Macromol. Symp. ***2001****, 166, 157-163*

Influence of the guest molecules on the structural organization of the clathrates of syndiotactic poly(*p*-methylstyrene)

Domenico La Camera*, Vittorio Petraccone, Silvana Artimagnella, Odda Ruiz de Ballesteros

Dipartimento di Chimica, Università di Napoli "Federico II"
Via Mezzocannone 4, 80134 Napoli, Italy

SUMMARY: The influence of the shape and size of guest molecules on the structural organization of the α and β class clathrates of syndiotactic poly(*p*-methylstyrene) is described, through the analysis of the packing model proposed for the crystal structures of the clathrate forms containing *o*-dichlorobenzene and tetrahydrofuran. Preliminary data of the crystal structure of the s-PPMS clathrate containing benzene and a comparison with the crystal structure of the clathrate forms of syndiotactic polystyrene are also presented.

Introduction

Recently, it has been found that syndiotactic poly(*p*-methylstyrene) (s-PPMS) and syndiotactic polystyrene (s-PS) are able to co-crystallize with several molecules forming polymeric clathrates $^{1-4)}$. Some possible applications of these molecular compounds like, for instance, chemical separations and water or air purification from organic molecules have been recently pointed out $^{5,6)}$.

The clathrates of s-PPMS have been divided in two different classes (α and β) on the basis of the differences between their X-ray diffraction patterns, and of the different behavior with respect to suitable treatments involving the removal of guest molecules (e.g. annealing and/or acetone treatments) $^{2)}$. The α class includes the s-PPMS clathrates containing *o*-dichlorobenzene (*o*-DCB), *o*-xylene, *o*-chlorofenol, and *N*-methyl-2-pyrrolidone, which have similar X-ray diffraction patterns. The β class, instead, includes the clathrates containing tetrahydrofuran (THF), benzene (B), cyclohexane, cyclohexanone and 1,4-dioxane, whose X-ray diffraction patterns are similar to each other but different from those of α class clathrates. Moreover, α and β class clathrates are transformed into the crystalline forms I and II of s-PPMS respectively, upon

CCC 1022-1360/00/$ 17.50+.50/0

annealing or treatments with acetone $^{2)}$. These experimental observations suggested some structural differences between the molecular organization of the α and β class clathrates of s-PPMS. It is worth noting that the guest molecules forming α class clathrates are bigger than those of β class. Indeed, the first are *o*-substituted molecules, whereas the latter are cyclic molecules not substituted (with exception of cyclohexanone that, however, is only *mono*-substituted).

In this paper, the influence of the guest molecules on the structural organization of the two classes of s-PPMS clathrates is discussed, through the analysis of the different packing models proposed for the crystal structures of the clathrate forms of s-PPMS containing *o*-DCB $^{7)}$ and THF $^{8)}$, and through our preliminary data $^{9)}$ on the crystal structure of the s-PPMS clathrate with benzene. Moreover, the comparison with the crystal structure of the clathrate forms of s-PS permits to understand the effect, on the structures of the clathrates, of the addition to the phenyl rings of a methyl group in *para* position.

Results and discussion

All the reflections observed in the X-ray fiber diffraction pattern of the clathrate form of s-PPMS with benzene (not reported here) are accounted for an orthorhombic unit cell with constants a=19.5 Å, b=13.3 Å and c=7.7 Å. Packing energy and structure factor calculations have shown that the best agreement between the calculated and observed intensities is obtained for the space group $C222_1$ $^{9)}$. A preliminary packing model of the crystal structure of the s-PPMS clathrate containing benzene is shown in Figure 1A. The comparison between this model and that proposed $^{8)}$ for the crystal structure of the s-PPMS clathrate containing THF, shown in Figure 1B, permits to understand the structural features typical of the β class clathrates. In both the structures the guest molecules occupy cavities delimited by isomorphic helical chains and located around the 2-fold screw axes of symmetry of the lattice.

The shape and the dimension of the cavities characteristic of the β class are completely different from those of the α class clathrates. Figure 2 shows one of the two possible packing models of the crystal structure of the s-PPMS clathrate form with *o*-DCB, representative of α class.

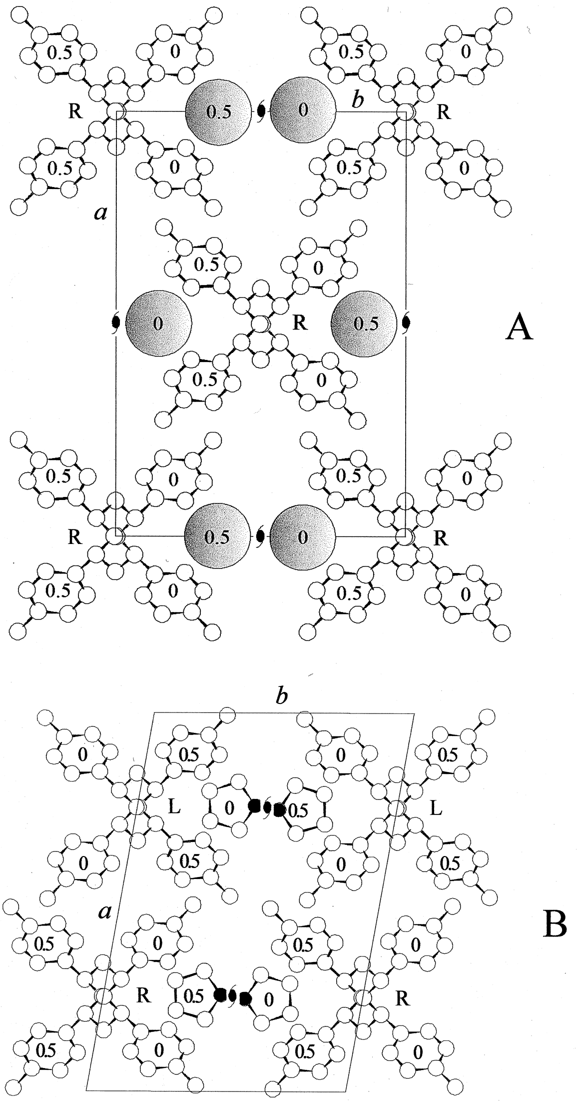

Fig. 1: Packing models proposed for the crystal structures of the s-PPMS clathrates containing benzene (A) in the space group $C222_1$ and THF (B) in the space group $P2_1/a$. Filled circles indicate the spaces in which the benzene molecules can be accommodated. R=right, L=left handed helix. The approximate z/c fractional coordinates of the barycenters of the phenyl groups and of the guest molecules are indicated. Some of the 2-fold screw axes of symmetry, normal to the ab plane, are also reported.

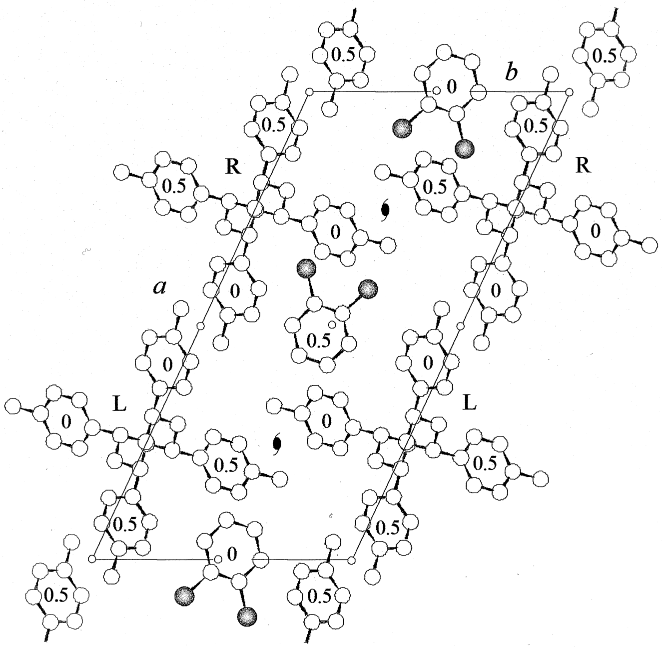

Fig. 2: Packing model proposed for the crystal structure of the s-PPMS clathrate containing *o*-DCB in the space group $P2_1/a$, showing one of the two possible positioning of the guest molecule. R=right, L=left handed helix. The approximate *z*/*c* fractional coordinates of the barycenters of the phenyl groups and of the *o*-DCB molecules are also indicated.

In this structure the guest molecules occupy cavities delimited by two enantiomorphic helical chains and located around crystallographic inversion centers.

A view of the cavities typical of the two classes of s-PPMS clathrates, showing the van der Waals encumbrance of carbon, chlorine and oxygen atoms, is reported in Figure 3. The significant differences in the packing of chains and guest molecules between the α and β classes are apparent. These differences are due to the different shape and size of the guest molecules. In fact, the molecules which forms the β class clathrates, like for instance THF, are small enough to enter into the cavities formed by the four phenyl rings of a single s-PPMS chain in the s(2/1)2 helical conformation. In this class the cavities are not isolated (see Fig. 3A), and the guest molecules could interact each other, since the distance between subsequent molecules, along the *c* axis, is about 4.0 Å. Bigger and *ortho*-substituted guest molecules, like for instance *o*-DCB, representative of the α class clathrates, cannot be accommodated in cavities generated by two adjacent isomorphic chains, as in the β class structures. Contrary to the β class, the α class clathrates presents isolated cavities (see Fig. 3B) and the distance between two subsequent *o*-DCB molecules, along the *c* axis, is about 8 Å, double than the distance between two subsequent guest molecules in the β class clathrates.

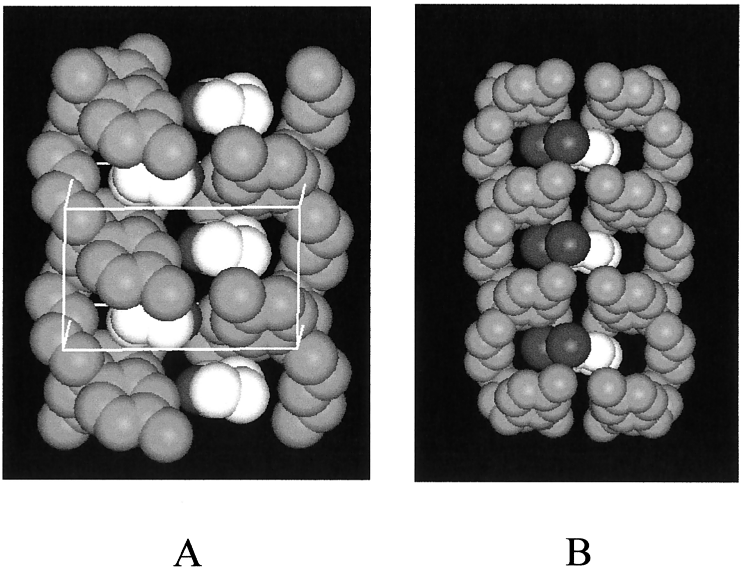

Fig. 3: Views of the cavities in the packing models of the s-PPMS clathrates containing THF (A) and *o*-DCB (B). Only the phenyl rings delimiting the cavities are represented.

It is interesting to compare the crystal structures of the s-PPMS clathrates with those of the s-PS; this permits to understand the effect, on the formation of clathrates, obtained by the addition to the phenyl rings of s-PS of a methyl group in *para* position. The crystal structures of the clathrates of s-PS containing toluene [4)], iodine [10)] and 1-2-dicloroethane [11)] have been solved so far. They are characterized by s-PS chains, in the s(2/1)2 helical conformation, similarly packed in monoclinic unit cells, according to the space group $P2_1/a$. It is remarkable that varying shape and size of the guest molecules only the volume of unit cells change, but dramatic changes in the packing of the s-PS chains, like those described for s-PPMS clathrates, have not been observed so far. In the crystal structures of the s-PS clathrates the guest molecules occupy isolated cavities formed by the phenyl rings of two adjacent enantiomorphic helices, as occurs in the s-PPMS clathrates belonging to α class. Crystal structures characterized by cavities analogous to those of the β class clathrates have not been observed so far for s-PS.

Finally, it is worth noting in the case of the clathrate of s-PPMS containing benzene, although the shape and the location of the cavities in the unit cell remain unaltered with respect to those of the clathrate with THF, an impressive change in the packing of the helices along the *a* axis occurs. In fact, in the packing model proposed for the crystal structure of clathrate with benzene *bc* layers of isomorphic chains are piled along *a* with *bc* layers of chains with equal chirality (Fig. 1A). In the model structure proposed for the clathrate containing THF, instead, *bc* layers of isomorphic chains alternate along *a* with *bc* layers of chains of opposite chirality (Fig. 1B). This difference could be a further effect of the guest molecules. In fact, the increased size of the guest molecules induces an increasing of the distance between two adjacent s-PPMS chains along the *b* axis (b_{THF}=12.7 Å, b_B=13.3 Å) and, consequently, influences the packing of the chains along the direction of *a* axis.

Acknowledgments

This work was supported by Ministero dell'Università e della Ricerca Scientifica e Tecnologica (PRIN 1998 titled "Stereoselective Polymerization: New Catalyst and New Polymeric Materials").

References

1. M. Iuliano, G. Guerra, V. Petraccone, P. Corradini, C. Pellecchia, *New Polym. Mater.* **3**, 133 (1992)
2. A. Dell'Isola, G. Floridi, P. Rizzo, O. Ruiz de Ballesteros, V. Petraccone, *Macromol. Symp.* **114**, 243 (1997)
3. A. Immirzi, F. De Candia, P. Iannelli, V. Vittoria, A. Zambelli, *Makromol. Chem., Rapid Commun.* **9**, 761 (1988)
4. Y. Chatani, Y. Shimane, T. Inagaki, T. Ijitsu, T. Yukinari, H. Shikuma, *Polymer* **34**, 1620 (1993)
5. G. Guerra, G. Milano, V. Venditto, F. Loffredo, O. Ruiz de Ballesteros, L. Cavallo, C. De Rosa, *Macromol. Symp.* **138**, 131 (1999)
6. G. Guerra, G. Milano, V. Venditto, P. Musto, C. De Rosa, L. Cavallo, *Chem. Mater.* **12**, 363 (2000)
7. V. Petraccone, D. La Camera, L. Caporaso, C. De Rosa, *Macromolecules* **33**, 2610 (2000)

8. V. Petraccone, D. La Camera, B. Pirozzi, P. Rizzo, C. De Rosa, *Macromolecules* **31**, 5830 (1998)
9. D. La Camera, V. Petraccone, S. Artimagnella, O. Ruiz de Ballesteros, *maunuscript in preparation*
10. Y. Chatani, T. Inagaki, Y. Shimane, H. Shikuma, *Polymer* **34**, 4841 (1993)
11. C. De Rosa, P. Rizzo, O. Ruiz de Ballesteros, V. Petraccone, G. Guerra, *Polymer* **40**, 2103 (1999).