDPE and iPP were RAPRA (Rubber and Plastics Research Association of Great Britain) products. The molecular weights were:

LDPE	$M_n = 24\,000$, $M_w = 215\,000$
HDPE	$M_n = 8000$, $M_w = 92\,000$
iPP	$M_n = 15\,600$, $M_w = 307\,000$

Film and fibre preparation

Films were prepared by compression moulding of pellets in a Carver laboratory press. The material was

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kept at the moulding temperature for 5 min under press load and then quenched at 0°C (water–ice bath). Films 0.4 mm thick were obtained.

Fibres were made by drawing dumbbell-shaped specimens from the films. The specimens were drawn using a dynamometer (Testometric 500 D of Daventest). The drawing rate was 1 min^{-1}. The drawing ratio λ ($\lambda = L/L_0$, actual over initial length) was determined by using ink marks on the samples. Only fibres having λ values homogeneous along all the sample were used for further analysis. This general procedure was followed to obtain LDPE, HDPE and iPP fibres, but moulding temperatures (m.t.) and drawing temperatures (d.t.) were different for the three different polymers:

LDPE	m.t. = 140°C, d.t. 25°C
HDPE	m.t. = 160°C, d.t. 60°C
iPP	m.t. = 200°C, d.t. 80°C

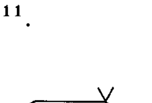
Under these conditions the maximum λ value obtained was 6, 18 and 11 for LDPE, HDPE and iPP respectively.

EXPERIMENTAL TECHNIQUES AND RESULTS

Paramagnetic probe method

The introduction of a stable radical into a polymeric matrix is a tool which permits one to obtain direct information on the mobility of polymer chains[9]. Analysis of the e.p.r. spectra of the polymer–radical system, and in particular the width of the spectral lines, gives a quantitative evaluation of the rotatory and translatory motions of the radical in the polymeric medium. In other words it gives an evaluation of the diffusion phenomena of the radical in the polymeric medium. It is well known[10] that the diffusion phenomena are directly connected with molecular mobility in the amorphous phase, and therefore the radical behaves as a probe sensitive to the molecular mobility of the medium. More specifically, the widening of the e.p.r. lines is determined by the correlation time τ_c, which is related to the rotary diffusion coefficient D_{rot} by $D_{rot} = 1/6\ \tau_c$. The quantity $\nu = 1/\tau_c$ is generally called the frequency of rotation of the radical; ν changes with temperature following an Arrhenius equation that gives the activation energy of the probe rotation, E_a[11]. Therefore, not only is τ_c related to mobility in the medium—and, if detected at different temperatures, it can be used to analyse how mobility changes with temperature T—but it also allows evaluation of the activation energy of the rotation phenomenon, which of course depends on the influence that the medium has on the probe motions[11].

Radicals



were employed as spin probes, the nitroxides being introduced into the polymers by absorption of its vapour at 30°C up to concentrations between 10^{-3} and 10^{-4} mol kg^{-1}.

The spectra were recorded on an X-band spectrometer RE-1306 (USSR). The 100 kHz modulation amplitude used did not exceed 0.2 mT and the microwave power was 0.5 mW.

The rotational correlation time τ_c in the rapid motion region ($5 \times 10^{-11} < \tau_c < 10^{-9}$) was calculated according to the equation:

$$\tau_c = 6.65 \times 10^{-10}[(I_+/I_-)^{1/2} - 1]\Delta H_+$$

where ΔH_+ is the linewidth in gauss of the low field[12].

In *Figures 1*, *2* and *3* we report the correlation time as a function of temperature for samples characterized by different λ values; *Figures 1* to *3* refer to LDPE, HDPE and iPP respectively. The e.p.r. spectra show that, at any given temperature, τ_c increases on increasing λ, as is to be expected for a fibre model in which the molecular mobility is reduced by the drawing process. In *Figure 4* we report τ_c as a function of λ at 25°C for the three different polymeric systems.

A second point regards the dependence of τ_c on temperature; the trend is a decrease in τ_c as the temperature increases, which indicates that rotational diffusion of the probe is easier at higher temperatures, and this result depends on the kinetic character of τ_c, as previously reported. Moreover, the slope of $\lg \tau_c$ vs. T depends on the temperature range. At low temperatures $\lg \tau_c$ vs. T for all samples at every λ value is linear up to a certain temperature, indicated as T_u. At temperature T_u a

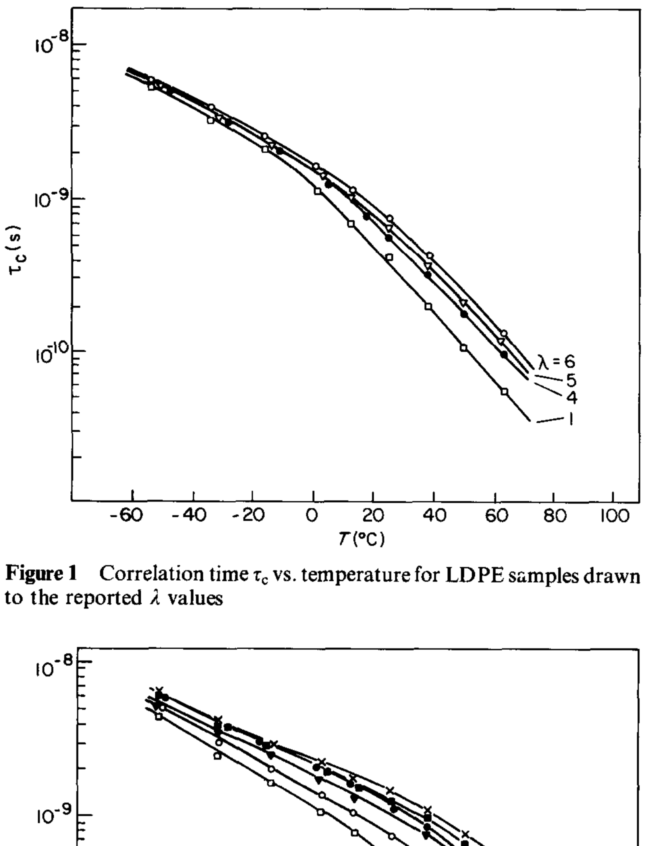


Figure 1 Correlation time τ_c vs. temperature for LDPE samples drawn to the reported λ values

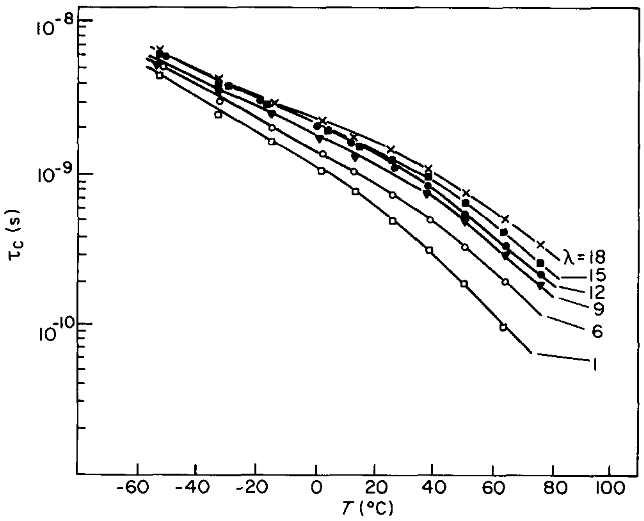


Figure 2 Correlation time τ_c vs. temperature for HDPE samples drawn to the reported λ values

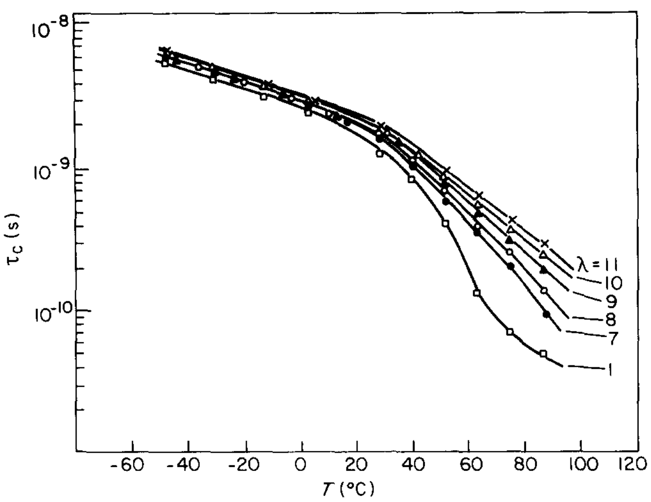


Figure 3 Correlation time τ_c vs. temperature for iPP samples drawn to the reported λ values

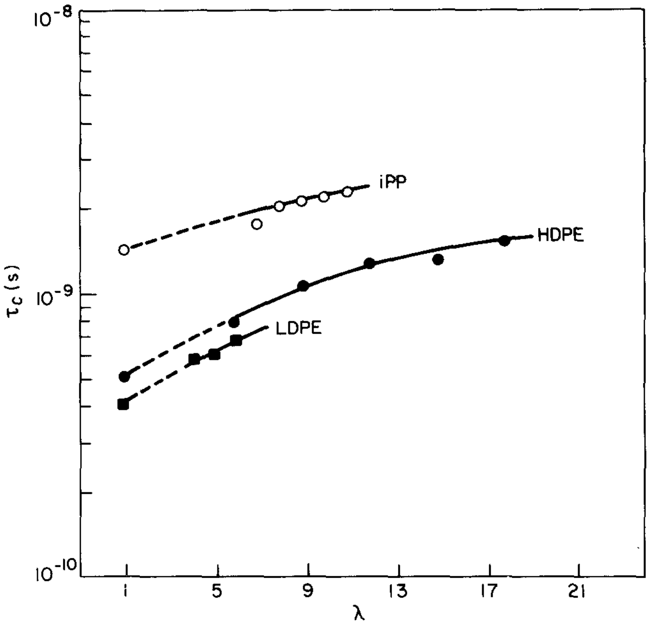


Figure 4 Correlation time τ_c detected at 25°C vs. degree of deformation λ for LDPE, HDPE and iPP

deviation from linearity occurs, giving rise, at higher temperatures, to a new dependence that can still be linear or weakly curved but is in all cases characterized by a higher slope of the function $\lg \tau_c$ vs. T. The change in derivative at the temperature T_u is indicative of a transition that in the literature is explained in terms of a transition from a frozen radical rotation to a condition in which the rotation becomes easier[13,14]. The transition temperature T_u (temperature of rotation unfreezing) is related to the glass transition T_g and can be equal to it, or higher or lower, depending on the nature of the polymeric system and the radical[9,13,14]. T_u, as previously defined (i.e. the temperature at which the deviation from linearity occurs) and as obtained from the data of *Figures 1* to *3*, is reported in *Figure 5* as a function of λ for the three polymeric systems. The general trend is an increase in T_u on increasing λ. It is important to point out another aspect, i.e. that the difference in slope between the low- and high-temperature ranges is indicative of a different activation energy E_a of rotational diffusion of the radical probe. The values of E_a can be derived by an Arrhenius plot of $\lg \tau_c$ vs. $1/T$. This analysis gives E_a in the low- and high-temperature ranges, approximating the weak curvatures to straight lines. The results are reported in *Table 1*. The error is ± 1 kJ mol^{-1} in the low-temperature range and ± 2 kJ mol^{-1} at high temperatures. *Table 1* shows a drastic increase in E_a on going from low to high temperatures; moreover, at a given temperature, E_a depends on λ, and decreases on increasing λ, with a dependence that is weak at low temperatures but significantly strong at high temperatures.

Elastic moduli

The axial elastic moduli were obtained as the slope of the stress–strain plots detected in a strain range within 1% of deformation; in this range the stress depends linearly on the strain, as is characteristic of an elastic trend. For each sample the modulus was detected as a function of temperature. The thermal scanning was carried out starting at −70°C, and the modulus was detected at intervals of 10°C.

The elastic modulus at different λ values is reported as a function of temperature in *Figures 6*, *7* and *8* for polymers

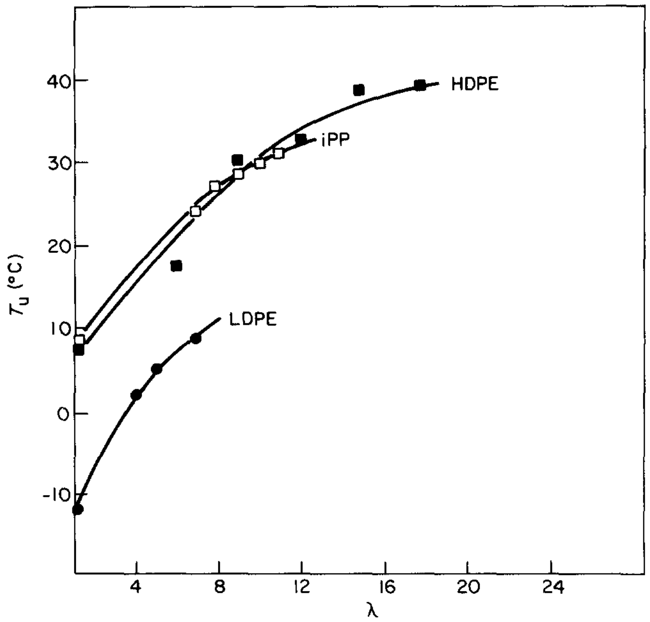


Figure 5 Temperature T_u as defined in the text vs. degree of deformation λ for LDPE, HDPE and iPP

Table 1 Activation energy of molecular probe rotation

Sample	Low-temperature E_a (kJ mol^{-1})	Higy-temperature E_a (kJ mol^{-1})
LDPE $\lambda=1$	9.0±1	45±2
$\lambda=4$	8.5	43
$\lambda=5$	8.0	42
$\lambda=6$	7.8	40
HDPE $\lambda=1$	11.8±1	43±2
$\lambda=6$	10.7	39
$\lambda=9$	10.3	36
$\lambda=12$	10.2	34
$\lambda=15$	10.1	33
$\lambda=18$	9.8	31
iPP $\lambda=1$	7.5±1	55±2
$\lambda=7$	7.5	47
$\lambda=8$	7.5	44
$\lambda=9$	7.0	41
$\lambda=10$	7.0	38
$\lambda=11$	7.0	36

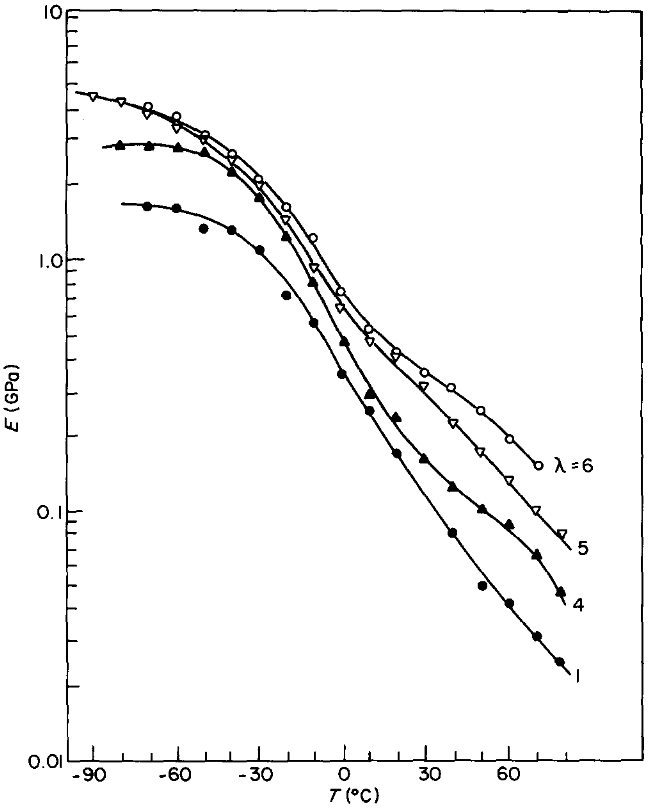


Figure 6 Elastic modulus vs. temperature for LDPE samples drawn to the reported λ values

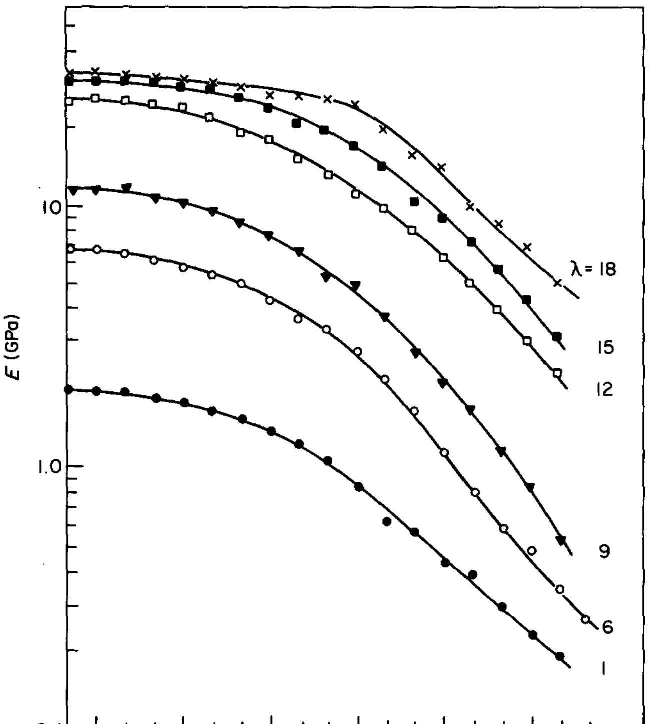


Figure 7 Elastic modulus vs. temperature for HDPE samples drawn to the reported λ values

LDPE, HDPE and iPP, respectively. For any given temperature, the modulus E increases on increasing λ, in agreement with results widely reported on this effect[15]. On the other hand, at each λ value, the elastic modulus decreases as the temperature increases; the slope $(\lg E)/T$ depends on the temperature range and is lower at lower temperatures. In some cases a transition between low- and high-temperature ranges can be identified, in particular when a sharp change in slope is localized over a few degrees (i.e. HDPE $\lambda=18$ or iPP $\lambda=11$). In other cases the slope changes with a continuous trend over a wide temperature range. In other words in a few cases a transition temperature can be identified; in other cases a transition range. Therefore we used an interpolation method as illustrated in *Figure 9* for the undrawn LDPE, HDPE and iPP samples; the interpolation allows one to describe the transition, calculating an average temperature interpolated in the transition range. The

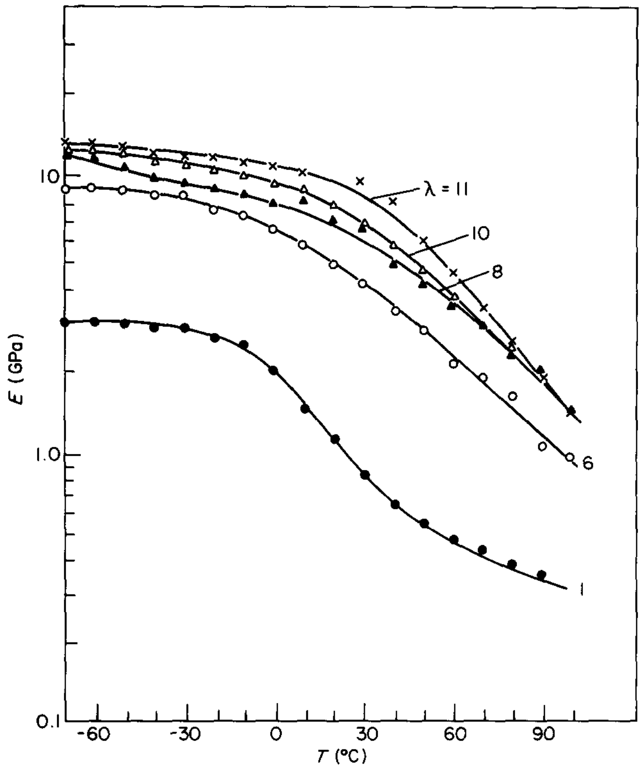


Figure 8 Elastic modulus vs. temperature for iPP samples drawn to the reported λ values

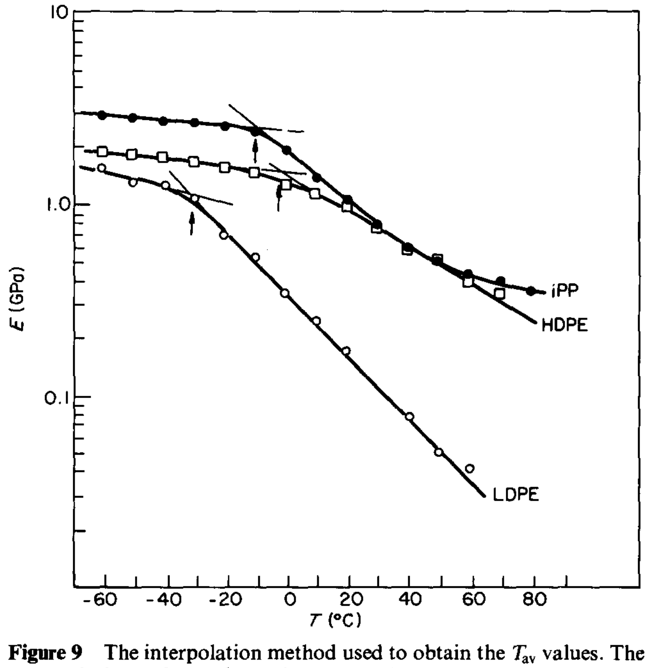


Figure 9 The interpolation method used to obtain the T_{av} values. The reported plots refer to the undrawn samples

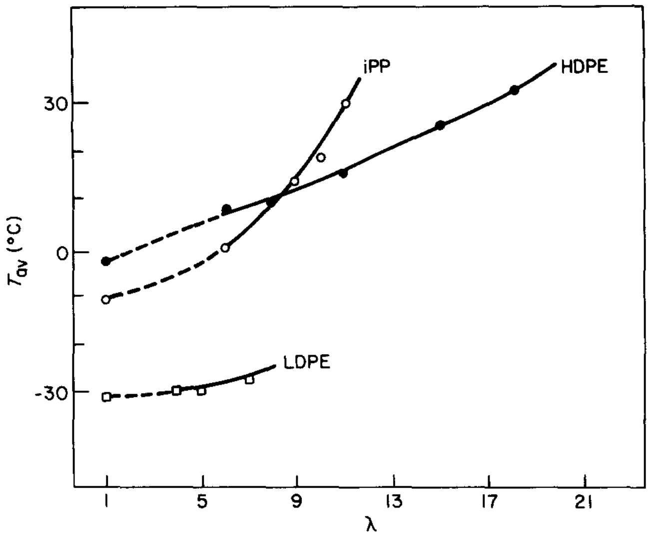


Figure 10 T_{av} values vs. degree of deformation λ for LDPE, HDPE and iPP samples

values thus obtained, indicated as T_{av}, are reported in *Figure 10* as a function of λ for the three different polymers.

DISCUSSION

The drawing of a semicrystalline polymer induces a wide and deep morphological rearrangement, and the initial spherulitic morphology is transformed into the final microfibrillar organization. A molecular model of the morphological transition explains features of the fibre structure such as the high anisotropy of the physical properties and the high elastic modulus[16]. The drawing generates blocks of folded chains as fragments of the initial structure; these blocks are displayed along the stretching direction generating the new morphological units, the microfibrils, that are characterized by an alternating sequence of crystalline and amorphous layers. The molecules which axially connect different crystalline blocks of the same or different microfibrils (tie molecules) become more and more taut as the degree of drawing increases[16]. The number and the tautness of such molecules (taut tie molecules, TTM) are responsible for the high axial modulus and induce drastic constraints on the interfibrillar amorphous layers. This effect reduces the free volume and, as a consequence, molecular mobility in the amorphous phase. The results obtained by analysing the transport properties of drawn samples strongly support this last point, and further support is provided by the e.p.r. data reported in this paper. The trend in τ_c vs. λ observed at 25°C and reported in *Figure 4* clearly indicates that the rotational diffusivity, that is $1/6\tau_c$, decreases on increasing λ. Considering that the radical probe diffuses in the amorphous component, the reduced mobility of the probe is the consequence of a reduced mobility of the chains in the amorphous phase. The influence of λ on probe rotation is present not only at 25°C but, as shown in *Figures 1* to *3*, in all the temperature range; however, the dependence of τ_c on λ appears more attenuated at low temperatures. The latter observation can be explained if we consider that at low temperatures the molecular mobility is so low as to reduce the effects of different λ values.

This picture agrees well with the E_a data reported in *Table 1*, where it is evident that E_a is a weak function of λ at low temperatures, while the dependence becomes more evident at high temperatures, where E_a decreases significantly as λ increases. In the fibres the reduced molecular mobility allows only motions of reduced dimensional scale, in such a way inducing a decrease in E_a. It is not surprising, therefore, that the effect of λ on E_a is less evident at low temperatures where the system is frozen and the dimensional scale of the motions reduced for thermodynamic reasons. The substantial difference observed in E_a on going from low to high temperature ranges can be discussed on the same basis: E_a at high temperatures is many times larger as a consequence of the greatly different dimensional scale of the molecular motions. It is important to point out once again that rotation of the probe is affected by the motions of the medium, and a higher activation energy of chain motion induces a higher activation energy of probe rotation. Therefore, a higher E_a is indicative of large-scale molecular motions activated by a higher energy. In this sense T_u, which separates temperature ranges characterized by different E_a values, can be considered as the temperature transition from a system characterized by a small and local mobility to a system in which long molecular sequences can move. Therefore T_u is not a T_g, as previously pointed out, but is directly and closely related to it[13,14]. *Figure 5*, which shows an increase in T_u on increasing λ, is indirectly indicative of an increase in T_g as the degree of drawing increases. The modulus data can be discussed taking into account the indication given by the e.p.r. results; the modulus trend reported in *Figures 6* to *8* partially reflects the increase in mobility on increasing the temperature, as clearly indicated by the τ_c values. The increased mobility activates relaxation phenomena that, by reducing the modulus of the amorphous component, affect the axial modulus of the fibre. Of couse the softening of the amorphous component is not the only process responsible for a modulus decrease, because, as is well known, phenomena occurring at the amorphous–crystalline interphase also play a role on the modulus value[1]. However, these phenomena become operative at temperatures higher than the range in which T_{av} values were interpolated; in this sense T_{av} separates two zones characterized by a different mobility in the amorphous component. Therefore, just like T_u, T_{av} is not a T_g, but is related to it. In particular, considering the interpolation method used to obtain T_{av}, with some approximation it can be connected to an average point of a transition range. Thus, the data of *Figure 10*, showing an increase in T_{av} on increasing λ, are indirectly indicative of an increase in T_g as the drawing degree increases. The T_{av} trend obtained does not disagree with the T_u data, particularly if the different experimental approach is considered. This result confirms the observations found when analysing the dynamic mechanical spectra of drawn iPP (ref. 17), which show an increase in the glass transition on increasing λ, in quantitative agreement with the T_{av} data in *Figure 10*. Moreover, *Figure10* seems to suggest that the observed effect is related to the degree of drawing that can be achieved. The relative increase in T_{av}, induced by drawing up to $\lambda = 6$ in LDPE, does not differ significantly from the increase induced in iPP by the same drawing, and only the possibility of achieving larger λ values allows one to induce a larger effect in iPP and HDPE. A similar trend was found in reporting, as a function of λ, the transport parameters obtained on drawn samples of different polymeric systems[18].

CONCLUSIONS

The T_u and T_{av} values obtained respectively from the e.p.r. spectra and the elastic modulus data can be qualitatively correlated to the glass transition temperature. The results reported seem indirectly to indicate that the glass transition in oriented semicrystalline systems increases on increasing the degree of drawing.

This evidence agrees well with a fibre model in which the molecular mobility in the amorphous component is strongly reduced by the action that the TTM exerts on interfibrillar amorphous layers.

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