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Polystyrenes in channels

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Abstract

Polystyrenes (PS) with various stereosequences have been modeled in narrow cylindrical channels corresponding to those found in polymer–inclusion compounds (ICs), such as those formed with host cyclodextrins (CDs), where the polymers reside as guests. Isotactic (i) PS is found to fit in channels with narrower diameters (D) than syndiotactic (s) PS, when both adopt conformations permitted by the Yoon, Sundararajan, Flory RIS conformational model of PSs, while atactic (a) PS can be included in channels with D intermediate to those for i- and s-PS. In ICs formed with host γ-CD and guest a-PS homopolymer and guest poly(ϵ-caprolactone) (PCL)-b-a-PS diblock copolymer it was observed that the a-PS homopolymer and the a-PS copolymer blocks were and were not included, respectively. Thus, it appears that a-PS is barely able to be threaded by γ-CD, whose internal diameter is ~8 Å. Because the channel conformers found for i- and s-PS have smaller and larger diameters, respectively, than those found for a-PS, we would expect i-PS to be complexed by γ-CD, while s-PS might not. As a consequence IC formation with γ-CD may provide a means to physically separate the stereoregular forms of polystyrene. In addition, only the mrm and rmr PS stereoisomers show channel conformations with significant probabilities, so we suggest that in situ polymerization of styrene monomer in the narrow channels of its IC formed with γ-CD might produce a new stereoregular form of PS with regularly alternating m and r diads.

Keywords: Polystyrenes; gamma-cyclodextrin; Channel conformer

1. Introduction

Certain small molecules like urea, perhydrotriphenylene (PHTP), cyclotriphosphazines, and cyclodextrins (CDs) may act as hosts in the complexation with guest polymers to form crystalline guest polymer–host inclusion compounds (ICs) [1]. A common feature of polymer–host-ICs is the restrictive environment provided by the narrow channels of the host crystalline lattice for the guest polymer chains. For example, the internal diameters of the cyclo-amylose bracelets α-, β-, and γ-CDs range from ~5–10 Å. During the formation of polymer–CD-ICs, CDs must be threaded over the polymer chain to form host CD stacks, each including highly extended guest polymer chains, which are, in most instances, separated from neighboring guest polymers by the host CDs.

Polymer–host-ICs have at least three important attributes. First, the unique environment provided to the guest polymers by the host crystalline lattice make observations of the conformations and motions of the included chains important for understanding the conformations and mobilities of polymers in their ordered bulk phases, such as in their crystalline domains. Comparison of the conformations and mobilities of the extended and isolated polymer chains in the narrow channels of their ICs with those observed in their bulk crystals can permit an assessment of the relative importance of inherent chain flexibility and cooperative interchain interactions to the mobilities of polymers in their ordered bulk phases [2]. Second, because the guest polymers in polymer–host-ICs are extended and isolated from neighboring guest polymers, when they are coalesced from their ICs, the resulting consolidated bulk phase may have a structure, morphology, and even constituent chain conformations different from those found in bulk polymer samples formed from their disordered, randomly coiling, and possibly entangled melts and solutions [3]. In addition, when two or more chemically distinct polymers are included in a common IC and then are subsequently coalesced, the consolidated polymer blend that is produced may be intimate and well-mixed, unlike similar blends formed by casting from their common solutions or obtained by melt

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blending [4]. Third, because a polymer–host-IC can only be formed if the potential guest polymer is able to be accommodated in the narrow IC channels, formation of polymer–host-ICs can be utilized to separate polymers with different extended chain cross-sections resulting from distinct microstructures, such as stereosequences [5,6] (isotactic, syndiotactic, atactic) and linear and branched architectures, for example.

In this investigation, we seek to characterize the ability of polystyrenes (PSs) with different tacticities to form ICs with the host γ-CD. Previously, we have observed that when an IC was formed between the diblock copolymer poly(ϵ-caprolactone) (PCL)-PS, the PCL blocks were included [7], while the atactic (a) PS blocks were not. On the other hand, when a solution containing both a-PS and bis-phenol-A polycarbonate (PC) was used to from a γ-CD-IC, both polymers were included [4], and following coalescence from their common γ-CD-IC, well-mixed a-PS/PC blends were produced. Thus, it appears that a-PS with its large pendant phenyl side chains is near the edge of being able to be threaded by γ-CD rings to form a-PS–γ-CD-IC crystals. As a consequence, here we report a search for extended PS conformations narrow enough to be included in the channels of γ-CD-IC, where PS stereosequence is explicitly accounted for.

2. Search for PS channel conformers

In Fig. 1, the PS tetramer fragment tested for inclusion in cylindrical channels with radii r_c is presented. The search was begun in the same manner as that conducted previously [8] for polypropylene (PP) channel conformers, by calculating the x, y, z coordinates of all atoms in the PS tetramer fragment as expressed in the Cartesian coordinate system affixed to the middle (○) of the first C–C backbone bond. Of course, these atomic coordinates depend on one or more of the set of seven backbone rotation angles φ_1, φ_2, φ_3, φ_4, φ_5, φ_6, φ_7. The Yoon, Sundararajan, Flory (YSF) [9] conformational model for PS was adopted. As can be seen in the Newman diagrams of PS shown in Fig. 2, each of the backbone bonds is reasonably limited to the *trans* (t) and one *gauche* (g) conformations, so the YSF rotational isomeric state (RIS) model of PS is a two conformational state description, where φs are restricted to $\varphi_t \sim 20°$ and $\varphi_g \sim 100°$, respectively, to relieve somewhat the steric interactions between the substituted backbone carbon CH and the sidechain phenyl ring (Φ) or backbone CH_2 groups present in the perfectly staggered rotational states $\varphi_t, \varphi_g = 0°, 120°$. We have chosen to let each backbone rotation angle adopt values $\varphi = 10$, 30, 90, and 110° to permit a greater range of PS conformations in our search for channel conformers. As a consequence, $(4)^7 = 16{,}384$ conformations in all were tested for each of the six possible PS tetramer fragments [mmm (see Fig. 1), rrr, mmr = rmm, rrm = mrr, mrm, rmr].

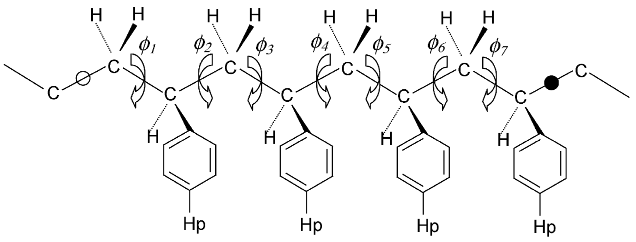

Fig. 1. PS tetrad fragment (mmm = dddd) used in the search for channel conformers.

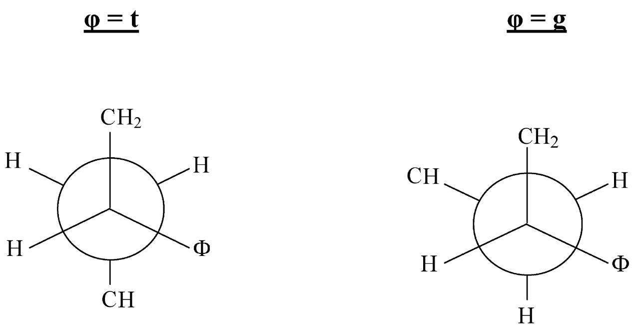

Fig. 2. Newman diagrams illustrating the t (0°) and g (120°) PS conformations.

The x, y, z tetramer atomic coordinates calculated for each conformation ($\varphi_1, \varphi_2, \varphi_3, \varphi_4, \varphi_5, \varphi_6, \varphi_7$) were transformed to a Cartesian coordinate system x', y', z' whose z'-axis connects the mid-points(○,●) of the terminal bonds. The radius, r, of the corresponding cylindrical coordinate system with coincident z'-axis is $r = ({x_2}' + {y_2}')^{1/2}$, and $\theta = \arctan(y'/x')$ for each fragment atom. If the r's for all fragment atoms are $\leq r_c$, then the conformation is considered a channel conformer. To this point our search for PS channel conformers is analogous to that conducted previously [8] for PP stereoisomers. However, unlike the ~1.53 Å distance between the backbone CH and sidechain CH_3 carbons in PP, the distance between the backbone CH carbon and the proton (Hp) at the *para*-position of the attached phenyl ring is ~5.5 Å, which approximates the distance between the carbon atoms terminating five backbone carbon fragments of PS adopting the extended $\varphi_i, \varphi_{i+1} = t, t$ conformation. Because of the highly asymmetric nature of the PS repeat units caused by the large phenyl ring sidechains attached to the backbone, we had to modify our search for PS channel conformers.

This was accomplished by making the following adjustments to the coordinate systems for all channel conformers tested that had one or more phenyl groups whose Hp atoms protruded ($r > r_c$) from the cylindrical coordinate system z', r, θ defined above and used previously in our PP modeling [8]. For the most protruding phenyl group, i.e. whose $r = r_{max} > r_c$, the z'-axis was shifted along the x'- and y'-axes by amounts $\Delta x'$ and $\Delta y'$, respectively, until $r \leq r_c$. Then the same $\Delta x'$ and $\Delta y'$ increments were added to the x' and y' coordinates of all remaining atoms in the PS tetramer fragment, their r's were recalculated, and tested against $r \leq r_c$. Each tetramer conformation with all atoms passing this test was then considered a channel conformer.

The probability of each channel conformation identified above was obtained from the statistical weight matrices $U(\varphi_i, \varphi_{i+1})$ described in the YSF [9] RIS model for PS, where $U(\varphi_i, \varphi_{i+1}) = U'$ for bond pairs on either side of the substituted backbone carbon atom and $U(\varphi_i, \varphi_{i+1}) = U_{\mathrm{m}}''$ or U_{r}'' for the bond pairs between substituted backbone carbon atoms belonging to m = meso and r = racemic PS diads, respectively. Statistical weights $\eta = 0.8\{\exp[400(\mathrm{cal/mol})/RT]\}$, describing the preference of $\varphi = t$ over $\varphi = g$ first-order interactions (see Figure 2), and ω or $\omega' = 1.3[\exp(-2000/RT)]$ and $\omega'' = 1.8[\exp(-2200/RT)]$ to account for the second-order interactions between CH_2 and CH_2 or phenyl groups (Φ) and between two phenyl groups, respectively, were used as suggested by the YSF RIS model for PSs. The sum of statistical weights, or the partition function z, for the i-PS (mmm) tetramer displayed in Fig. 1 is $z_{\mathrm{mmm}} = U_1''U'U_{\mathrm{m}}''U'U_{\mathrm{m}}''U'U_{\mathrm{m}}''$, where U_1'' is the first row of U_{m}''. The probability that the mmm tetramer adopts the all *trans* conformation, for example, is obtained from the product of statistical weights $[U_1''(1)U'(1,1)U_{\mathrm{m}}''(1,1)U'(1,1)U_{\mathrm{m}}''(1,1)U'(1,1)U_{\mathrm{m}}''(1,1)]$ after dividing by z_{mmm}.

3. Results and discussion

In Table 1, we present a summary of our search for potential channel conformers for the tetrad stereoisomers of PS. The most striking observation to be made is the disparity in the channel sizes (D) required to accommodate the different PS stereoisomers. While the i-PS stereoisomer (mmm) requires an ~8.5 Å channel, the s-PS stereoisomer (rrr) cannot be accommodated in a cylindrical channel with a $D < 10.5$ Å, or an ~25% greater cross-section than that of the narrowest channel conformer found for the i-PS stereoisomer.

Also note that with the exception of the mrm and rmr PS tetrads, the probabilities of channel conformers found for the PS stereoisomers are very small. In this connection, it should be remembered that if each of the 16,384 conformations permitted for a PS tetrad were equally likely, then each would have a probability of 1/16,384 = 0.00006. In contrast, the probability for the mrm PS stereoisomer channel conformer is nearly two orders of magnitude higher. In addition to the mrm isomer, only the rmr tetrad channel conformer has a substantial probability (0.00005). This would imply that the free-radical polymerization of styrene in the narrow channels of its IC formed with γ-CD, for example, might produce a PS with alternating m and r diads rather than a-, i-, or s-PSs. This suggestion is made by analogy to our previous modeling [8] of PP stereoisomers in channels with diameters ($D \sim 5.5$ Å) appropriate to ICs formed with PHTP and urea hosts. There it was observed that all PP tetrad stereoisomers could be included in a 5.5 Å channel, but the probability of the channel conformers for the rrr isomer, or s-PP, were again at least two orders of magnitude greater than those of the other stereoisomeric channel conformers. When propylene monomer was formed into an IC with PHTP and then free-radically polymerized in situ, the resulting PP was found [10] to be predominantly syndiotactic, as suggested by our modeling of PP stereoisomers in channels appropriate to PHTP-ICs.

Table 1
PS stereoisomer channel conformations

Stereoisomer	Channel diameter, Å	Conformer	Probability
mmm	8.5	tttttgg and gttttgg	0.0000003
mrm	9.0	ttgttgt	0.0012
rrm	9.2	tgttgtt	0.0000002
mmr	9.3	tttttgg	0.000007
rmr	10.4	tttggtt	0.00005
rrr	10.5	tgttttg and tgttgtt	0.000005

As a consequence of our modeling the tetrad stereoisomers of PS in narrow cylindrical channels, we can make the following suggestions: (i) while the formation of a γ-CD-IC with i-PS should be possible, it appears that s-PS may not be included in the ~8.5 Å channels of the γ-CD-IC crystalline lattice, and so the process of IC formation with γ-CD may be used to separate stereoregular i-PS from s-PS; and (ii) the free-radical initiated polymerization of styrene monomer in the narrow channels of the styrene-γ-CD-IC, if it is possible, is likely to produce an unusual PS with alternating m and r diads and therefore repeating mr, and rm, triads, which has never been reported.

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