On the Clathrate Structures of Syndiotactic Poly(*m*-methylstyrene)

Oreste Tarallo, Annamaria Buono, Valeria Califano, Vittorio Petraccone*

Dipartimento di Chimica, Università degli Studi di Napoli "Federico II", Complesso Universitario di Monte Sant'Angelo, Via Cinthia, 80126 Napoli, Italy

Summary: The crystal structures of clathrate forms of syndiotactic poly(*m*-methylstyrene) containing guest molecules having different steric hindrance (CS_2, benzene and *orto*-dichlorobenzene) are presented. The structures are all characterized by polymer chains in s(2/1)2 helical conformation and guest molecules packed in an orthorhombic unit cell according to the space group *Pcaa*. All the presented clathrates belongs to β class indipendently from the dimensions of the guest molecule. In this aspect they differ both from clathrate forms of syndiotactic polystyrene, all belonging to α class, and from clathrate forms of syndiotactic poly(*p*-methylstyrene) that belong to α or β class according to the steric hindrance of the guest molecule.

Keywords: clathrates; crystal structure; host-guest system; syndiotactic poly(*m*-methylstyrene); WAXS

Introduction

Syndiotactic poly(*m*-methylstyrene) (s-PMMS) presents a complex polymorphic behaviour, which has been recently described.[1] Three different polymorphic forms have been found so far. Form I is characterized by chains in s(2/1)2 helical conformation and can be obtained by crystallization from the melt. The same conformation of the chains has been hypothesized also for form II, which can be obtained by crystallization from solutions of solvents that do not form clathrate structures. Form III, obtained in oriented fibers by stretching amorphous films, is a mesomorphic modification characterized by chains in *trans*-planar conformation.

s-PMMS shows the interesting property to cocrystallize with low molecular weight substances forming polymeric clathrates, as found for syndiotactic polystyrene[2] (s-PS) and syndiotactic poly(*p*-methylstyrene)[3] (s-PPMS). Some possible applications of these molecular compounds like chemical separations, water and air purification, have been recently pointed out for s-PS.[4] As far as s-PS clathrate forms are concerned, all the studied structures are very similar[2e,f,g] and may be grouped in only one class where the guest molecules occupy isolated centrosymmetric

 DOI: 10.1002/masy.200351310

cavities delimited by eight benzene rings of two adjacent enantiomorphous chains. Two different classes of clathrate forms (α and β) have been instead described for s-PPMS according to the steric hindrance of the guest molecule.[3g] α class clathrates (including bigger guest molecules) present a structure similar to s-PS clathrates. β class clathrates (including smaller molecules) are instead characterized by cavities positioned between two adjacent isomorphous chains related by a 2-fold screw axis of the lattice and formed by four benzene rings of the same polymer chain. Such cavities are not isolated and guest molecules may interact.

In this work, a characterization of clathrate structures of syndiotactic poly(*m*-methylstyrene) containing guest molecules having different steric hindrance is presented. In particular definitive results are reported for the clathrate form including carbon disulfide, while preliminary results are presented for benzene and *o*-dichlorobenzene (*o*-DCB) clathrates. A comparison with the clathrate structures of s-PS and s-PPMS is also shown.

Clathrates Preparation

The polymer was synthesized as described in ref. 1. Unoriented samples of the s-PMMS clathrates containing carbon disulfide and benzene were obtained by swelling at room temperature of amorphous samples, while unoriented *o*-DCB clathrate samples were prepared by casting procedures from 1 wt.% solutions. The X-ray diffraction patterns of unoriented samples of these three clathrates are reported in Figure 1.

Oriented samples of benzene and CS_2 clathrate were obtained by exposing at room temperature fibers of the mesomorphic form III to solvent vapours, keeping the fiber under tension. However, when fibers of the mesomorphic form III were exposed to *o*-DCB vapours, form I was obtained. Therefore oriented samples of *o*-DCB clathrate haven't been obtained yet.[1] It is worth noting that most of the solvents that give clathrates in the case of s-PS and s-PPMS induce the formation of form I and/or II for s-PMMS. As a matter of fact, the three clathrates discussed in this paper are the only ones obtained so far, nevertheless experiments of casting, swelling and exposition to vapours of several solvents have been done.

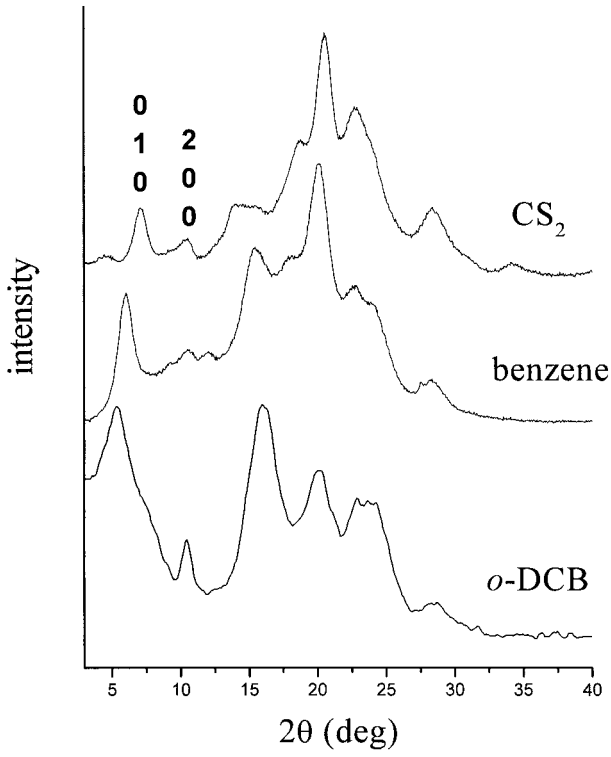

Fig. 1. Experimental X-ray diffraction patterns of unoriented samples of the clathrate forms of s-PMMS containing CS_2, benzene and *o*-DCB (Cu-Kα radiation).

It is relevant for the subsequent discussion to stress that swelling procedures and exposition to vapours of s-PMMS amorphous samples with several solvents that do not form clathrates give rise to X-ray diffraction patterns which we think may be interpreted in terms of small and imperfect crystals of forms I and/or II.[5] As an example, in Figure 2 the diffraction profiles of samples obtained by swelling of amorphous specimen of s-PMMS with tetrahydrofuran (THF), toluene and cycloexanone are shown together with the patterns of the pure crystalline forms I and II. It is evident that the diffraction patterns of the samples obtained by treatments with THF, toluene and cycloexanone are very similar to each other and are characterized by a strong reflection at $2\theta \cong 15°$, typical of both the pure forms I and II.

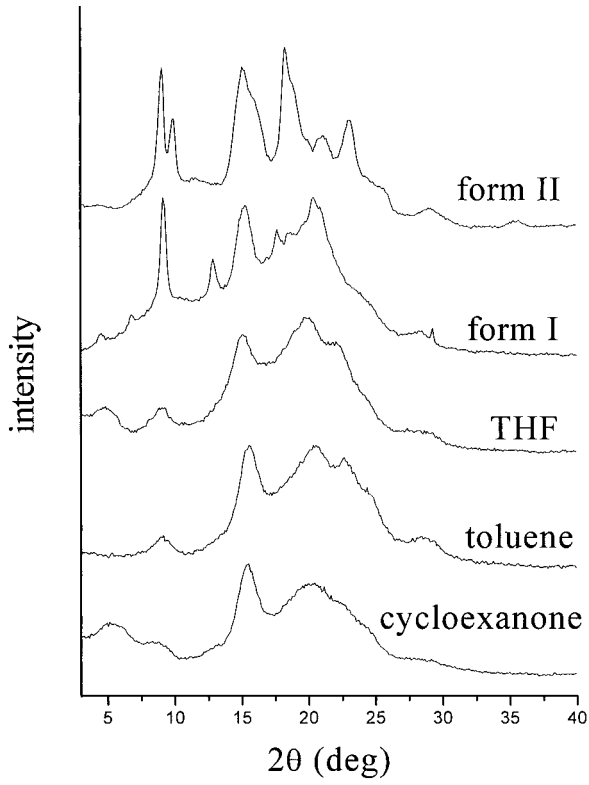

Fig. 2. Experimental X-ray diffraction patterns of unoriented samples obtained by swelling of amorphous samples of s-PMMS in THF, toluene and cycloexanone (Cu-Kα radiation).

Structure Models and Discussion

The crystal structure of the clathrate form of s-PMMS containing CS_2 has been solved by some of us on the basis of an X-ray fiber diffraction pattern with a discrepancy factor of 16%.[6] The structure is characterized by polymer chains in **s**(2/1)2 helical conformation and CS_2 molecules packed in an orthorhombic unit cell with axes a = 17.8 Å, b = 13.1 Å and c = 7.8 Å, according to the space group *Pcaa*. Figures 3a and 3b show *ab* and *bc* projections of the packing model proposed.

Comparing the X-ray profiles reported in Figure 1, we noted that the first reflection, indexed as (0 1 0) for the clathrate containing CS_2, on the basis of the proposed structure, shifts at lower

values of 2θ as the dimensions of the guest molecule increase (2θ = 7.0° for CS_2, 2θ = 6.0° for benzene and 2θ = 5.4° for *o*-DCB), while a reflection at 2θ ≅ 10°, indexed as (2 0 0) for the clathrate containing CS_2, is present at the same position for the other two clathrates. This fact suggested us that both benzene and *o*-DCB clathrate forms could have the same packing model of the s-PMMS clathrate containing CS_2, since in this hypothesis (cf. Figure 3a and 3b) the dimension of the *b* axis should increase as the guest molecule became more encumbering, while the dimension of the *a* axis should remain constant.

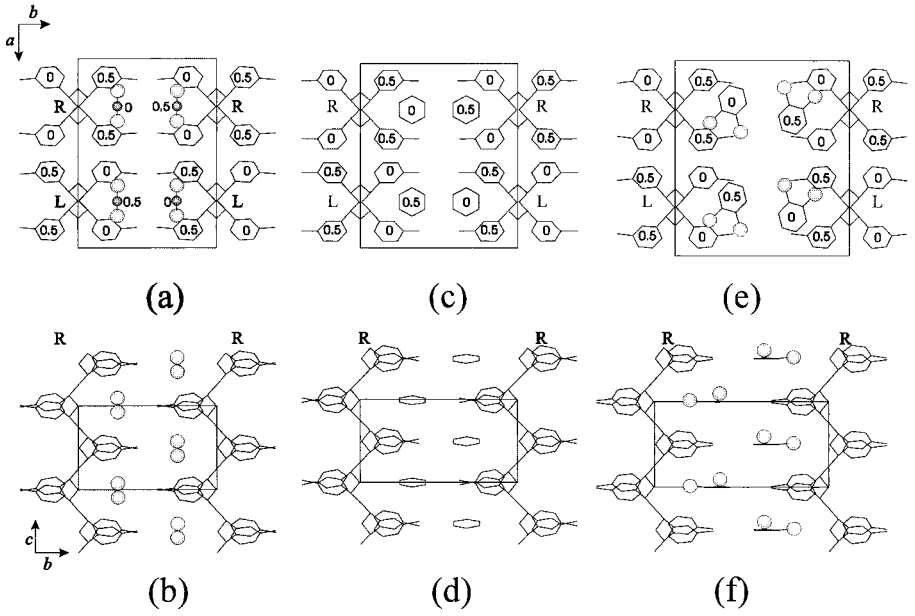

Fig. 3. *ab* and *bc* projections of the packing models proposed for the clathrate structures of s-PMMS containing CS_2 (a, b), benzene (c, d) and *o*-DCB (e, f). In (e) and (f) in each cavity only one of the two statistical positions of the *o*-DCB molecule is shown. The other one can be obtained by a rotation of 180° on the crystallographic 2-fold axes parallel to the *b* axes of the cell. The approximate *z/c* fractional coordinates of the barycenters of the phenyl rings and of the guest molecules are shown in (a), (c) and (e). R = right- L = left-handed chain.

Consequently, we have assumed for both the clathrate forms containing benzene and *o*-DCB orthorhombic cells and we have indexed the first reflections as (0 1 0) and the reflections at 2θ ≅ 10° as (2 0 0). The resultant cell parameters are *a* = 17.4 Å, *b* = 14.8 Å and *c* = 7.8 Å for

benzene clathrate form and a = 17.25 Å, b = 16.4 Å and c = 7.8 Å for *o*-DCB one. In the case of s-PMMS clathrate containing benzene this cell hypothesis is in agreement with the X-ray fiber diffraction pattern reported in ref. 1. Assuming also the same space group (*Pcaa*), the arrangement of the chains inside the cell results to be identical to that one already found for the clathrate form of s-PMMS containing CS_2. The position of the guest molecules (benzene and *o*-DCB) has been instead determined by molecular mechanics calculations using commercially available software (*Cerius*[2] by *Accelrys Inc.*). *ab* and *bc* projections of the packing model proposed for s-PMMS clathrate form containing benzene are shown in Figure 3c and 3d while the same projections for *o*-DCB clathrate are shown in Figure 3e and 3f respectively. All C-C and C-Cl non-bonded distances are higher than 3.5 Å for the proposed models. Calculated X-ray powder diffraction profiles for the clathrate structures containing benzene and o-DCB are presented in Figure 4. In the case of the *o*-DCB clathrate structure, the structure factors calculations were performed for a statistical model characterized by *o*-DCB molecules arranged statistically in one of the two positions related by a rotation of 180° on the crystallographic 2-fold axis parallel to the *b* axis of the cell. This result suggests that a positional disorder inside the structure is present.

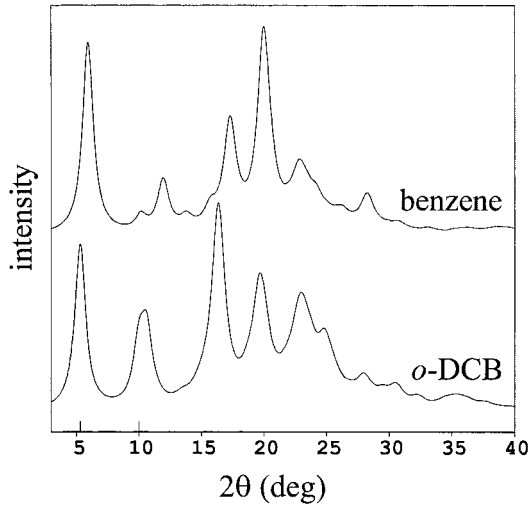

Fig. 4. Calculated Cu-Kα X-ray powder diffraction patterns of the proposed structures of the clathrate form of s-PMMS containing benzene and *o*-DCB.

From a comparison of these profiles with the experimental ones (reported in Figure 1), it is apparent that the agreement is fairly good for the model proposed for the s-PMMS clathrate form containing *o*-DCB, while is less satisfying in the case of the clathrate form containing benzene. Mainly, in the last case, our model is not able to reproduce the strong reflection at $2\theta \cong 15°$ that is present in the experimental X-ray diffraction pattern. This reflection could be due to the presence in all the samples of this clathrate we have obtained (including the oriented one[1]) of a certain amount of small and imperfect crystals of form I and/or II, as in the case already discussed in the precedent paragraph for solvents that do not form clathrates.

It is evident from these results that, despite the similarity of the two polymers, s-PPMS clathrates belong to different classes depending on the dimensions of the guest molecule (in particular bigger molecules, such as *o*-DCB give rise to α class clathrates,[3e] while smaller molecules, such as benzene, give rise to β class clathrates[3f]), while s-PMMS clathrate forms belong all to the β class, independently from the dimensions of the guest molecule. As far as the comparison with s-PS clathrates is concerned, we recall that all its clathrates belong to the α class independently from the dimensions of the guest molecule. In this respect it may be relevant to note that also in the case of a small molecule such as iodine, having shape and dimensions almost identical to CS_2, and for which it could be expected a β class clathrate, s-PS give rise to an α class clathrate.[2f] However, in this case, two guest molecules are accommodated in the cavity, giving a 2:1 ratio between the guest molecules and the polymer chains in the cell, typical of the β class clathrates. In order to rationalize these different behaviours, molecular mechanic calculations are in progress.

Acknowledgements

Financial support of MIUR (Prin 2000 and Cluster 26) is gratefully acknowledged.

[1] C. De Rosa, A. Buono, L. Caporaso, V. Petraccone. *Macromolecules,* **2001**, *34*, 7349.
[2] (a) Immirzi, A.; de Candia, F.; Ianelli, P.; Zambelli, A.; Vittoria, V.; *Makromol.Chem., Rapid Commun.* **1988**, *9*, 761; (b) Vittoria, V.; de Candia, F.; Iannelli, P.; Immirzi, A.; *Makromol.Chem., Rapid Commun.* **1988**, *9*, 765; (c) Guerra, G.; Vitagliano, M.V.; De Rosa, C.; Petraccone, V.; Corradini, P.; *Macromolecules* **1990**, *23*, 1539; (d) Chatani, Y.; Shimane, Y.; Inoue, Y.; Inagaki, T.; Ishioka, T.; Ijitsu, T.; Yukinari, T.; *Polymer* **1992**, 33, 488; (e) Chatani, Y.; Inagaki, T.; Shimane, Y.; Iijtsu, T.; Yukimori, T.; Shikuma, H.; *Polymer,* **1993**, *34*, 1620; (f) Chatani, Y.; Shimane, Y.; Inagaki, T.; Shikuma, H.; *Polymer,* **1993**, *34*, 4841; (g) De Rosa, C.; Rizzo, P.; Ruiz de Ballesteros, O.; Guerra, G.; Petraccone, V; *Polymer*, **1999**, *40*, 2103.
[3] (a) Iuliano, M.; Guerra, G.; Petraccone, V.; Corradini, P.; Pellecchia, C; *New Polymeric Mater,* **1992**, *3,* 133; (b) De Rosa, C.; Petraccone, V.; Guerra, G.; Manfredi, C; *Polymer,* **1996**, *37*, 5247; (c) Dell'Isola, A.; Floridi, G.; Rizzo, P.; Ruiz de Ballesteros, O.; Petraccone, V.; *Macromol. Symp.,* **1997**, *114*, 243; (d) Petraccone, V.; La Camera, D.; Pirozzi, B.; Rizzo, P.; De Rosa, C.; *Macromolecules*, **1998**, *31*, 5830; (e) Petraccone, V.; La Camera, D.; Caporaso, L.; De Rosa, C.; *Macromolecules*, **2000**, *33*, 2610; (f) La Camera, D.; Petraccone, V.; Artimagnella, S.; Ruiz de Ballesteros, O.; *Macromolecules*, **2001**, *34*, 7762; (g) La Camera, D.; Petraccone, V.; Artimagnella, S.; Ruiz de Ballesteros, O.; *Macromol. Symp.*, **2001**, *166*, 157.
[4] Guerra, G.; Milano, G.; Venditto, V.; Musto, P.; De Rosa, C.; Cavallo, L.; *Chem. Mater,* **2000**, *12*, 363.
[5] In the preliminary characterization of s-PMMS (cf. ref 1) the diffraction profiles of similar samples were interpreted as indicative of clathrate forms.
[6] V. Petraccone, O. Tarallo, V. Califano *Macromolecules* submitted.