

Polymer Communication

The conformation of poly(dimethylsiloxane) in the crystalline state

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Received 24 August 1999; accepted 15 September 1999

Abstract

The problem of the polymer chain conformation in crystalline poly(dimethyl siloxane) has been revisited using X-ray diffraction techniques. It is shown that the crystallites belong to the centered tetragonal system. A four-fold helical configuration of the polymer chain is proposed, with four monomers per turn and a pitch of ca. 1.2 nm: it corresponds to an extended configuration of the siloxane backbone with oxygen atoms located close to the 4_1 symmetry axis and methyl groups pointing outwards. These results are in deep contrast with the previously accepted monoclinic structure and ribbonlike chain conformation. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(dimethylsiloxane); Centered tetragonal system; X-ray diffraction

1. Introduction

It is known that highly crystalline materials can be obtained by cooling poly(dimethylsiloxane) (PDMS) oils or rubbers [1–3]. For high molecular weight polymers, the melting endotherm observed by differential scanning calorimetry is in the temperature range 233–236 K [1,2]. Since the early work of Damaschun [4] in 1962, it is generally admitted that the crystalline phase belongs to the monoclinic system and that the polymer adopts a twofold helical conformation with six monomers per turn associated with a periodicity of 0.83 nm. It results in a ribbonlike aspect of the chain, forming large lateral loops. This model was based on the analysis of the low-temperature X-ray fiber pattern from a highly stretched PDMS rubber filled with silica (35 wt%; extension ratio $\lambda = 4$). Two points led us to question this description. The first one is a publication by Schilling et al. concluding that there is an incompatibility of the model with ^{29}Si and ^{13}C NMR results [5]. Indeed single resonances are observed for both nuclei in the crystalline state, instead of multiple resonances as expected from the conformational heterogeneity of the model. The second point was an apparent incoherence between the X-ray texture pattern reproduced in Damaschun's work and our own observations on weakly stretched PDMS rubber samples. To our knowledge, no structural investigation using X-ray diffraction has been undertaken since 1962.

2. Experimental section

Different samples are used in the present study: PDMS oils containing linear polymers of different masses referred respectively to as O1 ($M_w = 14,600$ g/mol; heterogeneity index, 1.67) and O2 ($M_w = 200,000$ g/mol; unspecified heterogeneity index), and PDMS rubbers in the form of 1 mm thick foils, referred as R1 (unfilled sample)¹ and R2 (silica filled, 30 wt%). The X-ray setup consists of a low-temperature diffractometer mounted on a rotating anode generator (copper anode) equipped with a doubly curved graphite monochromator. A small traction apparatus can be housed in the cryostat and externally operated. Diffraction patterns are recorded onto photostimulable imaging plates or with a position-sensitive detector when more quantitative intensity measurements are required. X-ray absorption measurements have been performed on a rubber foil that could be set perpendicular to the incident beam and escaped by 90° rotation, allowing primary and transmitted intensities to be successively measured.

3. Results and discussion

3.1. Sample characterization

The melting temperature and crystallinity amount have been determined for the different samples (see Table 1).

¹The unfilled rubber is prepared by hydrosilylation of a PDMS oil ($M_w = 26,300$; M_w/M_n , 1.76) using pentadimethylcyclopentasiloxane as reticulating agent.

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Table 1
Melting temperatures and crystallinity amounts for the different samples

Sample	Melting temperature (K)	Amount of crystallinity (%)
O1	242.7	66 (59 K); 65 (183 K)
O2	239	49 (59 K); 41 (183 K)
R1	237	60 (59 K); 54 (183 K)
R2	237	41 (183 K)

Melting temperatures are associated with the complete disparition of Bragg scattering whereas crystallinity amounts are estimated by comparison between amorphous and Bragg scattering.

3.2. Crystallographic assignment

X-ray fiber patterns have proved to be helpful for line indexation in polymer crystallography. The diagram reproduced in Fig. 1 has been obtained on a silica-filled rubber previously weakly stretched at room temperature ($\lambda = 1.5$; R2 sample) and cooled at a rate of 1 K/min (it has been verified that the presence of a filler has no qualitative effect on the texture diagram). It clearly presents the characteristics of a fiber pattern with a fiber-axis repeat distance of ca. 1.2 nm; the corresponding layers are visualized by horizontal dashed lines. The indexation procedure is started by noting the meridian position of the fourth-order reflection (d -spacing is ca. 0.3 nm; see black arrow), accordingly indexed as (004). Indeed θ - 2θ scans recorded before and after stretching of the sample and subsequent cooling show a strong reinforcement of the (004) and (008) reflections while other (001) orders are systematically absent. The condition for possible reflection $l = 4n$ is an indication of a 4_1 screw axis, of helical pitch $c \approx 1.2$ nm. This symmetry is compatible with both cubic and tetragonal systems; however, the cubic assignment may be discarded as it implies unobserved equatorial reinforcements of the (004) diffraction ring.

The second tetragonal parameter is deduced from the location of the equatorial reflection pointed to by a white arrow on Fig. 1; a close examination of the diffraction

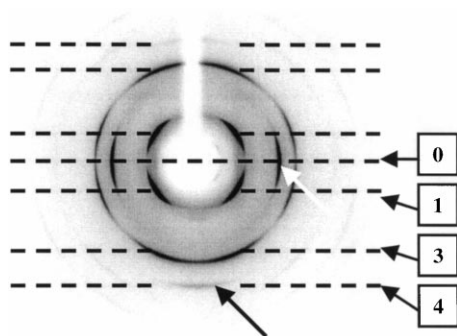


Fig. 1. Low temperature X-ray pattern of a 30 wt% silica filled PDMS rubber submitted to vertical extension (sample R2; $\lambda = 1.5$; exposure time, 20 min).

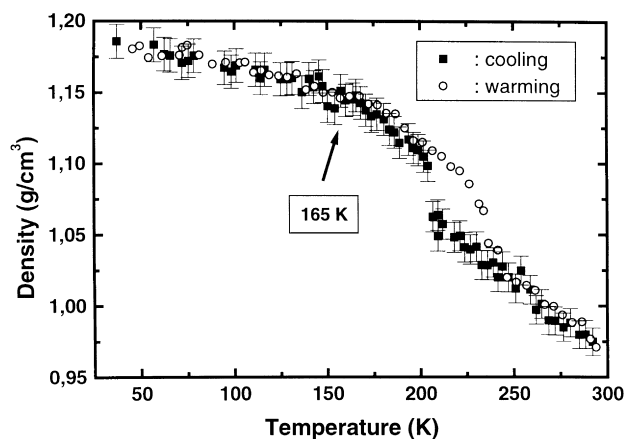


Fig. 2. Temperature dependence of the density of a PDMS rubber; the measurement is performed by X-ray absorption² (sample R1).

pattern suggests a (2,0,0) indexation associated with a crystallographic parameter $a \approx 0.83$ nm. Under these assumptions, the positions of all diffraction lines and the general aspect of the texture diagram are precisely accounted for; this point is illustrated in Table 2 which compares some experimental d -spacings and azimuthal angles to calculated values. The condition for possible reflection $h + k + l = 2n$ is systematically observed indicating a body-centered lattice. Crystallographic parameters are listed in Table 3 for samples O1 and O2 at two representative temperatures.

The number of monomers per unit cell is deduced from the density of the crystalline phase. It is possible to evaluate the sample density by X-ray absorption measurements assuming isotropic thermal contraction of the sample.² The experiment has been conducted on a free-hanging pure PDMS rubber foil, assuming a room temperature (20°C) density of 0.974 g/cm³ [6]. A data set obtained during a complete thermal cycle is plotted on Fig. 2; supercooling is clearly visible as expected [7]. The break observed at ca. 165 K can be associated with the glass transition ($T_g \approx 150$ –153 K [1,8]). Crystalline densities are obtained after subtraction of the amorphous contribution knowing the sample crystallinity; for this purpose, the low-temperature density of the amorphous phase is reasonably derived by linear interpolation of the data obtained before crystallization down to 165 K and assumed to vary in a way similar to the crystalline density below this temperature. The different densities thus obtained are collected in Table 4 at two temperatures. The additional knowledge of the unit cell volume allows the determination

² For a sample of thickness d , transmitted and incident intensities are related by the well-known equation: $I_{\text{trans}}/I_{\text{inc}} = \exp(-\mu d)$, where μ is the linear absorption coefficient of the material, proportional to its density ρ . Assuming an isotropic thermal contraction, relative variations of d and ρ are related by: $\Delta\rho/\rho = -3\Delta d/d$ and hence $\Delta(\mu d)/(\mu d) = (2/3)\Delta\rho/\rho$; supposing the density at some temperature T_0 to be known, the density at any temperature can be thus derived from a measure of the absorption coefficients by the relation: $\rho(T) = \rho(T_0)((\mu d)(T)/(\mu d)(T_0))^{3/2}$.

Table 2

Comparison between observed and calculated d -spacings and δ angles; δ is the angular position of the intensity reinforcement measured with respect to the fiber axis (sample O1, 183 K)

(h,k,l) -indices	Experimental d_{hkl} (nm)	Calculated d_{hkl} (nm)	Experimental δ angle (deg.)	Calculated δ angle (deg.)
(0,1,1)	0.685	0.684	54.9	54.9
(0,2,0)	0.417	0.417	88.9	90
(1,2,1)	0.358	0.356	72.8	72.2
(0,1,3)	0.358	0.358	19.4	22.5
(0,0,4)	0.298	0.298	0.6	0
(1,2,3)	0.272	0.272	43.3	44.6
(1,3,2)	0.242	0.241	65.1	64.8
(0,2,4)	0.242	0.242	31.2	31
(0,3,3)	0.228	0.228	53.5	52.6
(0,4,0)	0.209	0.209	89.2	90

Table 3

Crystallographic parameters for the tetragonal lattice of crystalline PDMS

Sample	a (nm)	c (nm)	Cell volume (nm ³)
O1 at 183 K	0.835	1.192	0.831
at 53 K	0.825	1.179	0.802
O2 at 183 K	0.836	1.200	0.839
at 53 K	0.825	1.187	0.808

of the number of monomers per unit cell, found very close to eight. It can be noticed that the crystalline density calculated at 183 K by G. Damaschun is 1.07 g/cm³, outside the error limits of our experimental data.

At this point of the discussion, it is worth briefly discussing the reasons that led to the above-mentioned inappropriate monoclinic assignment. It can be first noticed that, due to weaker X-ray sources, the indexation procedure was applied to a very restricted number of diffraction lines. A second important point is a qualitative modification of the texture pattern for samples submitted to high extension ratios, as done in Damaschun's study: in these conditions, the tetragonal symmetry is more difficult to work out. A detailed study of this effect is the object of a forthcoming paper.

3.3. Structure discussion

The preceding discussion is purely based upon diffraction observations and does not require any structural hypothesis. It is now assumed that, for the weak extension ratios presently considered, polymer chains preferentially align along the stretching axis; in these conditions, it can be proposed that the chains adopt a fourfold helical configuration with four monomeric units per turn and a helical pitch

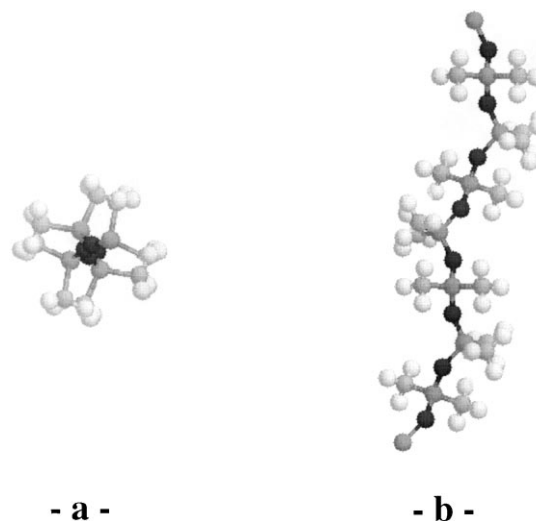


Fig. 3. Model of PDMS chain presenting a fourfold helical conformation. (a) top view, (b) side view (oxygen atoms are in black).

of ca. 1.2 nm. Due to the centering condition, this leads to eight monomers per unit cell, as found experimentally. Based upon geometrical parameters found in the literature [9], a model satisfying these assumptions can be proposed: it is sketched on Fig. 3 and corresponds to an extended conformation of the siloxane backbone with the oxygen atoms located close to the 4_1 symmetry axis and methyl groups pointing outwards. In this model, all silicon atoms are equivalent, in perfect agreement with the observation of a single NMR resonance for ²⁹Si nuclei [5]. The two methyl groups attached to each silicon atom are not symmetry related; however, they present the same intramolecular conformation which determines chemical shifts and

Table 4

Densities obtained from X-ray absorption measurements (sample R1); the number of monomers per unit cell is deduced from the crystalline density knowing the cell volume

Temperature (K)	Density (g/cm ³)	Amorphous density	Crystalline density	Number of monomers per unit cell
183	1.124	1.086	1.156	7.84
59	1.180	1.140	1.207	7.89

accounts for the observation of a single ^{13}C resonance. A structure determination is in progress and the addition of some disorder appears necessary to account for the experimental line intensities.

4. Conclusion

The problem of the crystalline structure of PDMS has been revisited using classical X-ray diffraction techniques. It is shown to be centered tetragonal in contradiction with the previously admitted monoclinic assignment; X-ray absorption measurements allowed crystalline densities to be evaluated and a number of eight monomers per unit cell is found. Assuming that polymer chains align along the stretching direction, it is deduced that: (i) the chains present a fourfold helical configuration; and (ii) each unit cell is crossed by two chains running along the tetragonal axis. A model characterized by an extended conformation of the siloxane backbone is proposed.

Acknowledgements

This work owes much to the helpful participation of A. Anthore and S. Murriss. Samples were friendly provided by B. Deloche and B. Haidar who must also be thanked for interesting discussions.

References

- [1] Clarson SJ, Dodgson K, Semlyen JA. *Polymer* 1985;26:930.
- [2] Helmer JD, Polmanteer KE. *J Appl Polym Sci* 1969;13:2113.
- [3] Ohlberg SM, Alexander LE, Warrick EL. *J Polym Sci* 1958;27:1.
- [4] Damaschun G. *Kolloid-Z* 1962;180:65.
- [5] Schilling FC, Gomez MA, Tonelli AE. *Macromolecules* 1991;24:6552.
- [6] Mark JE. *Physical properties of polymer handbook*, New York: Woodbury, 1996.
- [7] Ebenghou RH, Cohen-Addad JP. *Polymer* 1994;35:2692.
- [8] Friedrich J, Rabolt JF. *Macromolecules* 1987;20:1975.
- [9] Darsey JA. *Macromolecules* 1990;23:5274.