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Thermal Expansion Coefficients of the Axes of the Unit Cell of Syndiotactic 1,2-Poly(1,3-Butadiene)

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Summary: Samples of syndiotactic 1,2-poly(1,3-butadiene) subjected to different thermal and mechanical treatments have been characterized by DSC and X-ray. The treatments induce changes in the crystallinity, crystal size and size of the unit cell, but do not evidence polymorphism. Values of the thermal expansion coefficients of the axes of the unit cell have been determined by X-ray measurements at various temperatures.

Keywords: crystal structures; thermal expansion; unit cell; X-ray

Introduction

Syndiotactic 1,2-poly(1,3-butadiene) [sPBD12] is a thermoplastic elastomer of industrial interest due to its properties of both plastics and rubbers. It has a wide range of applications; in fact, it is used for better resistance against wetting and slippage, films in 'packagingbreathing' items for fruits, vegetables and seafood, rubber goods, molded bottles, adhesives, oil paints, photosensitive resins, plastic material, footwear soles, tubes and hoses.[1]

sPBD12, obtained by Natta and Porri[2] in 1955, was the first prepared syndiotactic polymer. The crystal structure of sPBD12 was determined by Natta and Corradini[3] by X-ray investigations. The crystal structure is characterized by highly extended chains in the planar zigzag conformation, packed in an orthorhombic unit cell with $a = 10.98$ Å, $b = 6.60$ Å and $c = 5.14$ Å, space group *Pcam*.

Some of us performed in the past years molecular mechanics calculations concerning both the chain conformation[4,5] and the crystal structure[6] of sPBD12, which gave results in very good agreement with experimental data. The conformational analysis of the chains of sPBD12 showed the presence of two minima, the absolute minimum corresponding to a highly extended chain having **t***cm* symmetry and a slightly higher energy minimum corresponding to a helical chain having **s(2/1)2** symmetry. Moreover, a packing analysis of chains having **t***cm* symmetry, performed by taking into account all the orthorhombic space groups in which the symmetry elements of the chains are also crystallographic symmetry elements, indicated that the best mode of packing is realized in the *Pcam* space group.

Following the discovery of catalytic systems able to yield syndiotactic polymers having controlled constitution and configuration, the study of sPBD12 has been stimulated in the last years. As a consequence, various papers concerning the synthesis, the thermal behaviour, the crystallization kinetics and the morphology have been published.[7–12]

In the light of both the industrial and the renewed scientific interest for sPBD12, and considering that the properties of polymeric materials are closely related to stereoregularity, crystallization process, degree of crystallinity and polymorphism, we have examined the possibility of structural changes induced by thermal and mechanical treatments and by crystallization conditions, taking into account that

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polymorphic forms characterized by helical chains could be realized with a low energy cost for this polymer.

By the joint use of molecular mechanics and X-ray determinations we have recently performed structural studies on samples of sPBD12 having different degree of constitutional and configurational regularity, giving a clear indication of the compatibility of configurational defects in the crystal phase.[13] We report in this paper experimental data on samples of sPBD12 obtained by crystallization from the bulk, and the results of the analysis of the structural variations induced by thermal and mechanical treatments. Finally, we evaluate the thermal expansion coefficients of the axes of the unit cell.

Experimental Part

The polymer sample having ~97% of 1,2 content and ~62% of [rrrr] pentads was synthesized with catalyst systems based on chromium complex and methylaluminoxane in the laboratory of Prof. Porri (Politecnico di Milano, Italy), as described in Ref. [7]. Differential scanning calorimeter measurements were performed with a Perkin-Elmer DSC7 calorimeter in a flowing nitrogen atmosphere. Powder diffraction patterns were collected with a Philips PW3710 automated diffractometer operating in the conventional $\theta/2\theta$ Bragg-Brentano geometry, using the Ni-filtered CuKα radiation ($\lambda = 1.5418$ Å). An Anton-Paar TTK 450 low-temperature camera was used for the X-ray measurements at the various temperatures. A Pt_{100} thermocouple, inserted into the sample holder was used for high-precision measurements and for the control of the working temperature.

Characterization of the Polymer Sample

The sample was characterized by DSC and X-ray analysis. The DSC scans were performed at heating and cooling rates of 10 °C/min. Figure 1 shows the DSC traces obtained heating the as received sample up to ~30 °C above the melting temperature (a), cooling the melt down to room temperature (b) and heating the bulk crystallized sample up to ~30 °C above the melting temperature (c). The scans exhibit one broad endothermic peak with maximum at 154.3 °C in the first case, two exothermic peaks due to crystallization in the second case, and one very broad endothermic peak with maximum at 140.7 °C in the third case.

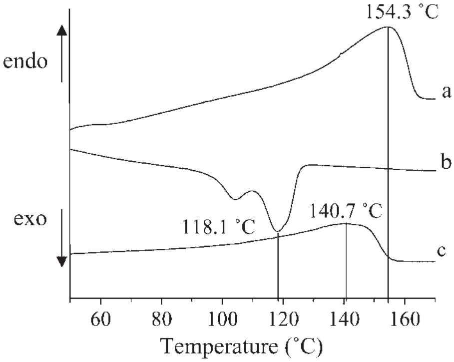

Figure 1.
DSC traces of sPBD12 performed at rates of 10 °C/min. a: heating scan of the as received sample; b: cooling scan of the melt; c: heating scan of the bulk crystallized sample.

X-ray powder profiles of sPBD12 were collected both on the as received sample and on samples compression moulded at various temperatures in the range between 175 °C and 210 °C. The compression moulded samples were cooled by different treatments: i) quenching in a mixture of ice and water or in liquid nitrogen at various setting times, from 1.5 to 20 minutes, in the cold liquids; the quenched samples were also annealed for different annealing times at various temperatures up to 140 °C; ii) cooling in the air at different rates. Figure 2 shows the X-ray powder profiles of the as received sample, of a quenched sample, of an annealed quenched sample and of a compression moulded sample cooled in the air. These treatments do not induce substantial modifications of the polymer samples, in the sense that the number and the positions of the reflections remain unchanged, while changes are observed as far as the crystallinity, the crystal size and

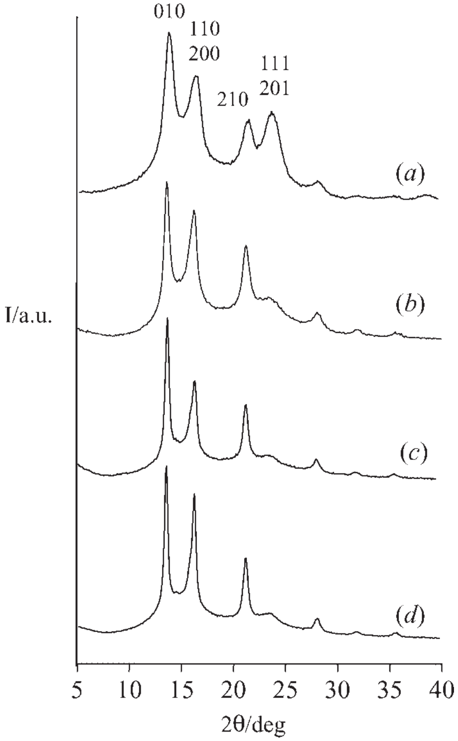

Figure 2.
X-ray powder profiles of samples of sPBD12: (a) as received sample, with the indication of the indices of the most intense reflections according to the crystal structure [3,13]; (b) sample compression moulded at 200 °C for 5 minutes and quenched in liquid nitrogen for 20 minutes; (c) sample compression moulded at 200 °C for 5 minutes, quenched in liquid nitrogen for 20 minutes and annealed at 140 °C for 6.5 hours; (d) sample compression moulded at 200 °C for 5 minutes and cooled in the air.

the intensity of the reflection at $2\theta = 24.5°$ are concerned. The treated samples are characterized by larger crystals with respect to the as received sample, as evidenced by the smaller half widths of their reflections. The intensity of the reflection at $2\theta = 24.5°$, which is given by the superimposition of the (111) and (201) reflections, is much higher in the powder spectrum of the as received sample, indicating that this sample exhibits a higher order along the *c* direction, while the other samples have some amount of disorder which can be interpreted by the inclusion of configurational defects in the crystal phase.[13] The crystallinity of the as received and of the quenched samples appears to be roughly the same, while higher crystallinity and higher crystal size are exhibited by the annealed and by the slowly cooled samples. These experimental evidences indicate that a rapid crystallization from the melt favours the formation of larger crystals, but disfavours the ordering process along the *c* direction, even if the samples are annealed. On the contrary, the slow formation of polymer in solution (as received sample) favours the ordering along the *c* direction, even if smaller crystals are formed. All these results can be explained assuming that during the rapid crystallization the portions of chain contaning configurational defects are not included in the crystal.

We also collected X-ray powder profiles of the as received sample at various temperatures, from room temperature to temperatures above the melting point. They are shown in Figure 3. The shapes of the profiles from room temperature to 130 °C are practically the same, the only

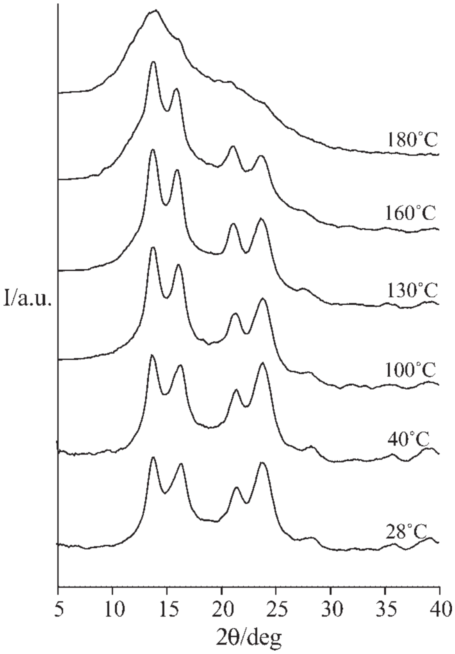

Figure 3.
X-ray powder profiles of the as received sample of sPBD12 collected at various temperature.

changes being slight variations in the positions of the reflections due to the expansion of the unit cell with increasing temperature. The profile collected at 160 °C exhibits also a decrease of the crystallinity and variations of the intensities of the reflections. The profile collected at 180 °C appears prevailingly as that of an amorphous polymer.

Thermal Expansion of the Axes of the Unit Cell

In order to obtain a quantitative measurement of the influence of the temperature on the size of the unit cell we collected also X-ray powder profiles at various temperatures, starting from –20 °C up to 120 °C at intervals of 20 °C. For these measurements we used the compression moulded sample cooled in the air, whose powder profile exhibits sharp reflections (see profile (d) in Figure 2) so that the exact positions of the maxima could be detected. In order to determine the values of the *a* and *b* axes of the unit cell we collected more accurately, at each temperature, diffraction profiles of two chosen reflections by step size of 0.1° and time for step of 10 s. In particular we chose the (010) and (210) reflections because they are the only intense reflections not superimposed with other reflections. Figure 4 shows the profiles of the two reflections at the various temperatures. At each temperature the value of the *b* axis was directly determined from the 2θ value of the (010) reflection while the value of the *a* axis was obtained from the 2θ value of the (210) reflection using the value of the *b* axis at the same temperature. The values of the *a* and *b* axes at room temperature are practically coincident with those reported by Natta and Corradini.[3]

The values of the *a* and *b* axes as a function of the temperature are shown in Figure 5. The trends are linear and, therefore, constant values of the thermal expansion coefficients of the *a* and *b* axes are obtained. They are $2.8 \cdot 10^{-4}$ K^{-1} and $6.7 \cdot 10^{-5}$ K^{-1}, respectively. These values are similar, or at least on the same order of magnitude, to those found for other vinyl polymers,[14,15] as shown in Table 1.

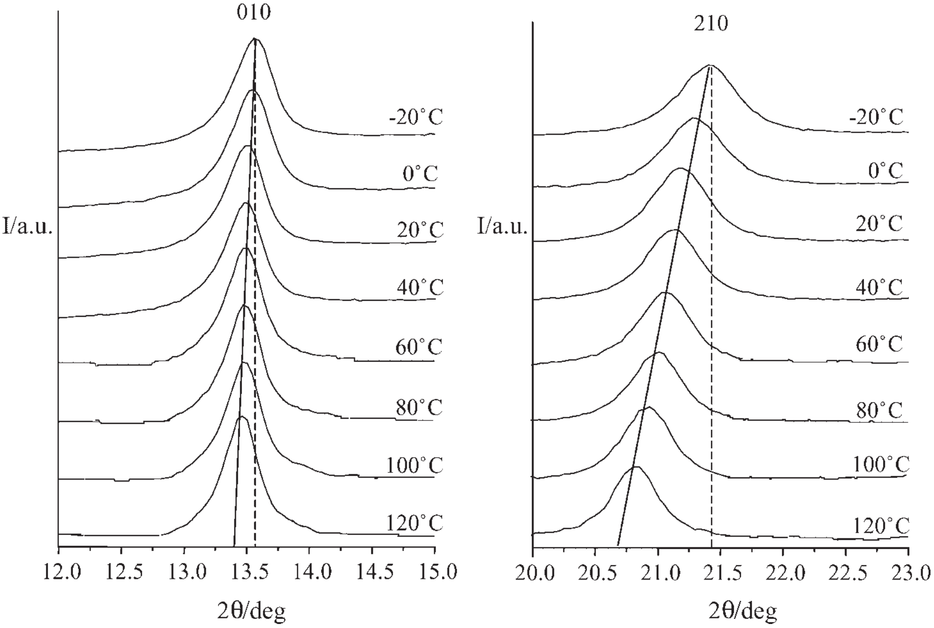

Figure 4.

X-ray powder profiles of the (010) and (210) reflections at various temperatures, collected by step size of 0.1° and time for step of 10 s on the compression moulded sample of sPBD12 cooled in the air.

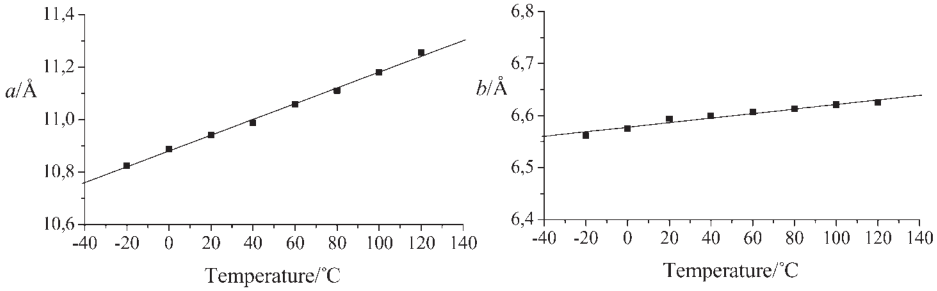

Figure 5.
Trends of the *a* and *b* axes of the unit cell of sPBD12 as a function of the temperature.

Table 1.
Thermal expansion coefficients of the *a* (λ_a) and *b* (λ_b) axes of sPBD12, in comparison with those of iPP[15] and of isotactic poly-1-butene [iPB].[14]

Polymer	$\lambda_a \cdot 10^{-4}$ K^{-1}	$\lambda_b \cdot 10^{-4}$ K^{-1}
sPBD12	2.8	0.67
iPP, α_1 form	1.08	2.26
iPP, α_2 form	0.623	1.50
iPB, form 1	1.65	1.65
iPB, form 2	1.79	1.79
iPB, form 3	2.55	1.42

As for the value of the *c* axis, it is not easily obtainable because the X-ray powder profile does not present isolated non-equatorial reflections. On the other hand, the value of the *c* axis, depending only on chain conformation, is generally invariant with temperature. This was verified for other polymers, as reported in previous papers.[14–16]

By using the thermal expansion coefficients we calculated the values of the *a* and *b* axes of the unit cell of sPBD12 at 0 K. The values of the axes of the unit cells of polymers extrapolated at 0 K from experimental determinations are generally comparable with those obtainable performing structural predictions by molecular mechanics calculations because the potential functions do not take into account thermal vibrations and defects. Table 2 shows the extrapolated values of the axes of the unit cell in comparison with those obtained by us[13] by minimizations of the conformational and packing energy of sPBD12 with three different set of potential functions.[17–19] The extrapolated values are very similar to the calculated ones, the average deviations being 2.6% for the *a* and *b* axes, and 0,9% for the *c* axis.

Conclusions

The experimental data indicate that sPBD12 does not exhibit structural variations in the range of temperature from −20 °C to the melting point, except for the size of the unit cell. Therefore, this polymer can be used as plastic material also at the low temperatures typical of cold countries. We underline that no other polimorphic form of sPBD12 is found when the polymer sample is subject to various thermal and mechanical treatments, tough the conformational energy calculations indicate the presence of helical minima having low energy.[4,5] On the contrary, other

Table 2.
Values of the axes of the unit cell of sPB12 extrapolated at 0 K in comparison with those obtained by energy minimizations with three different force fields.

	Extrapolated	Universal 1.02[17]	Dreiding[18]	Compass[19]
a/Å	10.13	10.462	10.561	10.174
b/Å	6.47	6.257	6.393	6.262
c/Å	5.15	5.111	5.239	5.134

syndiotactic polymers exhibit various polymorphic forms characterized both by helical chains and by highly extended chains.[5] In particular, for syndiotantic polystyrene, having planar lateral group as sPBD12 and exhibiting both trans planar and helical conformational minima,[20] various crystalline polymorphic forms, some differing for the conformation of the polymer chain and some others for the packing arrangements, were found.[21–23] This suggests that, under particular treatments, also sPBD12 could crystallize in some other polymorphic form.

The thermal expansion coefficients of the axes of the unit cell, determined by X-ray measurements, are constant in a wide range of temperatures and are on the same order of magnitude of those of polymers of olefins. Finally, the values of the axes of the unit cell, extrapolated at 0 K, are in very good agreement with those calculated for models of crystal structure obtained with various set of potential functions, showing that these potential functions are reliable for the prediction of structural features of sPBD12.

Work is in progress in order to analyse morphological features and to study the chain folding of this polymer.

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