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Nanoporous Crystalline and Cross-Linked Polymeric Materials

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ABSTRACT: Cosyndiotactic copolymers of styrene (S) and divinylbenzene (DVB) have been obtained by a catalytic system based on $CpTiCl_3$. These copolymers have been characterized as for their composition, configuration, cross-linking (solubility and swelling), and polymorphism. The paper is mainly devoted to the influence of the chemical cross-linking on the formation, thermal transitions, and guest sorption of the nanoporous δ phase. Chemically cross-linked s-PS exhibiting a high degree of crystallinity of the nanoporous δ phase and the related high sorption ability can be achieved by copolymerizations with DVB content lower than 2 mol %. These cross-linked, and hence insoluble, nanoporous crystalline samples can be relevant for molecular separations, mainly in organic media.

Introduction

Polymeric adsorbents have found, for almost half a century, several applications in industrial and analytical processes. The most successful adsorbent polymers are those based on amorphous polystyrene cross-linked with divinylbenzene, P(S−DVB), which present high porosity and large surface area and have been largely used as adsorbent resins as well as matrixes for the preparation of ion-exchange resins.[1]

In recent years, a new class of polymeric adsorbents has been proposed which presents high porosity in crystalline phases rather than in amorphous phases.[2] These materials are based on un-cross-linked semicrystalline syndiotactic polystyrene (s-PS), i.e., a stereoregular polymer obtained by coordination polymerization catalysis[3] and exhibiting a very complex polymorphic behavior.[4] In particular, two crystalline phases of s-PS, i.e., the deeply studied δ phase[5] and the recently discovered ε phase,[6] constitute the first examples of polymeric crystalline phases with a density lower than the corresponding amorphous phase, and their empty space is distributed as isolated cavities and channels, respectively. Materials presenting these nanoporous s-PS phases are promising for applications in chemical separations (mainly air/water purification)[2] as well as in molecular sensorics.[7]

These nanoporous crystalline s-PS materials present several advantages with respect to the traditional nanoporous amorphous P(S−DVB). In particular, by suitable polymer processing, films can be obtained exhibiting three different kinds[8] of uniplanar orientation[9] as well as axial or uniplanar−axial[9] orientations of their nanoporous crystalline phases. Guest transport studies have shown that, at low guest activities, the sorption occurs nearly only by the nanoporous crystalline phase and that the guest diffusivity can be controlled by the kind of orientation of the host crystalline phase.[10] It is worth adding that these nanoporous crystalline phases are readily transformed into cocrystalline phases[11] by sorption of suitable guest molecules and that polymer cocrystalline films presenting active guest molecules have been proposed as advanced materials, mainly for optical applications.[12]

The nanoporous crystalline s-PS materials, however, are less solvent resistant than the nanoporous cross-linked amorphous P(S−DVB). In fact, nanoporous crystalline s-PS samples are swollen and even dissolved by several concentrated chlorinated and/or aromatic compounds, mainly at temperatures higher than 50 °C, i.e., not far from the polystyrene glass transition temperatures. This can be a problem for molecular separation processes in organic media. Of course, for s-PS, the solubility can be eliminated, and the swelling can be reduced by chemical cross-linking.

In this paper, copolymerizations of styrene and DVB have been conducted by syndiospecific catalytic systems based on $CpTiCl_3$, aiming to obtain cosyndiotactic copolymers between S and DVB, i.e., s-P(S−DVB), and looking for sorbent materials being both cross-linked and nanoporous crystalline. The obtained copolymers have been characterized, mainly as for their polymorphic behavior and, in particular, as for their ability to form the nanoporous δ phase. Moreover, cross-linked δ form samples have been characterized as for their thermal behavior, degree of crystallinity, and related ability to absorb low-molecular-mass guest molecules from diluted solutions.

Experimental Section

General Polymerization Procedure. All the operations were performed under a nitrogen atmosphere by using conventional Schlenk-line techniques. Styrene and divinylbenzene were purchased from Aldrich and distilled over calcium hydride under reduced pressure and stored at −20 °C. Toluene was refluxed over sodium diphenylketyl for 48 h and distilled before use. Methylalumoxane was purchased by Witco and used, as a solid, after solvent distillation. $CpTiCl_3$ was purchased from Aldrich and used as received.

Styrene Homopolymerization. Polymerizations of styrene were carried out by the following procedure: A 100 mL round-bottom flask, equipped with a magnetic stirrer, was charged with MAO (based on Al) = 7.0×10^{-3} mol, styrene (10 ml, 8.6×10^{-2} mol), and toluene (15 ml). The flask was thermostated at 50 °C, and the run was started by introducing 1.6×10^{-5} mol of $CpTiCl_3$ complex dissolved in toluene (2 mL). The temperature of the reaction was kept constant during the run. Polymerization was stopped by introducing few milliliters of methanol, and the mixture was poured into acidified ethanol. The polymer was

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recovered by filtration, washed with fresh ethanol, and dried in vacuum at 60 °C.

Styrene−Divinylbenzene Copolymerizations. Copolymerizations were carried out by the following general procedure: in a 100 mL round-bottom flask, equipped with a magnetic stirrer, were charged with MAO (based on Al) = 7.0×10^{-3} mol, styrene (10 mL, $8.6{\times}10^{-2}$ mol), divinylbenzene, and toluene as specified in Table 1. The flasks were thermostated at 50 °C, and the runs were started by introducing 1.6×10^{-5} mol of $CpTiCl_3$ complex dissolved in toluene (2 mL). The temperature of the reactions was kept constant during the runs. The copolymerizations were stopped as usual, and the copolymers were recovered by filtration, washed with fresh ethanol, and dried in vacuum at 60 °C. The filtrates were extracted by water, and the organic phases were analyzed by ^{13}C NMR in order to determinate the amount of unreacted comonomers. Thus, it was possible establish the molar composition of the copolymers.

Extraction of the Soluble Polymer Fraction. The synthesized polymers were fractionated by exhaustive extractions with boiling chloroform in a Kumagawa extractor.

The degree of swelling of the insoluble polymer fractions has been evaluated as the ratio between the weight of the gel when filled by chloroform (immediately after the described extraction procedure) and the weight of the gel desiccated under vacuum at room temperature for 24 h.

Measurements. *^{13}C NMR Analysis.* ^{13}C NMR spectra were recorded on an AV 300 Bruker spectrometer operating at 75 MHz, using an inverse-gated-decoupling mode in order to eliminate the nuclear Overhauser effect (NOE) and, therefore, to assume that the areas of the resonances of the ^{13}C NMR spectra are proportional to the amounts of the different carbons. The following ^{13}C NMR acquisition parameters were used: acquisition time AQ=1.2 s, pulse delay D1=4 s, and pulse angle P1 = 8.25 μs (90°). The s-PS sample was prepared by dissolving polymer (40 mg) into tetrachlorodideuterioethane (0.5 mL). The spectrum was recorded at 100 °C using hexamethyldisiloxane (HMDS) as internal chemical shift reference. The concentration of r diads in the polystyrene was determined as reported in ref 3c. The organic phases were analyzed into $CDCl_3$ (0.5 mL). The spectra were recorded at RT using tetramethylsilane (TMS) as internal chemical shift reference.

FTIR Analysis. Infrared spectra were obtained at a resolution of 2.0 cm^{-1} with a Tensor 27 Bruker spectrometer equipped with deuterated triglycine sulfate (DTGS) detector and a Ge/KBr beam splitter. The frequency scale was internally calibrated to 0.01 cm^{-1} using a He−Ne laser. 32 scans were signal-averaged to reduce the noise.

Equilibrium sorption of 1,2-dichloroethane (DCE) from aqueous solutions was obtained by measurements of FTIR absorbances of conformationally sensitive peaks,[13] by using calibration curves analogous to those described in refs 13a, 13c, and 13d based on thermogravimetric (TGA) measurements.

X-ray Diffraction Analysis. Wide-angle X-ray diffraction patterns with nickel-filtered Cu Kα radiation were obtained, in reflection, with an automatic Bruker powder diffractometer. The degree of crystallinity of homopolymer and copolymer samples (being all unoriented) was determined resolving the diffraction patterns into two areas, A_c and A_a, that can be taken as proportional to the crystalline and the amorphous fraction of the polymer, respectively, and calculated through the expression $X_c = 100 \times A_c/(A_c + A_a)$, according to the classical Hermans−Weidinger method.[14]

DSC Analysis. Differential scanning calorimetry (DSC) measurements were carried out with a DSC 2920 TA Instruments in a flowing nitrogen atmosphere, at heating rate of 10 °C/min. For the examined cocrystalline samples, the quality of the first heating scans is poor, due to the large endothermic peak associated with the guest evaporation. As a consequence, the glass transition temperature (T_g) of the polymers has been determined in second heating scans, i.e., for completely amorphous samples as obtained after a first heating scan up to 300 °C followed by cooling at room temperature at a rate of 10 °C/min.

Results and Discussion

Copolymerization Tests and Copolymer Characterization. The polymerization experiments were performed at 50 °C, using a constant concentration of catalyst and styrene. The as-prepared polymers were extracted exhaustively with boiling chloroform in a Kumagawa extractor, for determining the amounts of the insoluble fractions and the swelling of polymers. The molar composition of the copolymers was evaluated by ^{13}C NMR of the organic phases containing the unreacted monomers. Copolymers with divinylbenzene molar fraction (X_{DVB}), in the range 1.7%−8.5%, have been achieved.

The main results of our polymerization studies are collected in Table 1. It is clearly apparent the occurrence of an ideal random copolymerization between the two monomers. In fact, the feed composition is nearly coincident with the copolymer composition for the entire explored range.

Table 1 also shows that the polymerization yields remain high for the whole considered composition range. The small yield decrease observed with increasing the amount of divinylbenzene in the feed could be due to lower solubility of the cross-linked growing chains, which could make difficult the migration of the monomers in the reaction medium.

All the as-polymerized copolymer samples are cross-linked and the fraction soluble in $CHCl_3$ is only 5 wt % for the sample with the minimum DVB content and negligible for higher DVB content. The cross-linking density, of course, increases with the DVB content as shown by the swelling with $CHCl_3$ of the insoluble fraction, which gradually decreases with the DVB content from 1.5×10^3% to 0.5×10^3% (sixth column of Table 1). The increase of cross-linking density also determines the substantial increases in the glass transition temperatures, which are reported in the ninth column of Table 1.

The ^{13}C NMR spectrum of the chloroform-soluble fraction of the s-P(S−DVB) copolymer with 1.7% of DVB clearly shows that the content of syndiotactic diads is higher

Table 1. Information Relative to Runs of Copolymerization of Styrene (S) with Divinylbenzene (DVB)[a]

sample[b]	X_{DVB}[c] (feed) (%)	yield (g)	X_{DVB}[c] (copol) (%)	insoluble fraction in $CHCl_3$ (%)	swelling (%)	degree of crystallinity of the clathrate samples[d] (%)	degree of crystallinity of the δ form samples[d] (%)	T_g[e] (°C)
s-PS	0	6.5	0	0		37	37	93
s-P(S−DVB) 1	1.7	5.5	1.7	95	1.5×10^3	33	27	96
s-P(S−DVB) 2	4.2	4.5	4.2	100	1.0×10^3	30	21	101
s-P(S−DVB) 3	5.9	4.3	5.8	100	0.6×10^3	25	13	109
s-P(S−DVB) 4	8.5	4.0	8.5	100	0.5×10^3	0	0	133

[a] DVB molar composition in the feed, polymerization yield. Information relative to the obtained copolymers: DVB molar composition, insoluble fraction, degree of swelling, degree of crystallinity, and glass-transition temperature. [b] Polymerization conditions: solvent toluene, total volume 25 mL; $CpTiCl_3 = 1.6 \times 10^{-5}$ mol; MAO (based on Al) $= 7.0 \times 10^{-3}$ mol; styrene in the feed $= 8.6 \times 10^{-2}$ mol; temperature = 50 °C; time = 5 min. [c] X_{DVB} = mol of DVB/(mol of S + mol of DVB). [d] Determined by X-ray diffraction. [e] Determined by differential scanning calorimetry.

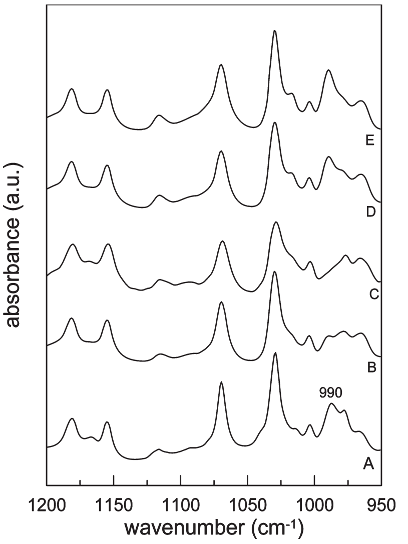

Figure 1. FTIR spectra in the wavenumber range 1200−950 cm^{-1} of an homopolymer s-PS film containing 2 mol % of nonreacted DVB (A), a copolymer with 1.7 mol % of DVB (B), a copolymer with 1.7 mol % of DVB obtained in similar conditions of (B) but for longer polymerization times (C), and a copolymer with 4.2 mol % (D) and 5.9 mol % of DVB (E) obtained for the polymerization time used for the sample of curve B.

than 98%, as for the s-PS homopolymer. This indicates the formation of cosyndiotactic S−DVB copolymers.

The occurrence of chemical cross-linking is possibly determined by coordination to the metal center and insertion into a cosyndiotactic growing chain of pendant *p*-vinyl groups of already formed copolymer chains. To evaluate the fraction of residual *p*-vinyl pendant groups (i.e., of those not involved in the cross-linking reaction), the copolymer samples of Table 1, after complete removal of residual unreacted monomers by supercritical CO_2 extraction,[15] have been examined by Fourier transform infrared (FTIR) analysis.

In Figure 1 are reported the FTIR spectra of the copolymer with 1.7 mol % of DVB (curve B) as well as of the copolymer having the same DVB content, as obtained in similar conditions but for longer polymerization times (curve C). The FTIR spectrum of a homopolymer s-PS sample having 2 mol % of nonreacted DVB (curve A) as well as the spectra of copolymers with 4.2 mol % (curve D) and 5.9 mol % (curve E) of DVB are also shown in Figure 1.

The peak typical of the vinyl groups located at 990 cm^{-1},[16] which is well apparent in the homopolymer s-PS film containing 2 mol % of nonreacted DVB (curve A) is barely detectable for the copolymer having 1.7 mol % of DVB obtained after short polymerization times (curve B) and is essentially absent for the copolymer having the same amount of DVB but obtained after longer polymerization times (curve C). For copolymers having higher DVB contents, the 990 cm^{-1} vinyl peak is instead clearly apparent (curves D and E).

These results clearly show that for suitable polymerization conditions, at least for the copolymer with the lowest DVB content, most *p*-vinyl groups are involved in the cross-linking reaction.

Crystallinity of the As-Prepared and Extracted Copolymers. The X-ray diffraction patterns of the as-polymerized samples of Table 1, shown in Figure 2, indicate that, for DVB content lower than 6 mol %, the S−DVB copolymers present a crystallinity only slightly reduced with respect to that one observed for the s-PS homopolymer (seventh column of Table 1). In particular, the patterns of Figure 2A−D are typical of clathrate cocrystalline phases of s-PS with the styrene monomer.[15a] Thermogravimetric scans indicate that the residual monomer content, in the homopolymer and copolymer samples, is in the range 11−15 wt %. In this respect, it is worth adding that, for the s-PS homopolymer, the styrene guest corresponds to 25 mol % of the cocrystalline phase, i.e., to nearly 9 wt % of the semicrystalline sample.

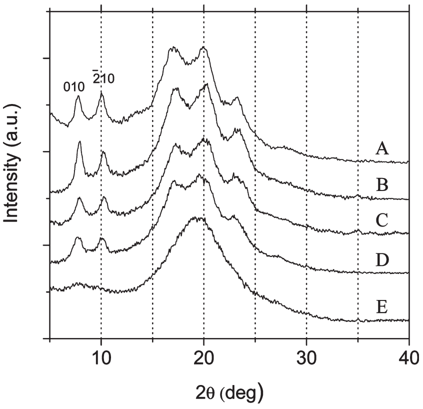

Figure 2. X-ray diffraction of as-polymerized samples: s-PS homopolymer (A); s-P(S-DVB) copolymers with 1.7 mol % (B), 4.2 mol % (C), 5.9 mol % (D), and 8.5 mol % (E) of DVB.

For DVB content lower than 6 mol %, not only the crystallinity but also the correlation lengths of the crystallites (at least in the directions perpendicular to the helical polymer axis, as evaluated by the width of the (010) and ($\overline{2}10$) diffraction peaks located at $2\theta_{Cu\,K\alpha} \approx 7.9°$ and 10.5°, respectively) remain essentially unaltered. This indicates that the cosyndiotactic configuration, clearly observed by ^{13}C NMR spectra for the soluble fraction, is also present in the cross-linked insoluble fraction and also suggests that a substantial fraction of the $-CH{=}CH_2$ pendant groups can be accommodated in the cocrystalline structure.

For the highest DVB content (8.5 mol %), the sample is essentially amorphous (Figure 2E). It is worth noting that, for other syndiotactic copolymers of styrene, the native clathrate crystallinity is maintained up to a comonomer content as high as 30 mol %.[17] The more difficult crystallization of s-P(S−DVB) copolymers, for high comonomer content, is of course due to the increase of the cross-linking density, reducing the length of the crystallizable stretches as well as their mobility.

The X-ray diffraction patterns of the as-prepared samples of Figure 2A−D, after 15 h of extraction by supercritical CO_2,[15] are shown in Figure 3A−D, respectively. It is well known that this extraction procedure, for the s-PS homopolymer, leads to a complete guest removal from cocrystalline phases and to formation of the nanoporous δ phase, as clearly shown by the 010 reflection becoming more intense and being shifted from $2\theta_{Cu\,K\alpha} \approx 7.9°$ to $2\theta_{Cu\,K\alpha} \approx 8.4°$ ($\underline{d} =$ 1.06 nm) and by a nearly complete disappearance of the $\overline{2}10$ reflection, being located for the clathrate with styrene at $2\theta_{Cu\,K\alpha} \approx 10.5°$ (compare Figure 2A and Figure 3A). As for the s-P(S−DVB) copolymers, the extraction procedure with CO_2 produces, as usual, a complete guest removal from the cocrystalline phase, as pointed out by thermogravimetric analyses. However, differently from the case of all known s-PS δ-clathrate and intercalate cocrystalline phases, for the s-P(S−DVB) copolymers, the $\overline{2}10$ is clearly visible also after complete guest extraction and the intensity ratio between the $\overline{2}10$ and 010 reflections increases with the DVB content (Figure 3B−D).

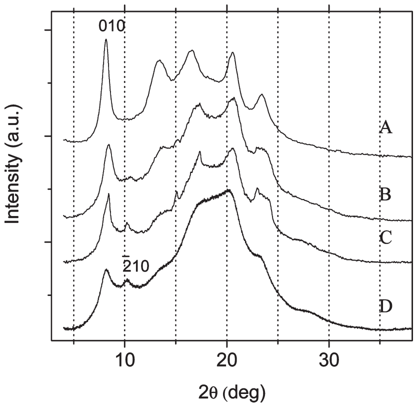

Figure 3. X-ray diffraction of as-polymerized samples of Figure 2A−D after extraction by supercritical CO_2: s-PS homopolymer (A); s-P(S-DVB) copolymers with 1.7 mol % (B), 4.2 mol % (C), and 5.9 mol % (D) of DVB.

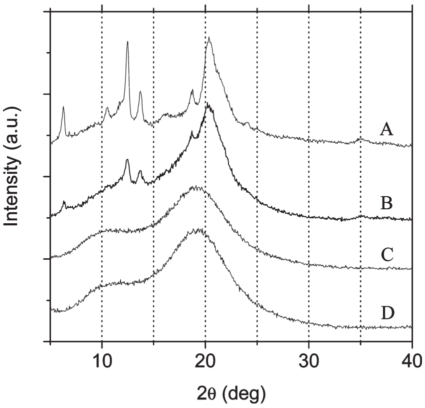

Figure 4. X-ray diffraction patterns of the as-polymerized samples of Figure 2A−D, after sudden annealing at 220 °C for 12 h: s-PS homopolymer (A); s-P(S-DVB) copolymers with 1.7 mol % (B), 4.2 mol % (C), and 5.9 mol % (D) of DVB.

These results can be easily rationalized by assuming that, in the clathrate phase, a small fraction of the cavities is occupied by the vinyl pendant groups in *para* positions of the phenyl rings, which of course cannot be removed by extraction procedures. In this respect, it is worth noting that the molar content of pendant vinyl groups for the copolymer of Figure 2B−D is expected to be smaller than the average comonomer content (in the range 1.7%−5.9%) while in the δ phase the number of the cavities is equal to 25% of the monomeric units of the crystalline phase. Hence, the crystalline cavities including pendant vinyl groups are expected to be always less than 20%.

The degree of crystallinity, as evaluated on the basis of the X-ray diffraction patterns of Figures 2 and 3 for the as-polymerized and extracted samples, is reported in the seventh and eighth columns of Table 1, respectively. It is apparent that the guest extraction procedure, which transforms δ-clathrate phases in nanoporous δ phases, occurs with some crystallinity loss, which markedly increases with the DVB comonomer content. For instance, for the sample with 5.9 mol % of DVB the degree of crystallinity decreases from 25% down to 13% (compare Figure 2D with Figure 3D).

A substantial crystallinity loss, as a consequence of guest removal procedures leading to δ-clathrate → δ-empty transitions, has been also observed for other cosyndiotactic copolymers of styrene with *para*-substituted styrenes.[17]

In this respect it is worth adding that, as usual for s-PS homopolymer[18] and copolymer samples,[17] the higher degrees of crystallinity of the cocrystalline phases can be easily restored by suitable guest sorption procedures.

Crystallinity of the Annealed Copolymers. For s-P(S−DVB) copolymers with DVB content higher than or equal to 4.2 mol %, all the attempts to obtain different crystalline phases by annealing of clathrate or of nanoporous δ phases were unsuccessful. Only for the copolymer with DVB content of 1.7 mol %, both γ[8a,8d,19] and α[21] phases can be obtained by annealing at 120 °C and subsequent annealing at 180 °C, respectively. Moreover, for this copolymer sample also the β phase[20] can be obtained, as usual, by sudden annealing at high temperature of the clathrate sample.[4a] Just as an example, the X-ray diffraction patterns of the as-prepared samples of Figure 2A−D, after annealing at 220 °C for 12 h, are shown in Figure 4A−D, respectively. The selected annealed procedure produces β phases only for the homopolymer and for the comonomer with lower DVB content, with a degree of crystallinity of 40% and 15%, respectively (see also Figure 5) .

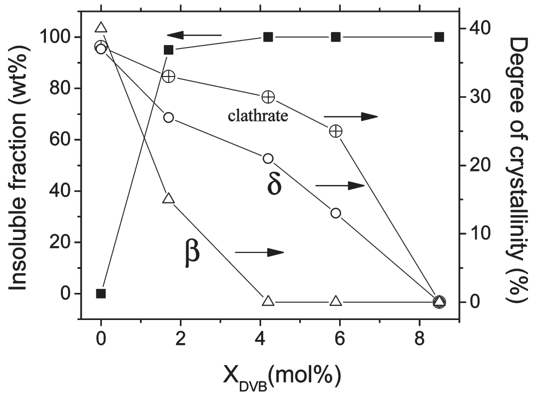

Figure 5. Polymer-insoluble fraction in $CHCl_3$ (■, left scale) and degree of crystallinity (right scale) of the native cocrystalline (⊕), of the desiccated nanoporous δ (○), and of the trans-planar β (Δ) samples, versus the S−DVB copolymer composition.

Previous studies of the polymorphic behavior of cosyndiotactic copolymers of styrene with *para*-substituted styrenes have already shown that the *para*-phenyl ring substitution destabilizes[17] the crystalline phases with respect the cocrystalline phases and the dense γ phase ($\rho \approx 1.07$ g/cm^3)[22] with respect to the less dense α phase ($\rho \approx 1.03_4$ g/cm^3).[21] However, both for copolymers with *p*-methylstyrene and *p*-chlorostyrene, the nanoporous δ phase ($\rho \approx 0.98$ g/cm^3)[5a] remains definitely less stable than the α phase. In particular, the empty δ phase has been obtained only for *p*-methylstyrene and *p*-chlorostyrene content lower than 10 mol %, while the α phase has been observed at least up to comonomer content as high as 30 mol %. The present study shows instead that, for the s-P(S−DVB) copolymers with a DVB content higher than 1.7 mol %, the only achievable s-PS crystalline phase is the lowest density nanoporous δ phase. This is possibly due to its ability to accommodate, in its crystalline cavities, the bulky vinyl pendant groups of the DVB comonomer units.

Sorption of Organic Molecules from Dilute Aqueous Solutions. The data relative to the polymer cross-linking (insoluble fraction in $CHCl_3$) and to the degree of crystallinity of the native cocrystalline or desiccated nanoporous δ samples (fifth, seventh, and eighth columns of Table 1, respectively) have been compared in Figure 5. The plot clearly shows that a high degree of cross-linking, associated with high degree of crystallinity of the nanoporous δ phase, can be achieved for

DVB comonomer content not far from 2 mol %. These insoluble copolymers, exhibiting the nanoporous δ phase, can be easily anticipated as sorbent materials suitable for molecular separations.

In particular, the equilibrium uptake of 1,2-dichloroethane (DCE) from diluted aqueous solutions, for the extracted samples of Figure 3, has been investigated. The choice of DCE is motivated by the additional information, which comes from its conformational equilibrium. In fact, as described in detail in previous papers,[13] since essentially only its trans conformer is included into the clathrate phase while both trans and gauche conformers are included in the amorphous phase, quantitative evaluations of vibrational peaks associated with these conformers allow to establish the amounts of DCE confined as guest in the clathrate phase or simply absorbed in the amorphous phase. The choice of DCE was also motivated by its presence in contaminated aquifers and by its resistance to remediation techniques based on reactive barriers containing Fe(0).[23]

The DCE equilibrium uptake, as obtained by FTIR measurements, from a 50 ppm aqueous solution by the homopolymer of Figure 3A is nearly 5 wt %, i.e., close to the values reported for different s-PS δ-form samples (films,[10b] powder or aerogels[2f]). The DCE sorption of the s-P(S−DVB) copolymer samples of Figure 3B,D, presenting 1.7 and 5.9 mol % of DVB, is close to 3 wt % and lower than 0.5%, respectively. Moreover, the DCE equilibrium sorption is negligible for all the amorphous or β-form copolymer samples, like for instance those of Figure 4.

The FTIR analysis also shows that, as already well known for DCE sorption in the nanoporous δ form homopolymer samples,[13] also for the δ form s-P(S−DVB) copolymer sample of Figure 3B the 1234 cm^{-1} peak relative to the trans DCE conformer is largely predominant over the 1284 cm^{-1} peak of the gauche DCE conformer. This clearly indicates that most DCE molecules are absorbed as guest into the cavities of the nanoporous crystalline phase of the cross-linked polymer.

Conclusions

Cosyndiotactic copolymers of styrene and DVB, with comonomer molar content in the range 1.7%−8.5%, have been obtained by using a polymerization catalytic system based on $CpTiCl_3$. The as-polymerized copolymer samples are cross-linked, and the fraction soluble in $CHCl_3$ is only 5 wt % for the sample with the minimum DVB content and becomes negligible for higher DVB content. A FTIR analysis has shown that, for the copolymers with low DVB content, most *p*-vinyl groups are involved in the cross-linking reaction.

The copolymers exhibiting a comonomer content lower than 6 mol % present a high degree of crystallinity (comparable to that one of the s-PS homopolymer) in the native clathrate cocrystalline phase and, after guest removal, can be obtained in the nanoporous δ crystalline phase. On the other hand, the γ and α crystalline phases as well as the thermodynamically stable β phase have been obtained only for the copolymer with the lowest DVB content (1.7 mol % of DVB).

The reduced stability of all the crystalline phases with respect to the δ nanoporous phase for s-P(S−DVB) copolymers is an unprecedented phenomenon and is possibly due to the ability of the δ phase to accommodate in its crystalline cavities the residual pendant *p*-vinyl groups, as clearly suggested by high intensity ratios between the $\bar{2}10$ and 010 reflection, also after complete guest removal procedures.

Combined FTIR and thermogravimetric analyses have shown that the cross-linked δ form s-P(S−DVB) samples present a high sorption capacity of low-molecular-mass guest molecules, also from dilute solutions. In particular, δ form samples with 1.7 mol % of DVB are able to absorb, from 50 ppm aqueous solutions, up to 3 wt % of 1,2-dichloroethane, essentially only as guest of the crystalline cavities of the nanoporous δ phase.

In summary, chemically cross-linked s-PS exhibiting the nanoporous δ phase and its high sorption ability can be easily achieved by syndiospecific copolymerization of S with a minor amount of DVB (lower than 2 mol %). The achieved insolubility of the nanoporous sorbent material can be relevant for molecular separations in organic media.

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