Clathrates with tetrahydrofuran of styrene-*p*-methyl styrene co-syndiotactic copolymers

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SUMMARY: Clathrates with tetrahydrofuran of styrene–*p*-methyl styrene co-syndiotactic copolymers have been characterized by wide-angle X-ray scattering and differential scanning calorimetry. Stable clathrate structures with THF molecules have been observed in whole range of composition. In particular, syndiotactic polystyrene like and syndiotactic poly-*p*-methylstyrene like clathrate phases are obtained for *p*-methylstyrene contents lower and higher than 35% by mol, respectively.

Introduction

The syndiospecific homopolymerization [1-6] and copolymerization [5-7] of styrene and *p*-methyl styrene (*p*-MS) have been reported in recent years.

Several clathrate forms have been described for syndiotactic polystyrene (*s*-PS).[8-10] The crystal structures of clathrate forms including toluene,[8] iodine[9] and 1,2-dichloroethane,[10] present the same crystal monoclinic symmetry and similar dimensions of the unit cell.

At variance with *s*-PS, for poly-*p*-methylstyrene (*s*-PPMS) two different classes of clathrate forms, have been described.[11] They have been classified on the basis of X-ray diffraction patterns similarity as well as of their different polymorphic behaviors as a consequence of thermal treatments.

The crystal structures of *s*-PPMS clathrates containing tetrahydrofuran (THF) [12] and *o*-dichlorobenzene (*o*-DCB)[13] has been recently reported and the proposed models could be considered as representative of the crystal structures of the β class and of the α class clathrates, respectively.[12]

A common feature is the presence of s(2/1)2 helical chains in the monoclinic cells, according to the space group $P2_1/a$ (as for *s*-PS clathrate structures). Relevant differences are concerned with the position of the guest molecules in the unit cell. In the structure of the *s*-PPMS clathrate with *o*-DCB,[13] the guest molecules are in isolated cavities delimited by the phenyl rings of two enantiomorphic helical chains. This kind of cavities are very similar to the cavities present in the crystal structure of the clathrate forms of *s*-PS.[8-10] In the crystal structure of the clathrate of the *s*-PPMS with THF,[12] the guest molecules are small enough to

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enter into the cavity formed by the four phenyl rings of a single *s*-PPMS chain. In this structure the cavities are not isolated.

It is well known that the presence of a comonomer can influence the polymorphic behavior of a crystalline polymer.[14-17] A first structural study on syndiotactic random copolymers of styrene and *p*-MS has shown changes in the polymorphic behavior of *s*-PS after introduction of small amounts (2-20mol%) of *p*-MS comonomeric units.[16]

In this paper the crystallinity and the possible formation of clathrate structures for co-syndiotactic copolymers of styrene and *p*-MS have been investigated in the complete range of composition.

Results and discussion

The X-ray diffraction patterns of as polymerized homopolymers and copolymers (M_w in the range 3-4 10^5 u.m.a.), obtained, following the procedures described in ref. 4, at 20°C using $CpTiCl_3$ (Cp = cyclopentadienyl) and methylaluminoxane as catalysts, are shown in figure 1.

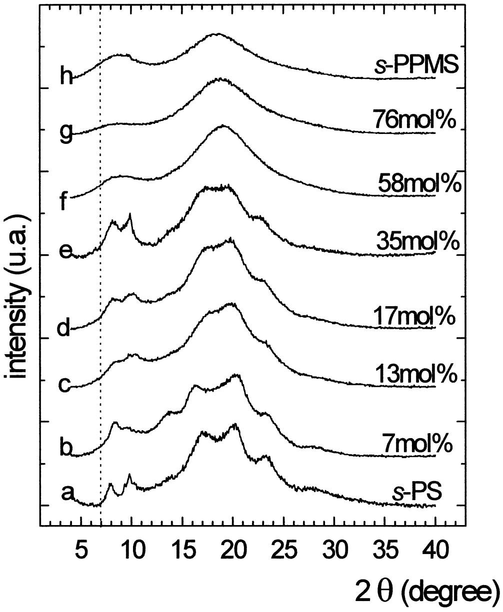

Figure 1. X-ray diffraction patterns of (Cu Kα) of as polymerized samples. The *p*-MS molar contents are indicated.

The patterns of copolymers with *p*-MS content lower than 35mol% (figure 1, b-e) are similar to that one of *s*-PS clathrates (figure 1, a).[8-10] The presence of weak and broad peaks correspond to low crystallinity and small size of crystallites.

As polymerized copolymers with higher *p*-MS content, as well as *s*-PPMS homopolymer are amorphous (figure 1, f-h).

High crystalline clathrate samples are instead obtained, in the whole range of composition, after exposure to THF vapor. The X-ray diffraction patterns of samples treated for 12h by THF are reported in figure 2.

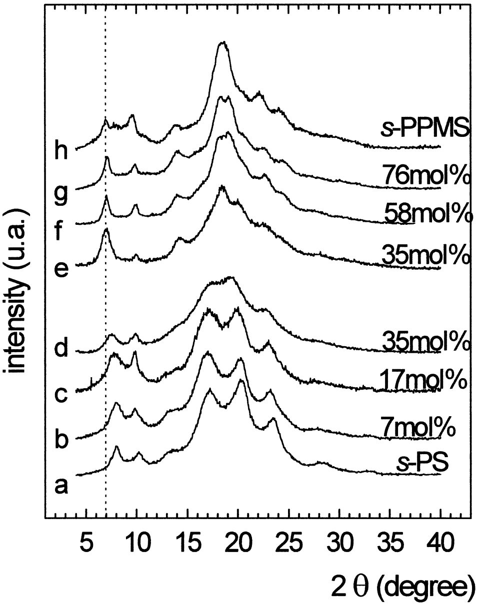

Figure 2. X-ray diffraction patterns (Cu Kα) of THF clathrate samples, the *p*-MS molar content is indicated.

Copolymers with *p*-MS content lower than 35mol% have X-ray diffraction patterns typical of the *s*-PS clathrates (figures 2, b-c).

The X-ray diffraction patterns of the samples with *p*-MS content higher than 35mol% (figures 2, f-g) are typical of the *s*-PPMS clathrate that includes THF molecules (figure 2, h) and belong to β class clathrates.

The X-ray diffraction patterns of the THF clathrate samples with *p*-MS content of 35mol% can be largely different depending on the their history. *s*-PPMS like clathrates are generally obtained (figure 2, e). *s*-PS like clathrates are, instead, obtained by THF vapor treatments of *s*-PS like clathrates with different guest molecules (e.g., as prepared samples or these samples treated by 2-butanone). For instance, the X-ray diffraction pattern of 2-butanone clathrates treated for 5 hours by THF vapor is reported in Figures 2, d. For this sample the replacement of 2-butanone by THF guest molecules has been verified by FTIR spectra.

Crystallinity indexes in the range of 25-30% have been evaluated, on the basis of the X-ray patterns of figure 2, for all the homopolymer and copolymer samples. These data indicate that the comonomeric units are able to cocrystallize into both *s*-PS like and *s*–PPMS like clathrate forms.

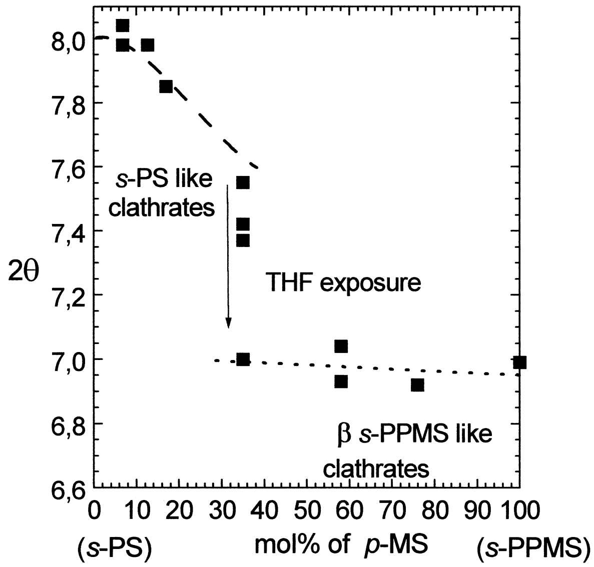

Figure 3. 2θ diffraction angles (of the region typical of 010 reflection of *s*-PS clathrates) of the THF clathrates samples as a function of *p*-MS content

For all *s*-PS like clathrates (*p*-MS content lower than 35mol%) a gradual decrease of the 2θ diffraction angle at about 7° (corresponding to the 010 reflections) with increasing *p*-MS content, is apparent (figure 3). This behavior is due to introduction of the bulky *p*-MS comonomer in the *s*-PS crystal lattice. For *s*-PPMS like THF clathrates (*p*-MS content higher than 35mol%), the 2θ diffraction angle at 7° is constant with *p*-MS content (figure 3). This indicates that the introduction in the *s*-PPMS lattice of styrene comonomer units, smaller than *p*-MS, has scarce influence on the size of crystal unit cell.

The transition temperatures corresponding to the melting of the clathrate phases (determined by endothermic peak of the first heating differential scanning calorimetry scans) and to the glass transition temperatures (determined by endothermic peak of the second heating differential scanning calorimetry scans) of the copolymer samples are reported as function of *p*-MS content in figure 4.

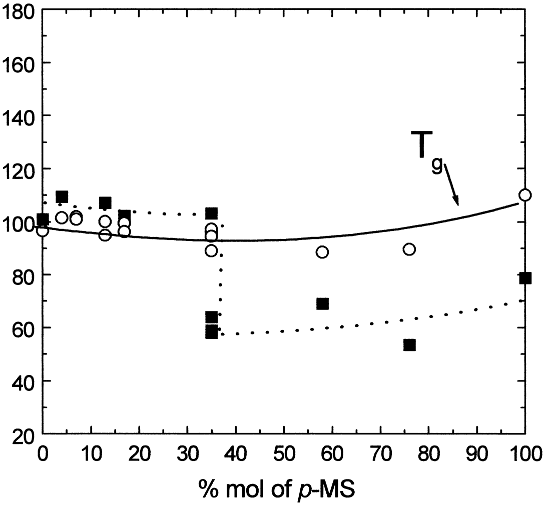

Figure 4. The maximum temperatures of stability of THF clathrates ( ) and the glass transition temperature ( ), determined by differential scanning calorimetry, as a function of *p*-MS content.

As already observed in the X-ray analysis, stable clathrate structures are obtained for the copolymer samples in the whole range of composition.

As for copolymers with *p*-MS content lower than 35mol% a transition from the clathrate to a different crystalline phase is observed. As for copolymers with *p*-MS content higher than

35mol% only the clathrate form, which transforms in the amorphous phase upon heating, is observed.

Lower clathrate transition temperatures are observed for *s*-PPMS like THF clathrates (60-70°C) with respect to *s*-PS like clathrates (100-110°C) indicating that they are less stable than *s*-PS like THF clathrates.

Conclusions

Syndiotactic copolymers of styrene with *p*-MS have been obtained for different copolymer compositions. All copolymer samples are able to form clathrates including THF molecules. The observed similar crystallinity indexes indicate that the comonomeric units co-crystallize into clathrate phases in the whole range of composition.

A *s*-PS like clathrates phase is observed for *p*-MS content lower than 35% by mol, which is stable up to 100-110°C. A *s*-PPMS clathrates phase is observed for *p*-MS content higher than 35% by mol, which trasform into the amorphous phase for heating at temperatures higher than 60-70°C.

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