Chemical Separations by Nanoporous Crystalline Samples of Syndiotactic Polystyrene

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SUMMARY: Chemical separations based on absorption phenomena into syndiotactic polystyrene samples including a nanoporous crystalline phase are described. These separation phenomena are due to the presence into the crystalline phase of cavities whose size and shape have been studied through sorption experiments relative to linear hydrocarbons and through calculation procedures relative to the available crystalline structures of different polymorphic and clathrate forms of syndiotactic polystyrene.

Introduction

Syndiotactic polystyrene (s-PS) presents a very complex polymorphic behavior, which, making some simplification, can be described in terms of two crystalline forms, α and ß, containing planar zig-zag chains and two forms, the γ and δ, containing s(2/1)2 helical chains1). In particular, the term "δ-form" has been used to indicate different clathrate structures1), for which the intensities and the precise locations of the crystalline reflections in the X-ray diffraction patterns change with the kind and amount of the included guest molecules1-5). The crystalline structures of the clathrate forms including toluene3), iodine4) and 1,2 dichloroethane5) have been characterized by X-ray diffraction studies. The clathrate forms can be obtained by solution crystallizations as well as by sorption of suitable compounds in amorphous or semicrystalline s-PS samples being in the α, or γ form2-5). By removal of the guest molecules from the different clathrate forms, by suitable solvent treatments6,7), an empty δ form can be obtained, whose nanoporous crystal structure has been recently described8). Sorption studies from liquids and vapors into the

CCC 1022-1360/99/$ 17.50+.50/0

empty δ form have shown that it is able to absorb some organic substances also when present at very low activities[9,10], thus suggesting this thermoplastic material as promising for applications in chemical separations as well as in water purification. In this paper some examples of chemical separations driven by enthalpic or entropic effects are presented. Moreover, the possibility of size-exclusion separations, based on these nanoporous polymeric materials, has been explored by sorption experiments of linear aliphatic hydrocarbons from hexane to decane. Furthermore the empty space available for guest molecules in the nanoporous crystalline phase of s-PS has been evaluated by applying a numerical procedure to available crystalline structures, of different polymorphic and clathrate forms of syndiotactic polystyrene.

Separation experiments

All reported experiments refer to s-PS powder samples presenting surface areas of nearly 4 m^2/g . Sorption kinetics of DCE from saturated (8100 ppm) and 100 ppm aqueous solutions by s-PS samples are shown in Fig. 1.

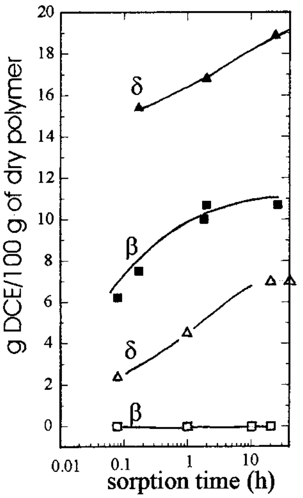

Fig. 1 Absorption kinetics of DCE from saturated (8100 ppm, filled symbols) and diluted (100 ppm, empty symbols) aqueous solutions by powder s-PS samples, including β or δ crystalline phases.

Besides samples in the empty δ form also samples in the β crystalline form, which absorbs low molecular mass compounds only into the amorphous phase[11,12)], are considered. It is apparent that for the case of the δ form powders, few minutes are already sufficient to get substantial DCE absorptions from water solutions while the DCE sorptions from the β form powders are much smaller and slower. In particular, for low DCE activities, the sorption from β form powders, that is from the amorphous s-PS phase, is negligible.

Another example of chemical separation involving a preferential absorption by empty s-PS samples of a chlorinated hydrocarbon is the separation of the azeotropic solution acetone-chloroform (84.5 wt % acetone). In both cited examples the preferential sorption of the halogenated compound would be essentially enthalpy driven. In fact, for halogenated compounds stronger van der Waals interactions involving the host phenyl rings and the guest halogen atoms are possibly present [13)].

On the other hand, separation of cyclic volatile organic compounds from non-cyclic analogous can be also be performed. For instance, for short sorption times, essentially only cyclohexane is absorbed from hexane-cyclohexane solutions. The preferential sorption of the cyclic molecules is expected to be associated essentially to entropic effects. In fact, the enthalpy gains associated with host-guest interactions are expected to be similar for linear and cyclic aliphatic hydrocarbons while the entropy reduction is expected to be higher for linear hydrocarbons, which, as a consequence of inclusion in the host cavities, should reduce drastically their conformational freedom.

As regards chemical separations due to size exclusion, here we report some preliminary results relative to sorption experiments on the *n*-alkane series from *n*-hexane up to *n*-decane. The X-ray diffraction patterns of s-PS empty δ form powders after 1 hour of immersion in different alkanes are shown in Figure 2.

The X-ray diffraction patterns relative to samples treated with *n*-decane, *n*-nonane and *n*-octane remain essentially identical to that one of the empty δ form. On the other hand substantial changes occur for the samples treated with *n*-heptane and *n*-hexane for which the appearance of $\bar{2}10$ reflection (at $2\theta \approx 10°$ for CuKα radiation), indicated by arrows in figure 2, and the reduction of 010 ($2\theta \approx 8°$), 101 and $\bar{1}11$ reflections (both at $2\theta \approx 13°$) clearly indicate the clathrate formation[6,8)].

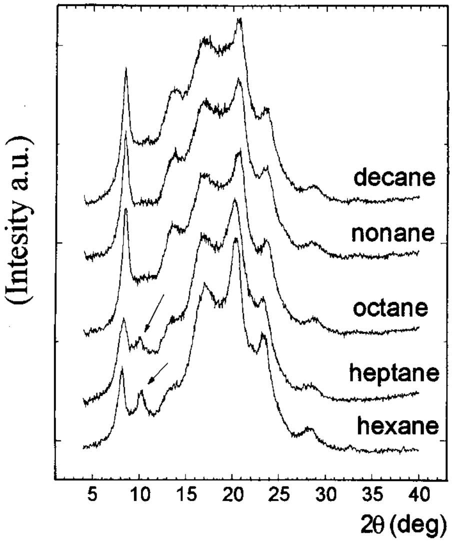

Figure 2 X-ray diffractions patterns of s-PS empty δ form powders after 1 hour of immersion in different *n*-alkanes

These results suggest that the volume of the cavities of the nanoporous crystalline form of s-PS could be intermediate between the van der Waals volumes of *n*-heptane (142 $Å^3$) and *n*-octane (161 $Å^3$) molecules. This evaluation of the cavity volume is in good agreement with the ability of the nanoporous samples of s-PS to clathrate naphtalene, whose molecules have a van der Waals volume of 145 $Å^3$.

Shape and volumes of the cavities

The fraction of empty volume (Φ_{empty}) in the unit cell can be defined on the basis of the volume which can be filled by an hypothetical probe sphere of radius r . For the α[14], β[15] and empty δ crystalline[8] forms of s-PS, the fractions of empty volume, calculated as a function of r, are reported in Figure 3.

The differences between the curves of Figure 3 are relatively small for low values of r (< 1Å) while become large for r values in the range 1-2 Å , corresponding to van der Waals radii of common atoms.

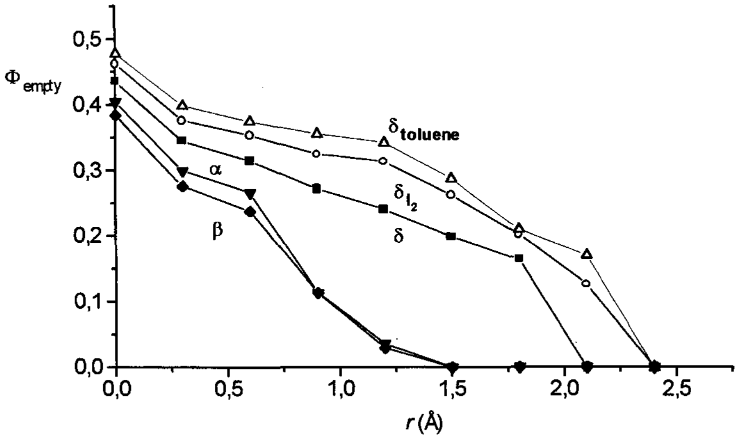

Figure 3 Calculated fraction of empty volume for unit cells of different polymorphic forms of s-PS (filled symbols). For two clathrate structures the hypothetical empty space calculated by ignoring the guest molecules (empty symbols) are reported

The region of empty space calculated for the empty δ form, by assuming r=1.8Å, that is a typical van der Waals radius of chlorine atoms or methyl groups$^{16)}$, is shown as a dotted region in the view parallel to the chain axes of figure 4.

The figure shows that this empty space corresponds to finite cavities (two per unit cell) centered on the center of symmetry of the crystal structure, whose boundary is essentially defined by ten phenyl rings.

This cavity has a volume of nearly 120 Å^3 (for r=1.8 Å) and its maximun dimension is nearly 8.1Å (essentially along the a–b direction) while its minimum dimension is nearly 3.4 Å (essentially along the a+b direction). Following the same procedure for the clathrate structures with iodine$^{3)}$ and toluene$^{4)}$, the shape and volumes of the hypothetical cavities generated by ignoring the presence of the guest molecules, have been evaluated (empty symbols in Figure 3. These are only hypothetical empty spaces which, however, give a measure of the possible expansion of cavities of the nanoporous crystalline structure, as a consequence of clathration.

For all the considered clathrate structures, the calculated cavities present shapes and orientations similar to those found for the empty δ form (Figure 4) while the volume evaluated for r=1.8 Å increases up to 160 Å^3.

These results are in good agreement with the cavity volume estimated on the basis of the sorption experiments of the previous section.

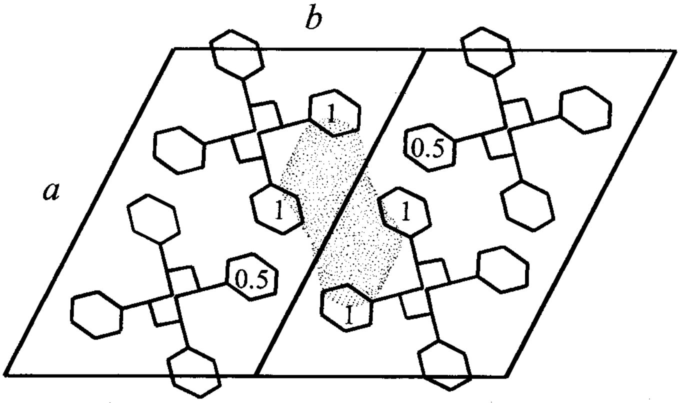

Figure 4 Model of packing for the crystal structure of the empty δ form of s-PS. Two cells along *b* are reported. The dotted region corresponds to the cavity as calculated for a probe sphere radius of 1.8 Å. The approximate fractional coordinates of the heights of the phenyl rings surrounding the cavity are also shown.

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