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Comparative Analysis of the Clathrate Forms of Syndiotactic Polystyrene, Poly (*p*-methylstyrene) and Poly (*m*-methylstyrene)

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Summary: The crystal structures of the clathrate forms of syndiotactic polystyrene (s-PS), poly (*p*-methylstyrene) (s-PPMS) and poly (*m*-methylstyrene) (s-PMMS) containing guest molecules having widely different steric hindrance are compared in detail. Common features and differences concerning the packing of the chains, the shape and the dimensions of the cavities and the stability of the forms deprived of the guest molecules are pointed out. A new clathrate form of s-PPMS containing CS_2 is also described.

Keywords: clathrates; crystal structure; host-guest system; syndiotactic polystyrene; WAXS

Introduction

Homogeneous catalytic systems, based on titanium or zirconium compounds and methylalumoxane, have allowed producing highly syndiotactic polystyrene and substituted polystyrenes. Some of these polymers (i.e. s-PS, s-PPMS and s-PMMS) are able to co-crystallize with low molecular weight substances to form polymeric clathrates. For this class of molecular compounds some promising applications have been suggested in the field of chemical separations, in particular for water or air purification from volatile organic compounds.

A common feature of all the clathrate forms of these polymers is that the polymer chains assume a minimum energy conformation corresponding to a s(2/1)2 helix with a repetition period of 7.7 – 7.8 Å, whose steric hindrance can be very schematically delimited in a prism with a rectangular base. This conformation is characterized by an orientation of the benzene rings generating on two opposite sides of the prism hollows in which properly shaped molecules can nest, a fact that is itself particularly favourable to the formation of clathrate

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structures. On the other hand, as far as the final shape of the cavities and the packing of the chains in the crystalline clathrates are concerned, appreciable differences can be found among these three polymers. A further relevant difference between the clathrates of these three polymers concerns the removal of the guest molecules at temperatures lower than the glass transition temperature.

The present note analyzes the differences of the various clathrate forms of these polymers and presents structural data for a new clathrate of s-PPMS containing CS_2.

Clathrate Forms of s-PS

In the framework of this class of polymers, the clathrate forms of s-PS have been the first ones studied.[1] In particular, Chatani *et al.* solved the structures of the clathrate forms containing toluene[2] and iodine.[3] They also emphasized that the clathrate structures of s-PS containing other solvents (i.e. benzene, *p*-xylene, chlorobenzene and so on) are all similar to each other and are all characterized by centrosymmetric cavities delimited by enantiomorphous chains. Subsequently, the clathrate structure of s-PS containing 1,2-dichloroethane (DCE) has been described.[4] This clathrate form, that is nearly isomorphous to the others already described, represents an example of the extreme selectivity of this type of cavities towards the absorption of guest molecules, since the DCE molecules absorbed into the crystalline phase of the clathrate sample are only in the *trans* conformation.

Structural data for these clathrate forms of s-PS are reported in Table 1. The crystal structure parameters of a metastable polymorphic form of s-PS (δ form), that is nanoporous and can be obtained by removal of guest molecules from clathrate samples by suitable solvent and thermal treatments,[5] are also reported. This form is of particular importance, since it is able to rapidly absorb selectively some organic substances from various environments, also when present at low concentration.[6,7]

Figures 1.a and 1.b show two projections of the crystal structure of the clathrate form of s-PS containing DCE and of the δ form of this polymer, respectively.

Clathrate Forms of s-PPMS

s-PPMS is able to give clathrate structures containing a wide range of guest molecules. The clathrate structures containing *orto*-dichlorobenzene (*o*-DCB),[8] tetrahydrofuran (THF),[9] and benzene[10] have been completely described. New structural data concerning the clatrate form of this polymer containing CS_2 are presented here for the first time.

A distinctive feature of s-PPMS is the fact that it forms two different types of cavities in which guest molecules can be hosted; therefore, the terms α class and β class have been introduced in order to differentiate the corresponding types of clathrates. Figure 2 shows projections of the structures containing *o*-DCB and THF, representative of the two types of cavities. The first type of cavity characterizes the clathrate form containing *o*-DCB, corresponding to the α class. This cavity is very similar to that observed in the clathrate forms of s-PS, and is realized by two enantiomorphous helices correlated by an inversion center. The clathrate form containing THF shows instead the second type of cavity, corresponding to the β class, in which isomorphous chains correlated by a 2/1 screw axis delimit the cavities. In this class, guest molecules may interact since the cavities are not isolated, as in the case of α class cavities, and the distance between contiguous guest molecules is about 4 Å.

Table 1. Crystal structure parameters, number of guest molecules per chain, class and calculated density for a totally empty form for the clathrates of s-PS, s-PPMS and s-PMMS described in literature.

	Ref.	*Space Group*	*a* *(Å)*	*b* *(Å)*	*c* *(Å)*	*γ* *(deg)*	$\rho_{clathrate}$ (b)	*n* (c)	*Class*	ρ_{empty} (d)
s-PS/TOLUENE	2	$P2_1/a$	17.5	13.3	7.7	121	1.11	1	α	0.90
s-PS/IODINE	3	$P2_1/a$	17.3	12.9	7.8	120	2.05	2	α	0.92
s-PS/DCE	4	$P2_1/a$	17.1	12.2	7.7	120	1.23	1	α	0.99
s-PS δ FORM (a)	5	$P2_1/a$	17.4	11.8	7.7	117	-	-	-	0.98
s-PPMS/*o*-DCB	8	$P2_1/a$	23.4	11.8	7.7	115	1.13	1	α	0.81
s-PPMS/THF	9	$P2_1/a$	18.8	12.7	7.7	100	1.07	2	β	0.87
s-PPMS/C_6H_6	10	$C222_1$	19.5	13.3	7.7	90	1.05	2	β	0.79
s-PPMS/CS_2	-	$C222_1$	20.0	12.5	7.7	90	1.08	2	β	0.81
s-PMMS/CS_2	13	*Pcaa*	17.8	13.1	7.8	90	1.14	2	β	0.86
s-PMMS/C_6H_6	14	*Pcaa*	17.4	14.8	7.8	90	1.04	2	β	0.78
s-PMMS/*o*-DCB	14	*Pcaa*	17.3	16.4	7.8	90	1.15	2	β	0.71

(a) Crystal form obtained by removing the guest molecules from the clathrates of s-PS (see Figure 1.b).
(b) Density (g/cm^3) for a crystal of a clathrate form having the cavities completely occupied by the guest molecules.
(c) Number of guest molecules per chain in a crystal of a clathrate having all the cavities occupied.
(d) Density (g/cm^3) for a crystal of a clathrate form completely emptied by the guest molecules.

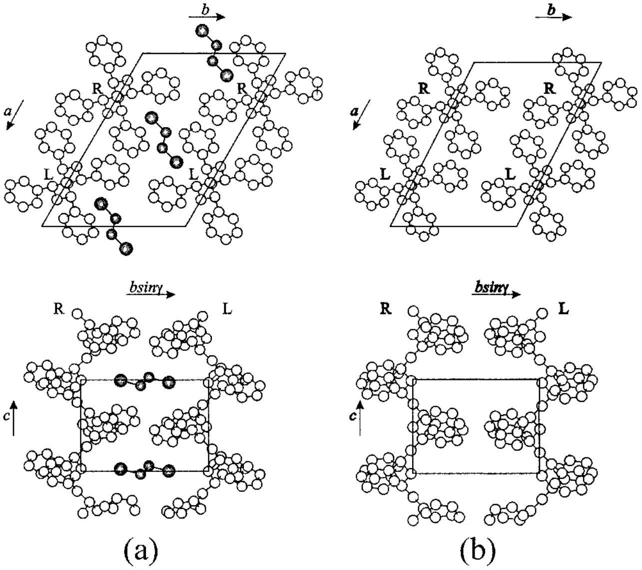


Figure 1. Schematic projections of the clathrate structure containing DCE (a) and of the pure form δ (b) of s-PS. In the lateral projection, only a couple of polymer chains, along the *a* axis, are reported. R = right-handed chain, L = left-handed chain.

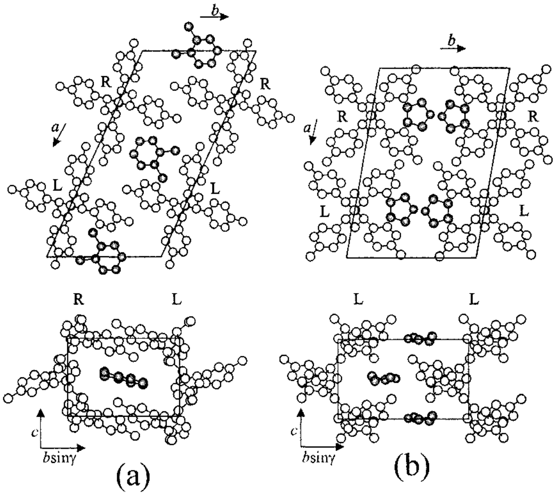


Figure 2. Schematic projections of the clathrate structures of s-PPMS containing *o*-DCB (a) and THF (b). In the lateral projection, only a couple of polymer chains, along the *a* axis, are reported. R = right-handed chain, L = left-handed chain.

The clathrate forms of s-PPMS containing benzene and CS_2 also belong to β class.

The crystalline structure of the clathrate form containing CS_2, presented here for the first time, has been deduced from a comparative analysis of the X-ray diffraction patterns of unoriented samples of the CS_2 clathrate and of the clathrate form containing benzene. The close similarity of the patterns made us assume an orthorhombic structure analogous to that already established for the clathrate form containing benzene. The position of the reflections that characterize the X-ray diffraction pattern is very well interpreted by an orthorhombic cell with axes a=20.0 Å b=12.5 Å c=7.7 Å.

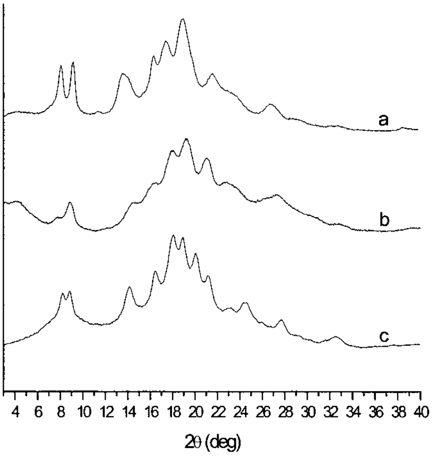


Figure 3. Experimental X-ray powder diffraction patterns of the clathrate form of s-PPMS containing benzene (a) and CS_2 (b). Calculated X-ray powder diffraction pattern for the clathrate form of s-PPMS containing CS_2 assuming a degree of crystallinity equal to 50% (c).

Through molecular mechanics calculations, assuming the same symmetry $C222_1$, we have obtained a structural model, whose simulated X-ray diffraction pattern is reported in Figure 3.c together with the experimental one (3.b). For comparison, in the same figure, the powder diffraction pattern of the clathrate form containing benzene (3.a) is also reported. The agreement between the experimental and the calculated diffraction patterns can be considered sufficiently good in order to classify this clathrate form within the clathrates of s-PPMS without making further refinements.

These last two clathrate forms show some peculiarities. First of all, although they are characterized by cavities very similar to that found, for the first time, for the clathrate with THF (and characterizing the β class), they show an orthorhombic packing of the chains. On the other hand, they represent two unusual examples of chiral crystalline phases in which all the polymer helices assume the same chirality in the lattice. Schematic projections of these structures are represented in Figures 4.a and 5.a in comparison with the corresponding clathrate structures of s-PMMS containing the same guest molecules (see next section). The structural data of the clathrates of s-PPMS are reported in Table 1.

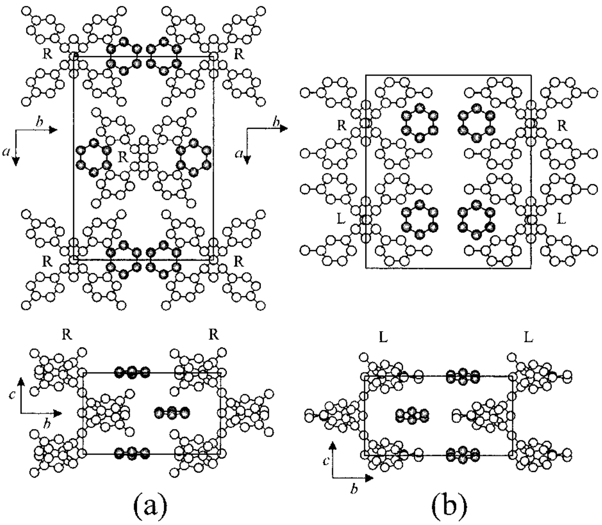
On the basis of X-ray diffraction experiments, as well as thermal treatments, it has been deduced that, for s-PPMS, clathrate forms belonging to the α class can be obtained also with other molecules with a large steric hindrance (such as *N*-methyl-2-pyrrolidone, *o*-chlorophenol, *o*-xylene), while smaller molecules (such as 1,4-dioxane, cyclohexane and cyclohexanone) induce the formation of β class clathrates.[11] It is concluded that, in the case of the clathrate forms of s-PPMS, the steric hindrance of the guest molecules determines the formation of one type of cavity or of the other.[12] Finally, it has to be noticed that, by removal of the guest molecules at any temperature, the clathrate forms of this polymer become completely amorphous or give rise to one or the other stable helical pure form of this polymer[11] that do not show any similarity with the microporous form described for s-PS.

Clathrate Forms of s-PMMS

As far as s-PMMS is concerned, it seems that the solvents that are able to induce the crystallization into clathrate forms are less numerous that for the other two polymers. In particular, only the clathrate structures containing CS_2, benzene and *o*-DCB, whose schematic projections are represented in Figures 4.b, 5.b and 6, have been described so far.[13,14]

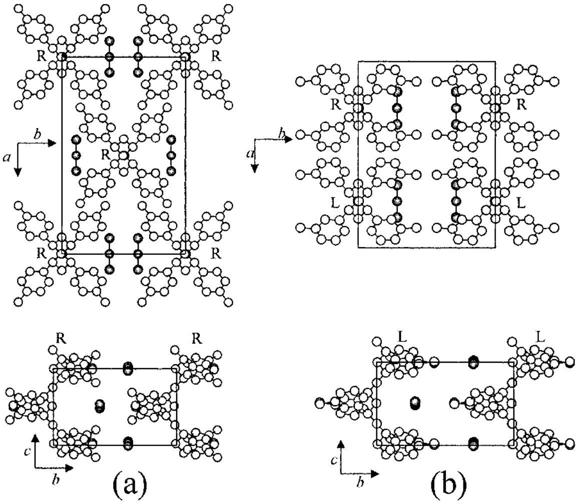
The structural data relative to these forms are listed in Table 1.

It may be noticed that all the clathrate forms of this polymer belongs to the β class despite of the great differences of the dimensions of the three guest molecules[13,14] Moreover, also in this case, by removing the guest molecules from the clathrate forms, no microporous form is generated but one of the pure forms is always obtained.[15]



(a) (b)

Figure 4. Schematic projections of the clathrate structures of s-PPMS (a) and s-PMMS (b) containing benzene. In the lateral projection, only a couple of polymer chains, along the *a* axis, are reported. R = right-handed chain, L = left-handed chain.



(a) (b)

Figure 5. Schematic projections of the clathrate structures of s-PPMS (a) and s-PMMS (b) containing CS_2. In the lateral projection, only a couple of polymer chains, along the *a* axis, are reported. R = right-handed chain, L = left-handed chain.

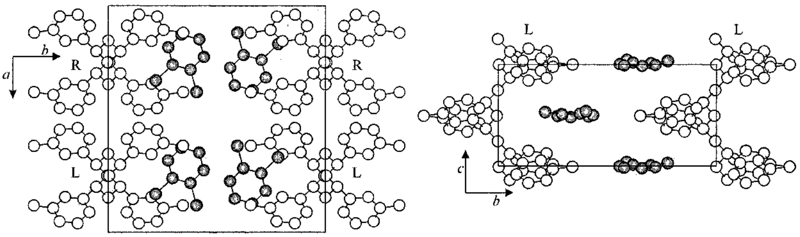


Figure 6. Schematic projections of the clathrate structures of s-PMMS containing *o*-DCB. In the lateral projection, only a couple of polymer chains, along the *a* axis, are reported. R = right-handed chain, L = left-handed chain.

Comparison and Conclusions

Despite the great similarity of the polymers that we have studied, the data presented in the previous sections show that the behaviour of these polymers is quite different with respect to the formation of clathrate forms.

s-PS give rise only to α class clathrates, while s-PMMS forms β class clathrates only. For each of these two polymers, all the known clathrates are characterized by the same symmetry (space group *P21/a* for s-PS and *Pcaa* for s-PMMS) and by an evident similarity in the lattice constants. Moreover, the formation of clathrate structures of these two polymers does not seem to be influenced by the dimension or by the shape of the guest molecule, except for the spacing between the chains forming the cavities, that coincides with the *b* axis of the unit cell for s-PMMS while in the case of s-PS is related mainly to this axis. As a matter of fact, the *a* axis, that depends primarily on the packing of the chains, remains almost unchanged.

The situation is much more complex in the case of s-PPMS. First of all, at variance from the other two polymers, s-PPMS can crystallize in both classes of clathrates. The analysis of the molecules that induce crystallization of clathrate forms in one or the other class show, in an evident way, that the choice is strictly dependent on the dimensions of the guest molecules. Small molecules (having dimensions comparable to the part of the cavity created by the chain itself, such as CS_2, THF and benzene) form β class clathrates, while larger molecules give rise to α class ones.

Moreover, it has to be noted that s-PPMS, within the β class, can crystallize with different symmetries. In particular, benzene and CS_2 clathrates crystallize in the $C222_1$ symmetry while the THF clathrate crystallizes in the *P21/a* symmetry. It is interesting to observe that the clathrate forms containing THF and CS_2, presenting cavities almost of the same dimensions (as we can see from the approximately equal values of the *b* axes that, in the case of β class clathrates, are directly proportional to the dimensions of the cavities), differ considerably for the values of the density relative to a completely emptied crystal (see Table 1). This difference of the density is to be attributed, without any doubt, to the different efficiency of the packing of the chains for the two clathrate forms. Consequently, it is surprising that the clathrate form containing CS_2 crystallize with a $C222_1$ symmetry rather than with a $P2_1/a$ symmetry.

Despite the extreme similarity of these host-guest systems, all the features we pointed out demonstrate that the influence of the factors that control the relative stability of the possible crystalline structures is scarcely predictable. Probably, in our case, an important role has to be attributed to the contribution that the interactions between the chains have in determining the total packing energy of the clathrate structures. We believe that this contribution is particularly relevant in the case of the clathrate forms of s-PS. In this respect, it may be useful to compare the densities of the emptied clathrate forms that we have examined, listed in the last column of Table 1. It is seen that the clathrate forms of s-PS are characterized by densities, relative to the packing of the chains only (without guests), appreciably higher than those of the other two polymers (to be compared with the density of the amorphous phase, always in the range 1.02-1.05 g/cm^3). Moreover, in the clathrates of s-PS the removal of the guest molecules, also in the case in which the cavities are larger, may lead through a negligible rearrangement of the chains to the packing of the δ form, that has a density not too far from the amorphous one. Consequently, the clathrates of s-PS, by removal of the guest molecules at temperatures lower than T_g, do not collapse in an amorphous phase or evolve in the thermodynamically stable γ form, at variance with the behaviours of s-PPMS and of s-PMMS.

Acknowledgements

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