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Polymorphism and mechanical properties of syndiotactic polystyrene films

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Abstract

The dynamic–mechanical behaviour and the tensile moduli of unstretched and stretched semicrystalline s-PS films, presenting different polymorphic forms (α, γ, δ and clathrate) but similar crystallinity and orientation, have been compared. The main aim is to elucidate the possible influence of different crystalline phases, being largely different in chain conformation and density, on mechanical properties of s-PS semicrystalline samples. For unstretched films presenting a preferential perpendicular orientation of the chain axes, the highest elastic modulus is observed for films with the high density γ phase while for uniaxially oriented films the highest modulus is observed for films with the trans-planar α phase. As for the clathrate films, the guest molecules when only included into the crystalline clathrate phase, have no plasticizing effect.

Keywords: Syndiotactic polystyrene; Polymorphism; Mechanical properties

1. Introduction

A precise knowledge of the physical properties (mechanical, thermal, electrical, solvent resistance, etc.) of the different polymorphic forms of a given polymeric material can be advantageously used for possible applications [1].

In particular, as for mechanical properties, it is well known that different polymorphic forms can present largely different crystallite moduli. Differences between crystallite moduli along the chain axes have been generally evaluated by measurements on oriented semicrystalline fibers [2] and often well compare with values calculated with simple molecular mechanics methods [3]. Moreover, it has been well established that substantial variations of crystallite moduli along the chain axes are mainly due to large variations in the chain conformations [4].

Syndiotactic polystyrene (s-PS) presents a very complex polymorphic behavior [5,6] and, making some simplification, four different crystalline forms have been described. By melt crystallization procedures both high melting α [7] and β [8] forms, which include trans-planar chains, can be obtained. By solution crystallization procedures, besides the β form, the thermally unstable γ [9] and δ [10] forms as well as several clathrate [11] forms, all including s(2/1)2 helical chains, can be obtained. Besides the crystalline and clathrate forms, two mesomorphic forms, containing trans-planar [12] or s(2/1)2 helical [13] chains have also been described.

The s-PS crystalline phases are largely different as for their densities. In fact, densities differences of the γ (1.10 g/cm^3), β (1.078 g/cm^3), α (1.034 g/cm^3) and δ (0.977 g/cm^3) phases with respect to the amorphous phase (1.05 g/cm^3), are of nearly +5, +2.5, −1.5 and −7%, respectively. The unusual strong reduction of density of the δ crystalline phase with respect to amorphous phase is due to the presence of well characterized crystalline cavities [10a,c].

These large density differences generate a completely different behaviour as for sorption of low molecular mass compounds. In fact, the high density trans-planar β-phase presents an extremely high solvent resistance with respect to the other crystalline phases [14,15a], which when exposed to several molecules, being suitable guests, can be transformed into clathrate phases[14,15a]. On the other hand, the lowest density nanoporous δ-phase is able to absorb efficiently a high number of guest molecules also when present in traces [15a,b,d,j,k,16]. In fact, δ form samples appear to be relevant for possible applications in molecular separations [15] and molecular sensors [16]. It is also worth adding that suitable clathrate phases can be relevant for optical applications (e.g. optical recording and fluorescent materials) [17].

The main aim of this paper is to elucidate if the formation of different crystalline phases, being largely different in chain conformation and density, can have a significant influence on mechanical properties of s-PS semicrystalline samples.

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Several papers dealing with the dynamical-mechanical behaviour of s-PS samples have been reported in the literature [18]. Two of them compare the behaviours of quenched amorphous and melt crystallized samples [18a,d]. A paper of de Candia et al. compares the dynamical mechanical behaviour of films crystallized by several different solvents and shows effects of phase transitions and solvent release on the relaxation phenomena [18c].

As for the tensile moduli, some data have been reported only for amorphous and semicrystalline films presenting the α crystalline phase. In particular, large differences have been observed above T_g by dynamical mechanical data and stress-strain tests, for α-form samples presenting different crystallinity and morphology [19].

In this work, we compare dynamic-mechanical behaviour and tensile modulus of unstretched and stretched amorphous and semicrystalline s-PS films presenting different polymorphic forms (α, γ, δ and clathrate).

As for the clathrate films, we have considered those including 1,2-dichloroethane (DCE), as low molecular mass guest. This guest choice was motivated by the additional information, which comes from its conformational equilibrium. In fact, as described in detail in previous papers [15b,c], essentially only the DCE trans conformer is included into the clathrate phase while both trans and gauche conformers are included in the amorphous phase. Hence, from quantitative evaluations of vibrational peaks associated with these conformers it is possible to evaluate the amounts of DCE confined as guest in the clathrate phase or simply absorbed in the amorphous phase.

In order to have a meaningful comparison between different crystalline phases, films with similar degrees of crystallinity and presenting a same kind and similar degree of crystalline phase orientation have been selected. Moreover, to minimize the morphological changes, all the considered films have been obtained by different treatments of s-PS/DCE clathrate films.

2. Experimental section

The s-PS used in this study was manufactured by Dow Chemical Company under the trademark Questra 101. ^{13}C nuclear magnetic resonance characterization showed that the content of syndiotactic triads was over 98%. The weight-average molar mass obtained by gel permeation chromatography (GPC) in trichlorobenzene at 135 °C was found to be $M_w = 3.2\times10^5$ with the polydispersity index, $M_w/M_n = 3.9$.

Amorphous films nearly 100 μm thick were prepared by compression molding: the s-PS pellets were melted at 300 °C under a press at 10 MPa and immediately quenched in ice-water.

Stretched films were prepared by uniaxial drawing of amorphous s-PS films at draw ratio $\lambda = 3.3$, at strain rate of 10/min, in the temperature range 105–110 °C with a dynamometer INSTRON 4301.

Clathrate films including 1,2-dichloroethane (DCE) guest molecules have been prepared by exposition of amorphous unstretched and stretched s-PS films to vapors of the pure organic compound for three days at room temperature.

The content of DCE in clathrate films was determined by thermogravimetric measurements (TGA): it was nearly 20 and 8 wt% after 1 h and 1 week of DCE desorption at room temperature, respectively. Conformational [15b,c] and dichroism [20] analyses based on FTIR measurements (not reported) have shown that, for the lower concentration, most DCE molecules are included as guest in the crystalline phase while, for the higher concentration, DCE molecules are included in both amorphous (42%) and crystalline (58%) phases.

The films presenting different polymorphic forms of s-PS, which have compared in our study, have been all obtained by crystal-crystal transition on unstretched or stretched films presenting the s-PS/DCE clathrate phase. In particular, δ semicrystalline films were obtained by extraction procedures from DCE clathrate films by CO_2 at 40 °C and 200 bar for 5 h [10b], while γ and α semicrystalline films were obtained from DCE clathrate films, by increasing the temperature (∼2 °C/min) from room temperature up to 160 and 220 °C, respectively, and then maintaining the samples at that temperature for 30 min [5]. These procedures were aimed to minimize the morphology changes between the compared films. In this respect, it is worth adding, that the morphology of the stretched and unstretched films are fibrillar [21] and microspherulitic [22], respectively.

Films presenting the β phase have been not considered in our analysis since they can be obtained from the starting films only by procedures, which are expected to substantially change the polymeric morphology. In fact, β form films can be obtained from s-PS/DCE films [5a] or from the γ-phase film [23] by abrupt annealing at high temperatures (above 150 °C and above 210 °C, respectively) but only for highly swollen samples.

The degree of crystallinity has been evalued by the Fourier transform infrared (FTIR) spectral subtraction procedure described in Ref. [24]. FTIR spectra were obtained with a Brucker Vector 22 spectrophotometer. The wavenumber range scanned was 400–4000 cm^{-1} at resolution of 2 cm^{-1}.

Wide-angle X-ray diffraction patterns with nichel-filtered Cu K_α radiation were obtained by using a Bruker powder diffractometer.

The degree of crystalline phase orientation for uniaxially stretched films have been evaluated by using the Herman's orientation function and the standard X-ray diffraction method [25].

As for the kind and degree of crystalline phase orientation of the unstretched semicrystalline films, whose crystallinity has been solvent induced, the method described in Refs. [9b,26] has been applied. In particular, the degree of perpendicular orientation has been defined, as $f_{c,perp}$ ($f_{c,perp} = 0$ corresponds to absence of orientation while $f_{c,perp} = 1$ corresponds to all crystallites with preferential perpendicular orientation of their chain axes with respect to the film plane).

Tensile tests were carried out at room temperature, using a dynamometer INSTRON 4301 at a strain rate of 10/min and at a grip-to-grip distance of 20 mm. Elastic modulus was measured from initial force-elongation response. The maximum strain used in this procedure was 2%.

Dynamic-mechanical properties were studied using a rheometric dynamic mechanical thermal analyzer. The spectra were recorded in the tensile mode, obtaining the modulus E', and the loss factor, tan δ, at a frequency of 1 Hz, as a function of temperature. The heating rate was 5 °C/min in the range of −50, +250 °C. Mechanical and dynamical-mechanical properties for stretched samples were measured for directions both parallel and perpendicular to the drawing direction.

3. Results and discussion

3.1. Unstreched films

The X-ray diffraction patterns collected by an automatic powder diffractometer, of the starting compression molded film (A), then exposed to DCE vapours (B) and successively treated by CO_2 at 40 °C (C) and annealed at 160 °C (D) and at 220 °C (E) are reported in Fig. 1.

The pattern of Fig. 1(A) shows the two typical very broad amorphous s-PS halos centred at $2\theta = 9.8°$ and $2\theta = 19.4°$.

The pattern of Fig. 1(B) shows that the DCE treated film has been crystallized in the s-PS/DCE clathrate phase ($a = 17.11$ Å, $b = 12.17$ Å, $c = 7.7$ Å and $\gamma = 120°$) [11c].

The pattern of Fig. 1(C) shows that the CO_2 extracted clathrate film presents the monoclinic δ phase ($a = 17.4$ Å, $b = 11.85$ Å, $c = 7.7$ Å and $\gamma = 117°$) [10], as usual for these kinds of treatments [10b].

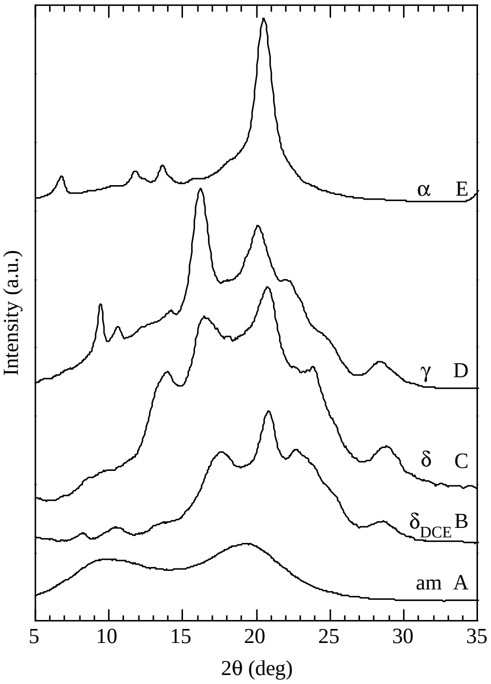

Fig. 1. X-ray diffractions patterns obtained by an automatic powder diffractometer of the starting compression molded film (amorphous, A) and of semicrystalline films obtained by successive treatments: exposition to DCE vapours (DCE clathrate, B) and extraction by CO_2 at 40 °C (δ phase, C), and annealing at 160 °C (γ phase, D) and annealing at 220 °C (α phase, E).

The pattern of Fig. 1(D) and (E) show the presence of the orthorhombic γ phase ($a = 19.15$ Å, $b = 17.0$ Å and $c = 7.7$ Å) [9] and of the hexagonal α phase ($a = 26.26$ Å, $b = 5.04$ Å and $c = 5.1$ Å) [8], as usual for slow thermal treatments at low and high temperatures [5], respectively.

As discussed in detail in Ref. [26b], s-PS films whose crystallization is induced by solvents, which are suitable as guests of s-PS clathrate phases, generally present a preferential perpendicular orientation of the chain axes with respect to the film plane. In particular, as for the films whose X-ray diffraction patterns are shown in (Fig. 1(B)–(E)), the degree of perpendicular orientation has been evaluated close to $f_{c,perp} = 0.55$. Moreover for all these films the degree of crystallinity is close to 40%.

Dynamic-mechanical scans of s-PS films with different polymorphic phases are shown in Fig. 2, as log E' and tan δ vs. the temperature.

For all samples, a wide and intense maximum of the loss factor (tan δ), corresponding to a relevant modulus decrease, clearly points out the glass transition temperature (T_g). The maxima of the tan δ peaks have been assumed as T_g and collected in Table 1.

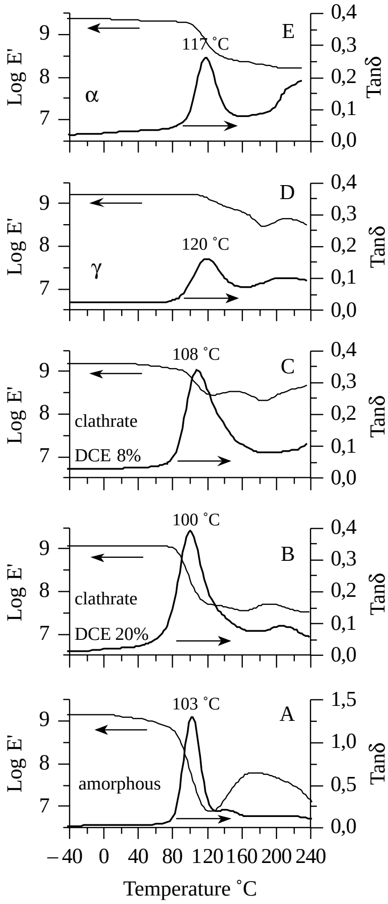

Fig. 2. Log E' and tan δ vs. the temperature, for the starting compression molded film (amorphous, A) and for semicrystalline films obtained by successive treatments: exposition to DCE vapours (clathrate DCE 20%, B; clathrate DCE 8%, C), annealing at 160 °C (γ phase, D) and annealing at 220 °C (α phase, E).

Table 1
Elastic modulus and T_g of unstretched s-PS films

Sample	Modulus (MPa)	T_g (°C)
Amorphous	1300 ± 80	103
Clathrate, DCE 20%	1120 ± 40	100
Clathrate, DCE 8%	1587 ± 30	108
δ	1529 ± 60	108
γ	1653 ± 60	120
α	1530 ± 50	117

Of course, the decrease of modulus at T_g is particularly large for the amorphous sample (Fig. 2(A)) (more than two orders of magnitude) as well as for the clathrate sample including DCE in both crystalline and amorphous phases (less than two orders of magnitude) (Fig. 2(B)). For all the other semicrystalline films (Fig. 2(C)–(E)) the decrease of modulus is close to one order of magnitude.

The dynamic–mechanical spectrum of amorphous s-PS (Fig. 2(A)) shows, above the glass transition, an increase in modulus that is caused by crystallization of metastable quenched amorphous material into the α phase [8].

The dynamic–mechanical spectrum of semicrystalline films with α phase (Fig. 2(E)) is very simple, showing only glass transition (markedly shifted at higher temperature with respect to the amorphous sample) and premelting and melting phenomena (above 210 °C) [18].

The dynamic–mechanical behaviour of semicrystalline films with γ phase (Fig. 2(D)) shows, beside the modulus decrease in the temperature range 120–165 °C associated with the glass transition, a steeper modulus decrease in the temperature range 165/185 °C, followed by a modulus increase up to 210 °C. The available knowledge relative to the polymorphic behavior of s-PS [5,6,13,27] allows attributing the steeper modulus decrease to melting of the γ form and the successive modulus increase to crystallization in the α form.

The dynamic–mechanical behaviour of semicrystalline samples with DCE clathrate phase (Fig. 2(C) and (D)), as well as for the semicrystalline sample with δ phase (not reported), show T_g which are close to that one observed for amorphous samples and two modulus maxima in the temperature ranges 125–150 °C and 180–220 °C. These maxima, according to previous studies of the s-PS polymorphic behavior (Fig. 4 of Ref. [13] or Ref. [27]), can be attributed to the clathrate (or δ) → γ and γ → α transitions, respectively (for additional information relative to interpretation of the dynamic-mechanical spectra, see also Section 3.2).

Values of elastic moduli are obtained by dynamic mechanical analyses like those of Fig. 2. However, more accurate room temperature values of tensile moduli, have been achieved by specific tensile measurements (average of 5–10 tests), and have been reported in Table 1.

The elastic moduli and T_g reported in Table 1 clearly show an increase of stiffness as a consequence of crystallization. In particular, for the considered samples with similar degree of crystallinity as well as with a same kind and similar degree of orientation, the stiffness is similar for films presenting trans-planar and helical crystalline phases, being significantly higher only for the γ form film. In this respect, it is worth noting that, since the crystallite chain axes are preferentially perpendicular to the film plane and hence to the tensile stresses, the crystalline phase moduli perpendicular to the chain axes are expected to be more relevant to the macroscopic behaviour than those parallel to the chain axes. Hence, it is not surprising that the highest modulus has been obtained for the highest density γ crystalline phase. It is worth adding that the higher stiffness of the γ form film could be in part associated with the higher constraint of amorphous domains, as suggested by the higher T_g value (Table 1).

As far as the clathrate films are concerned, it is worth noting that the DCE molecules, when only included as guest into the crystalline clathrate phase, have no plasticizing effect. In fact, the clathrate films with a DCE content close to 8% presents a modulus comparable to, and even higher than, δ and α form films. On the other hand, DCE molecules when also included in the amorphous phase have a relevant plasticizing effect. In fact, clathrate films including 20 wt% of DCE (nearly 11.5% in the crystalline phase and 8.5% in the amorphous phase) have elastic modulus markedly lower than for the other semicrystalline films and also lower than for the amorphous films.

3.2. Stretched films

To get additional information on the influence of polymorphism on mechanical properties of s-PS, dynamic-mechanical and tensile tests were also conducted on uniaxially stretched films.

X-ray diffraction patterns, collected by an automatic powder diffractometer, of samples obtained by uniaxial stretching of amorphous films of s-PS (trans-planar mesomorphic phase, A) followed by exposition to DCE vapors (clathrate phase, B), by guest removal by CO_2 (δ phase, C), by annealing at 160 °C (γ phase, D) and at 220 °C (α phase, E) are reported in Fig. 3.

The occurrence of strong molecular orientation is clearly pointed out by the substantial variation of the reflection intensities with respect to the unstretched samples of Fig. 1. The orientation of the crystalline phase in these samples is characterized by a high degree of parallelism of the chain axes with respect to the stretching direction. The degree of crystallinity and the degree of axial orientation are similar for all the considered films, being close to $x_c \sim 0.38$ and $f_c \sim 0.93$, respectively.

The dynamic–mechanical behaviour of the stretched films shows phenomena analogous to those observed for unstretched films (Fig. 2), although the transitions become more clearly apparent. This is shown for instance in Fig. 4, where the dynamic-mechanical behaviour of a semicrystalline stretched film including DCE only in crystalline phase (7 wt%) is reported for tensile test directions parallel (Fig. 4(A)) and perpendicular (Fig. 4(B)) to the drawing direction.

The observed behavior can be easily rationalized on the basis of previous IR and X-ray diffractions data, which have shown that above T_g, clathrate and δ phases are firstly disordered, leading to a helical mesomorphic phase (meso^h), which in turn only at higher temperatures is reorganized into

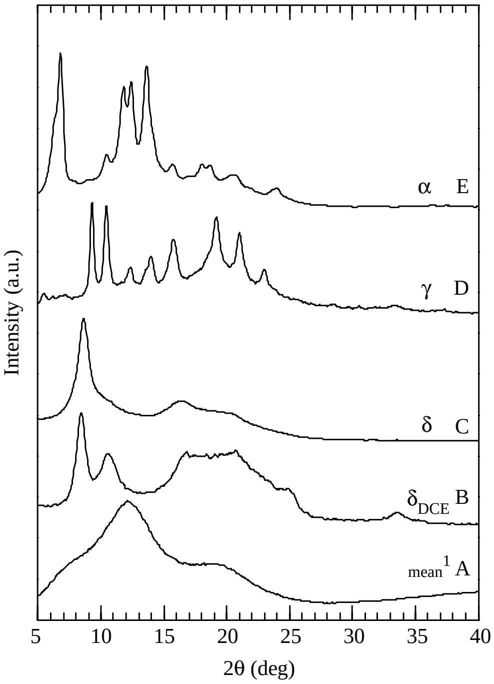

Fig. 3. X-ray diffraction patterns obtained by an automatic powder diffractometer of the compression molded films after successive treatments producing different crystalline phases: uniaxial stretching (mesomorphic trans-planar, A) followed by exposition to DCE vapors (clathrate phase, B), by guest removal by CO_2 (δ phase, C), by annealing at 160 °C (γ phase, D) and annealing at 220 °C (α phase, E).

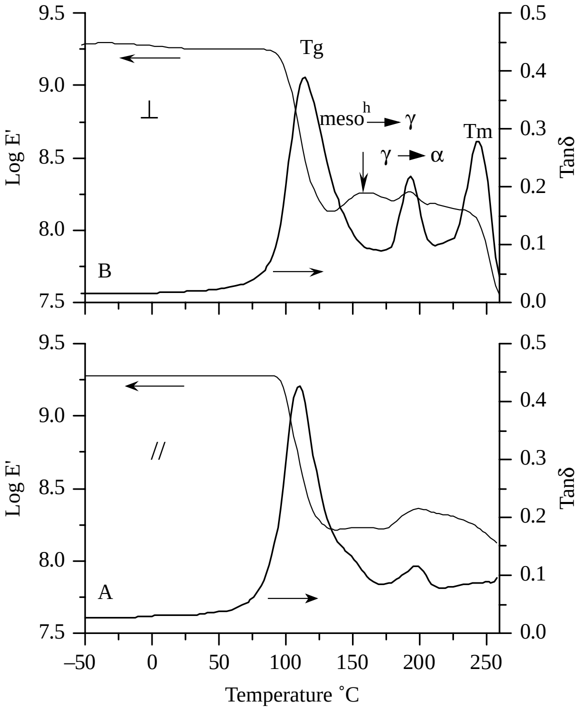

Fig. 4. Log E' and tan δ vs. the temperature, for a clathrate stretched film including DCE only in crystalline phase (7 wt%) for tensile test directions parallel (A) and perpendicular (B) to the drawing direction. The nature of the phase transitions has been explicitly indicated by labels close to modulus and tan δ peaks, in part B.

Table 2
Elastic moduli of stretched s-PS films

Sample	Modulus (MPa) test ‖	Modulus (MPa) test ⊥
Amorphous	2400 ± 200	1300 ± 60
Clathrate, DCE 19%	1780 ± 40	1320 ± 60
Clathrate, DCE 7%	2759 ± 60	1360 ± 40
δ	2714 ± 40	1200 ± 80
γ	2650 ± 100	1250 ± 60
α	3200 ± 100	1250 ± 50

the dense γ phase [13]. On this basis, the nature of the phase transitions has been explicitly indicated by labels close to the modulus and tan δ peaks in Fig. 4(B).

The elastic moduli obtained by tensile tests on uniaxially stretched films, for directions parallel (‖) and perpendicular (⊥) to the stretching direction, have been colleted in Table 2.

For all samples, the modulus for tensile tests perpendicular to the stretching direction (last column of Table 2) is not far from the modulus of the unoriented amorphous films (first raw of Table 1). This result can be easily rationalized by a 'series' Tanigami model [28], due to the usual low degree of orientation of the amorphous phase.

As usually observed for uniaxially stretched polymeric films, the tensile moduli for tests parallel to the draw direction are much higher than for tests perpendicular to the draw direction. However, the increase of modulus associated with axial orientation for the different s-PS films are substantially different (compare the second columns of Tables 1 and 2). In particular, for the semicrystalline films presenting helical crystalline phases (clathrate, δ, γ) modulus increases in the range 60–70% are observed. As for the amorphous film, the increase of modulus is larger (close to 85%) due to the formation, as a consequence of drawing, of the mesomorphic phase including trans-planar chains (meso^t) [12]. Much higher is the modulus increase (about 110%) associated to uniaxial drawing, for the semicrystalline α form film, which includes trans-planar chains.

This higher modulus hardening for the α form film can be easily rationalized on the basis of the higher along the chain moduli of crystalline phases with trans-planar chains with respect to crystalline phases with helical chains [4,29]. In fact, it is well known that the contour length of a chain sequence in helix conformation can change by low energy internal rotation around the skeleton bonds, while the length of zig-zag sequences can increase only by higher energy deformation of bond angles.

4. Conclusions

The dynamic–mechanical behavior and the tensile moduli of unstretched and stretched semicrystalline s-PS films presenting different polymorphic forms (α, γ, δ and clathrate) have been compared. The comparisons have been effected for samples presenting similar degree of crystallinity and the same kind and similar degree of crystalline phase orientation. Moreover, aiming to minimize the morphology changes, the comparisons have been effected between films, which have been obtained by solvent desorption or crystal-crystal transition on a same starting s-PS clathrate film.

As usual for samples presenting a high degree of axial crystalline phase orientation, the elastic moduli obtained by tensile tests parallel to the drawing direction are much higher for the crystalline phase including fully extended trans-planar chains (α form) than for the phases including helical chains (clathrate, δ and γ form).

As for the unstretched films, presenting a preferential perpendicular orientation of the chain axes with respect to the film plane, the highest elastic modulus is observed for films presenting the high-density helical γ phase. In this respect, it is worth noting that, since the crystallite chain axes are preferentially perpendicular to the film plane and hence to the tensile stress, the crystalline phase moduli perpendicular to the chain axes are expected to be more relevant to the macroscopic behaviour than the crystalline phase moduli parallel to the chain axes.

As for the clathrate films, it is worth noting that the DCE molecules, when are only included as guest into crystalline clatrate phase, have no plasticizing effect. In fact, the clathrate films with a DCE content close 8% present a modulus comparable to (and even higher than) δ and α form films, while clathrate films including about 20% of DCE (11.5% in the crystalline phase and 8.5% in the amorphous phase) have elastic modulus markedly lower than for the other semicrystalline films and also lower than for amorphous films.

The present study also confirms that dynamic-mechanical analyses are very useful to study polymorphic phase transitions. In particular, it is shown that the multiple successive transitions induced by annealing on clathrate or δ form samples (clathrate or δ → helical mesomorphic → γ → α) can be clearly pointed out by dynamic-mechanical analyses of uniaxially stretched films.

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