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Studies progress of preparation, properties and applications of hyper-cross-linked polystyrene networks

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Abstract Hyper-cross-linked Polystyrene (H-PS) are prepared by an extensive post-cross-linking of linear polystyrene in solution or poly(styrene-*co*-divinylbenzene) in a highly swollen gel state using bifunctional alkylating agents in the presence of Friedel-Crafts catalyst. H-PS resins differ from conventional porous polymer materials due to their unusual pore structure and outstanding swelling performances in thermodynamically good and poor solvent. In this paper, recent studies progress of preparation, properties especially physical properties and various applications are presented.

Introduction

Hyper-cross-linked polystyrene (H-PS) is microporous, low-density materials and represents a new class of polymeric networks. It was introduced by Davankov and co-workers using a novel method to prepare porous polystyrene materials in 1970s [1, 2]. The novel method involved an extensive post-cross-linking of linear polystyrene in solution or poly(styrene-*co*-divinylbenzene) in a highly swollen gel state using cross-linking agents. During the post-cross-linking, the styrenic precursors were swollen in a strongly solvating media such as 1,2-dichloroethane (DCE), accompanied by a Friedel-Crafts catalyst and a cross-linking agent, then heat was applied to the reactive system. Various bifunctional compounds can be used as cross-linking agent, e.g., monochlorodimethyl ether (MCDE), 1,4-*bis*-chloromethyldiphenyl (CMDP). After post-cross-linking reaction, a large number of rigid bridges were incorporated into the polystyrene chains. As a result, the products with extremely high cross-linking degree were obtained. From then on, the formation conditions, the pore structure and various applications of H-PS networks have been the research subject for many years [3, 4].

H-PS networks distinguished them from traditional styrene-divinylbenzene (St-DVB) copolymers in two important properties. First, H-PS networks are materials with considerably small pore size, very high surface area and porosity. Moreover, the higher the cross-linking degree of the networks is, the greater the specific surface area. Second, in spite of high cross-linking density, the networks almost exhibit the same ability to be swollen in thermodynamically good solvent, such as toluene and tetrahydrofuran, and in precipitating media, such as methanol and water [5, 6]. These excellent performances provide potential applications as improved sorbent for organic vapors [7], for recovering organic compounds from waste water [8–10], for removal of toxic trace metal [11], as ion-exchange resins [12], and packing materials for liquid chromatography [13]. Indeed, such materials are now available from several companies, such as Purolite International in the UK and USA, Dow Chemical in the USA, Jiangsu N&G Environmental Technology Co Ltd in China.

Davankov and co-workers [14–18] have extensively studied the preparation methods, the pore structure, various properties and applications of H-PS. Recently, Sherrington et al. [5, 6, 19] synthesized styrenic precursors via incorporating the third monomer of vinylbenzyl chloride (VBC), and obtained the H-PS networks with ultrahigh surface area by the following Friedel-Crafts reaction. The objective of this manuscript is to present recent research developments of H-PS networks achieved in recent years.

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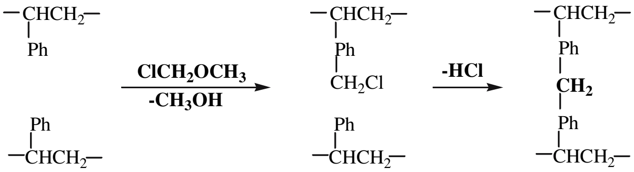
Preparation of H-PS networks

Preparation of H-PS networks includes two steps: synthesis of styrenic precusors and post-cross-linking of the precursor resins. In general, styrenic precursors are produced by traditional suspension polymerization. In order to introduce numerous rigid bridges into the precursors, monochlorodimethyl ether (MCDE) [18], 1,4-*bis*-chloromethyldiphenyl (CMDP) [1], *p*-xylylene dichloride (XDC) [3], dimethylformal (DMF) [15], tris-(chloromethyl)-mesitylene (CMM) [3] as well as *p, p′-bis*-chloromethyl-1,4-diphenylbutane (DPB) [34] have been used as cross-linking agents. Under appropriate temperature, a molecule of cross-linking agent can alkylate two (or three for CMM) phenyl rings in the presence of Friedel-Crafts catalysts (i.e., $FeCl_3$, $SnCl_4$). The hyper-cross-linking mechanisms of the first two cross-linking agents are shown as follow.

In the first case



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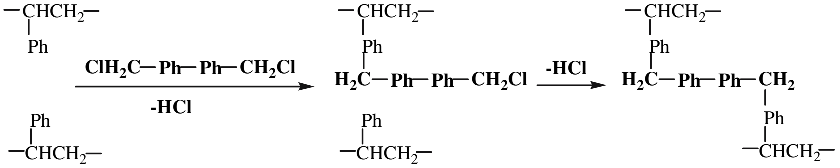


Cross-linking agents and Friedel-Crafts catalysts are homogeneously distributed throughout the whole reactive system before the hyper-cross-linking reaction. It is different from preparation of conventional copolymer networks that phase separation is not occurred during the post-cross-linking [4]. As the cross-linking reaction proceeds, more and more methylenes or other cross-linking groups are incorporated into the polymer chains to form bridges between phenyl rings. The initial solution is rapidly converted into a gel due to abrupt increasing of viscosity. As a consequence, the pre-existing intermolecular conformations in the networks are fixed and preserved via rigid bridges. The resulting resins exhibit an extremely high cross-linking density. After post-cross-linking reaction, the solvent, the unreacted cross-linking agents and the catalysts are removed via washing and extracting process.

Recently, Sherrington and co-workers [5, 6, 19] developed the H-PS networks through incorporating the third monomer of VBC into polymer chains. Gel-type or porous precursors are synthesized by traditional suspension polymerization or surfactant-free emulsion polymerization. And then, the precursors are swollen in DCE for several hours before the Friedel-Crafts catalyst are added. They investigated the effect of Lewis catalyst, reaction time and reaction media on the specific surface area of the final H-PS networks. The unreacted double bonds of poly(divinylbenzene) can be also utilized to further cross-linking, and the surface area and the pore size of the resulting species are on par with that of H-PS networks [20]. Our research group also prepared the H-PS networks using Sherrington's method, and evaluated the role of porogen used in synthesizing the VBC-DVB porous precursors and its influence on the final H-PS species.

Properties of H-PS networks

Pore structure of H-PS networks

The specific surface area of H-PS resins is much higher than that of conventional St-DVB copolymers. With the number of rigid bridges increasing, the specific surface area rises and achieves a relatively high value of 1,000 ~ 1,500 m^2/g, sometimes even up to 1,800 m^2/g for a higher cross-linking degree [4]. In addition, the value is also related to the type of cross-linking agents and the weight fraction of DVB in the monomer mixtures [3]. The H-PS networks prepared by Sherrington et al. [6] showed the specific surface area as high as 2,090 m^2/g, and $FeCl_3$ is the much more active Lewis acid catalyst for the hyper-cross-linking reaction than $AlCl_3$ and $SnCl_4$. Remarkably, the microporous structure is extremely well-developed after only 15 min reaction in DCE at 80 °C. The pore volume of H-PS resins is rather small for the most rigid networks cross-linked by MCDE, although the value increases on raising the cross-linking degree.

The values of the surface area and the pore volume suggest that almost all of pores inside H-PS networks are micropores. Research of H-PS pore structure by gel permeation chromatography indicated that the micropores are homogeneous, and the pore size lies in the range of about 1 nm, furthermore, there are no pores with diameter larger than 5 nm [21]. It has been demonstrated that porosity of H-PS networks is little affected by the synthetic conditions such as molecular weight of polystyrene and reaction media. However, concentration of starting polystyrene was proved to be a more important factor for porosity of H-PS networks [9]. This case is different for H-PS networks produced from the swollen St-DVB copolymer, whose porosity strongly relies on the amount of DVB in monomer mixtures [17]. Sherrington et al. [6] used gel-type (nonporous) and porous DVB-VBC resins as precursors to produce H-PS resins via Friedel-Crafts reaction. Figure 1 presents the internal morphologies of the resins before and after hyper-cross-linking reaction. They demonstrated that the H-PS resins prepared from gel-type and porous precursors have unimodal and bimodal pore size distribution, respectively.

More detailed information about specific surface area, pore volume, pore size and their measurement techniques of H-PS networks were given in reference [4], so it is not iterated here.

Physical properties of H-PS networks

It is well-known that amorphous linear polymers have three physical states: glassy, rubbery and viscous-flow states. After a large number of rigid bridges are introduced between the linear polymer chains, mobility of the chains will be restricted. However, H-PS networks are materials in a non-classical physical state due to the fact that the resins are shown to belong neither to typical glassy materials nor to typical elastomer [22]. The H-PS resins exhibit high deformation ability with no characteristics of glassy state from –70 °C to 300 °C, but show two fundamentally important features of the rubberlike state, namely large values of deformations and reversibility of deformations. Still, H-PS networks cannot be ascribed to materials in rubberlike state, because the non-elastic part of deformation requires a long heating of the resins or treating the sample with a solvent. Such kind of hindered relaxation is not characteristic of typical rubbers [22]. Moreover, the cross-linking degree (~100%) has not remarkable influences on the mechanical behavior of the H-PS resins [2]. Figure 2 provides a comparison of thermomechanical properties between traditional St-DVB and H-PS resins. In addition, the apparent density of H-PS networks produced from cross-linking St-DVB copolymer with MCDE lie in the range of 0.72–1.12 kg/m^3 [23]. Interestingly, the apparent density of the resins decrease with degree of post-cross-linking increasing, which is a trend opposite to the role of initial DVB-type crosslinks. Besides, H-PS networks exhibit unusual dilatometric properties in the range of 100–220 °C when cross-linking degree is far beyond 100%, this is followed by a sharp shrinking at higher temperature. The former is due to increased vibration intensity of the networks and partial relaxation of inner stress, and the latter is attributed to partial oxidation and degradation of polymer chains. However, the degradation is not accompanied by any loss in weight of the polymer but only results in a transformation into more dense conventional nonporous materials [23]. Many researches indicated that the unusual mobility of H-PS networks should be attributed to their strained, rigid openwork structure.

As was documented above, one of the outstanding properties of H-PS resins is the excellent swelling ability with any liquid and gaseous media, regardless the thermodynamic affinity of the media to the networks. Research results showed that swelling capacity of H-PS networks varies inversely with the concentration of DVB in the starting precursor resins. Furthermore, the swelling capacity of the resins based on St-DVB copolymers is distinctly less than that of polymers prepared from linear polystyrene [23]. Figure 3 presents the swelling tendency of H-PS networks in methanol, which is a typical precipi-

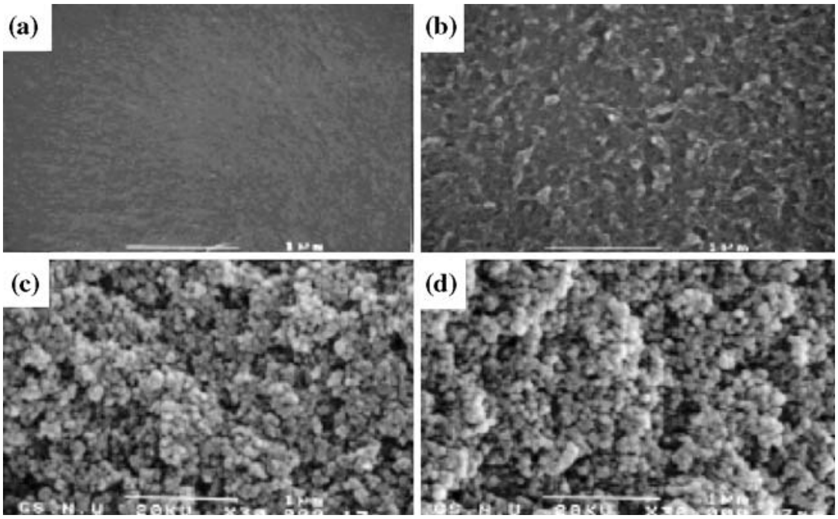
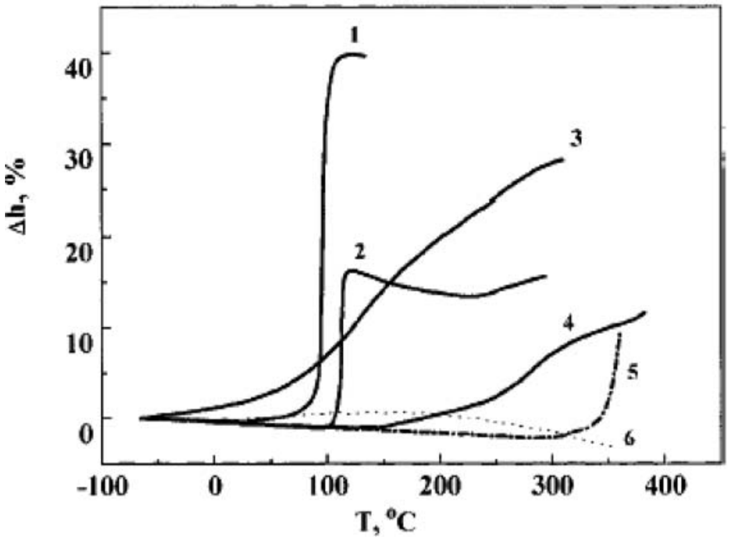


Fig. 1 Internal morphology of polymer beads before and after Friedel-Crafts hyper-cross-linking: gel-type precursor resins before (**a**) and after (**b**) hyper-cross-linked reaction; porous precursor resins before (**c**) and after (**d**) modification. Copied with permission from [6], copyright 2006, American Chemical Society. The scale bar is 1 micron

Fig. 2 Thermomechanical curves for St-DVB copolymers containing 3% DVB (1, 2), 34% DVB (5), poly(DVB) (6), and for the hyper-cross-linked polymer (3, 4). Loading, 10 g per bead (2, 4, 5) and 400 g per bead (1, 3, 6). Reproduced with permission from [22], copyright 1999, John Wiley & Sons Inc.



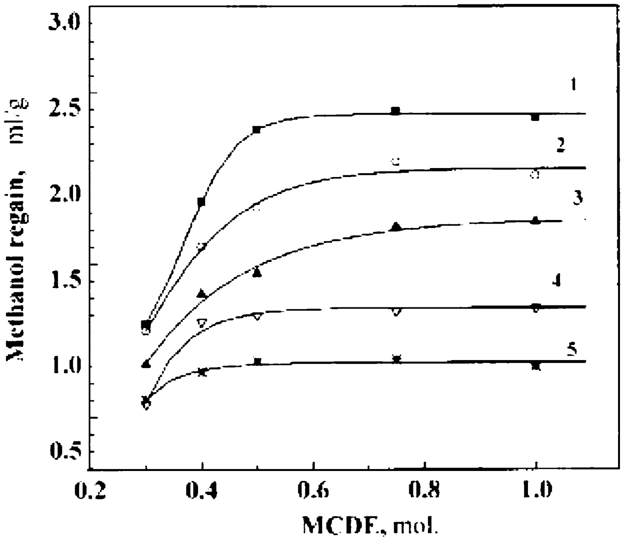


Fig. 3 Methanol uptake for H-PS networks prepared by post-cross-linking with MCDE of the copolymers of styrene with (1) 0.17, (2) 0.3, (3) 0.6, (4) 1.4, and (5) 2.7 mol% DVB. Reprinted from [23], copyright 2000, with permission from John Wiley & Sons Inc.

tating media for polystyrene. Davankov et al. [22] proposed that the unusual swelling capacity of H-PS resins in a non-solvating media is due to the strong inner stress, which originates from two opposite tendencies. One is the polymeric chains tend to form a dense packing during the solvent evaporating. The other is numerous rigid bridges between chains prevent the chains approaching each other. The contracting networks finally reach an equilibrium state. These inner stress form an additional strong driving force for the networks to be swollen in any media, that is to say, very weak interaction of H-PS networks with any non-solvent are sufficient for the networks to back into the swollen state under the inner stress [3]. However, there have been some debates in the literature regarding the sorption mechanism of thermodynamically incompatible species. For example, Sherrington et al. thought the most likely mechanism is due to the fact that all solvents, irrespective of thermodynamic compatibility with H-PS networks, return the dried networks to its lowest energy state formed under the conditions of hyper-cross-linking [6]. Therefore, there remain further questions to be answered for the swelling mechanism of H-PS networks.

Positronium annihilation of H-PS networks

Positron annihilation lifetime (PLA) spectroscopy is one of the most direct probe methods of measuring elementary free volume (EFV) in polymer materials [24]. Also, it can be applied in study of H-PS networks. Shantarovich and co-workers [25] investigated H-PS networks using PLA spectroscopy in a vacuum, in air, also in oxygen and nitrogen. Narrow size distribution of EFV with radius of about 1.5 nm and concentration estimated as about ~10^{19} cm^{-3}, are found in H-PS networks with cross-linking degree higher than 40%. Some of H-PS networks give positronium lifetime $\tau_5 > 50$ ns. On transition from the sample (St-0.3% DVB) to that with 66% of cross-linking degree, effective radius of EFV is changed from 0.2 nm to 0.3 nm up to 1.4 nm, but the integral number of EFV remains about the same, on the level of 5×10^{19} cm^{-3}. Thermal treatment does not change the characteristics of EFV of H-PS networks. Moreover, the annihilation rate of the longest-lived component in H-PS networks is found to increase linearly on raising temperature from 30 K to 370 K, at a lower temperature, the ortho-positronium (o-Ps) lifetime distribution in larger pores shifts to a longer value and becomes wider [26]. Dependence of the longest o-Ps and its intensity as a function of temperature are

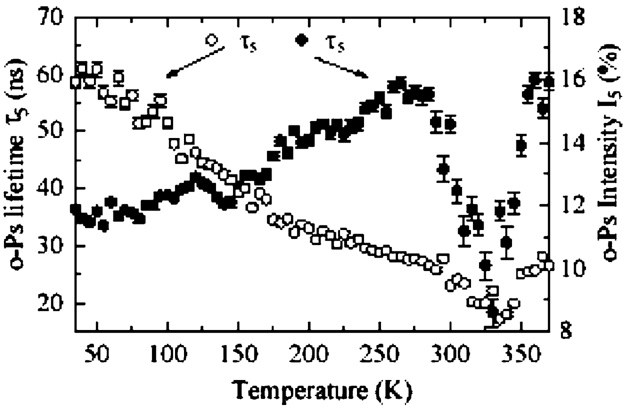


Fig. 4 Dependence of the longest *o*-fsPs lifetime of H-PS resins and its intensity as a function of the temperature in the range from 35 K to 370 K. Reprinted from [26], copyright 2003, with permissions from Elsevier

shown in Fig. 4. Remarkably, from 35 K to about 390 K, the longest o-Ps lifetime in large pores decreases, but its intensity continuously increases. Furthermore, they change significantly when the temperature ranges from about 290–370 K.

Whereas, the positron annihilation technique is an effective measurement method to provide reliable information on the porous structure of polymeric materials, it is preferable to compare the structural information obtained by positron annihilation with information resulted from several other methods, such as small-angle X-ray scattering, adsorption isotherms, size exclusion chromatography, NMR spectroscopy of adsorbed molecules, etc.

Solid-state ^{13}C-NMR of H-PS networks

In order to understand the structure of H-PS networks more clearly, Ford and co-workers [27] used the CP/MAS (Cross-Polarization Magic Angle Spinning) ^{13}C-NMR techniques to analyze the structure of H-PS networks in its solid and gel state. They found the CP/MAS spectra showed no signals from residual CH_2Cl groups. Moreover, gels of H-PS networks swollen in $CDCl_3$ and CH_3OH had residual static dipolar interactions, which enable cross-polarization and require MAS and high power ^{1}H decoupling to reduce chemical shift anisotropy from ~10^4 Hz to ~10^3 Hz. Unfortunately, the CP/MAS experiments failure to count carbon atoms in a highly quantitative manner. This shortcoming can be overcome by single pulse excitation (SPE) technique [28]. For example, Sherrington et al. [29, 30] used the technique to evaluate the structure of H-PS networks and highly cross-linked poly(DVB) resins. The SPE methodology can evaluate the real cross-linking level of poly(DVB), and simultaneously quantify the level of unreacted vinyl groups. Moreover, the H-PS resins prepared from lightly cross-linked St-DVB copolymers have very high quaternary aromatic contents, and approximately 10% of aromatic groups also retain a chloromethyl groups from incomplete methylene bridges. This result is inconsistent with Ford's. The discrepancy arises from different properties of polymer used in Ford's and Sherring's research. Ford et al. obtained H-PS networks by post-cross-linking of linear or lightly cross-linked polystyrene using chloromethyl methyl ether [27].

Applications of H-PS networks

H-PS materials represent a new class of polymeric networks. They are distinguished the traditional macroporous polymeric materials by considerably high specific surface area, relatively small pore size, unusual swelling and adsorption capacity in combination with an easy regeneration process. Due to the marked tendency of incorporating any organic solvents, H-PS resins provided a base for producing a series of novel adsorbents displaying unprecedented adsorption capacities. Up to now, H-PS materials have been widely used as starting materials of liquid chromatography, as materials for adsorption and separation, and as various support.

Adsorption and separation

The structure characters of H-PS networks decide its sorption behavior is always a combination of adsorption on ''surfaces'' of polymeric chains and adsorption by the bulk polymer, which are facilitated by expansion of the hyper-cross-linked networks and relaxation of the inner strains. It has been reported that the sorption capacity of H-PS resins is up to three times higher than that of conventionally macroporous materials [10]. The considerably high adsorption capacity makes H-PS materials to be a choice for concentrating trace organic compounds by solid-phase extraction (SPE) technique. For example, Sherrington et al. [19] evaluated sorption behavior of H-PS resins and several commercially available adsorbents via solid phase extraction of phenolic compounds, as shown in Fig. 5. From the plots it is clear that the higher retention are obtained for the two kinds of H-PS resins due to the presence of hydroxyl moieties, and the macroporous St-DVB resins exhibits much poorer results. Furthermore, the H-PS networks enable the on-line extraction of 300 cm^3 sample with recoveries higher than 80% for polar compounds such as oxamyl, methomyl or desisopropylatrazine [31]. Besides, acid analytes such as imazaquin, bensulfuron, fenoxaprop [32], aromatic sulfonates as well as chlorophenols [33] were successfully extracted by LiChrolut EN using SPE technique, sometimes without acidification of the sample.

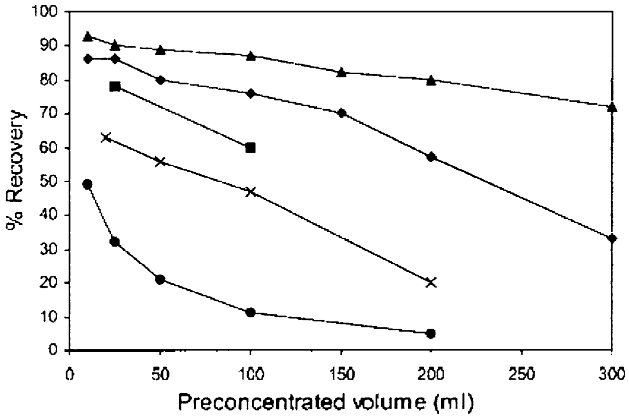


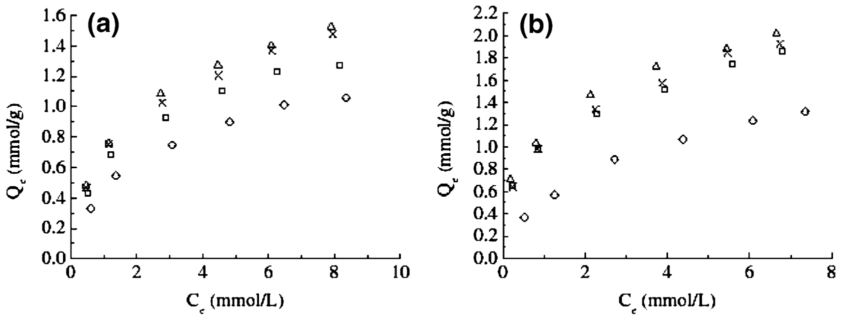
Fig. 5 Comparison of phenol recoveries using different resins: H-PS1 (▲) (908 m^2 g^{-1}); H-PS2 (♦) (1889 m^2 g^{-1}); Amberchrom GC-161 m (×) (900 m^2 g^{-1}); Lichrolut EN (■) (1,200 m^2 g^{-1}); macroporous St-DVB (●) (728 m^2 g^{-1}). Reprinted with permission from [19], copyright 2005, John Wiley & Sons Inc.

Hradil and co-workers [34] prepared heterogeneous membranes based on 4~32 wt.% of H-PS adsorbent with a poly(phenylene oxide) binder for separation of hydrogen from a isobutane/hydrogen mixture. They found the prepared membranes were superior to the homogeneous ones in permeability and to zeolite-filled membranes in selectivity, which reached a value of about 540 in H_2/isobutane separation. The sorption of hexane, 1,2-dichloroethane, tetrachloromethane and pyridine on macroporous and H-PS adsorbents were compared in the range of 70 ~ 150 °C, and H-PS adsorbents show some advantages in adsorption isotherms, retention volumes and breakthrough volumes due to their higher specific surface area and microporosity [8]. Adsorption capacities of H-PS resins markedly changed after some functionalized groups such as $-NH_2$, $-SO_3H$ are introduced into the networks. This variation may be due to hydrogen-bonding and π–π interaction between the polymer matrix and adsorbates or polar groups on the networks. For example, adsorption capacities of animated H-PS resins toward phenol acid and *o*-phthalic acid [35], *p*-nitrophenol and *p*-chlorophenol [36], sodium benzenesulfonate [37], resorcinol and catechol [38] remarkably increased in comparison with unfunctionalized H-PS resins. The adsorption discrepancies of resorcinol and catechol on H-PS resins and animated H-PS materials can be observed in Fig. 6. In the temperature range of 288~318 K, the sulfonated H-PS have higher adsorbing capacities toward aniline and 4-methylaniline in aqueous solutions than Amberlite XAD-4 [39]. In addition, a water-compatible H-PS adsorbent prepared by Zhang et al. exhibited higher adsorption capacities for phenolic compounds [40] and phenylhydrazine derivatives [41] from aqueous solutions than Amberlite XAD-4 due to partial polarity of H-PS networks and the better compatibility between the adsorbates and adsorbents.

Packing materials of HPLC

Mechanical robustness, inertness, pH stability, compatibility with both polar and non-polar organic solvents, here are desirable properties of modern high performance liquid chromatography (HPLC) packing materials. These requirements are best met by H-PS materials. These properties of H-PS resins make the packing rather versatile. And up to now, H-PS resins are used for packing materials of several different kinds of chromatography, such as reversed-phase, distribution, size exclusion chromatography modes. To be used for packing materials of chromatography, an outstanding and surprising property of H-PS resins is that the column efficiency of H-PS materials with micropores of 1–2 nm and macropores of ~100 nm in diameter declined very slowly with the flow rate of the eluent increasing to considerably high values [42]. This property contrasts clearly with the adsorption behavior of traditional macroporous polymer adsorbents and silica packings that are determined under identical conditions. The microporous open-work structure with an additional system of large transport pores, beads of the materials are possibly permeable to the eluent and allow some kind of permeation chromatography. Davonkov and co-workers, using commercially available H-PS sorbents ''Macronet Hypersol'', separated inorganic electrolytes such as $CaCl_2$, LiCl, KCl et al. [43] and minreral salts, acids and bases

Fig. 6 Adsorption isotherms of: (**a**) resorcinol and (**b**) catechol onto (◇) H-PS, (□) AH-1, (△) AH-2 and (×) AH-3 at 283 K. Reprinted with permissions from [38], copyright 2003, Elsevier



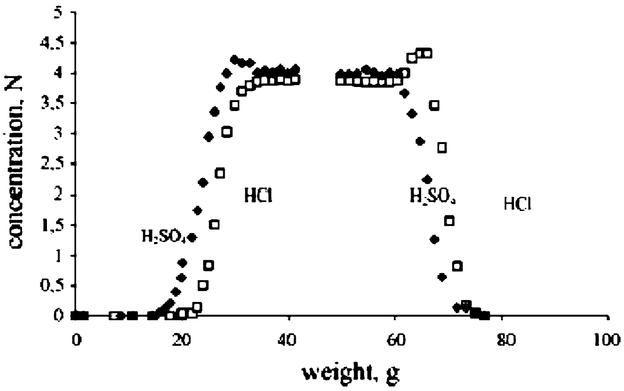


Fig. 7 Separation of 4N H_2SO_4 from 4N HCl on the H-PS resins. Reprinted with permission from [44], copyright 2000, Elsevier

[44] by size-exclusion chromatography (SEC). They found the selectivity of separation was determined by the largest ion in each pair electrolytes (Fig. 7, the hydrated sulfate anion is much larger than the chloride ion), and the productivity of separation increased on raising the concentration of the feed solution. Remarkably, the practical value of SEC can be further enhanced by the unique self-concentrating effect of both separated components [44].

Combining Chromalite 5HGN packing HPLC method with spectrophotometric detection, Nesterenko et al. [45] simultaneously determined and separated pyrocatechol, resorcinol, hydroquinone, *o*-, *m*- and *p*-aminophenols and *p*-phenylenediamine in commercial hair-color products, and found the detection limits of these compounds are in the range 0.05–0.16 kg/m^3. The neutral hydrophobic H-PS materials also exhibit unexpected anion-exchange properties in the pH range of 2.6–4.3 [11, 46]. When eluted with 0.1–0.4 mM perchloric acid, the order of anions elution is as following

$$F^-, H_2PO_4^- < Cl^- < IO_3^- < Br^- < BrO_3^- < NO_3^- < ClO_3^- \\ < NO_2^- < I^- < So_4^{2-}, ClO_4^- << SCN^- << IO_4^-.$$

Nevertheless, after impregnated the adsorbent with 4-dimethylamino-4′-sulfoazobenzene, it behaves rather like a cation-exchanger [12]. Using 0.3 mM $Ce(NO_3)_3$ as the eluent and pH = 5, unusual elution sequence for alkali, amimonium and alkaline-earth metal cations are observed

$$Na^+ < Li^+ \sim K^+ < Rb^+ < NH_4^+ < Cs^+$$

and

$$Mg^{2+} < Sr^{2+} < Ca^{2+} < Ba^{2+}$$

The sequence is distinctly different from that of sulfonated polystyrene resins. However, elution sequence of alkali metal cations on sulfonated H-PS resins with diluted nitric acid as eluent is very similar to that of the former: $Na^+ < Li^+ < K^+ < NH_4^+ < Rb^+ < Cs^+$ [12]. The sulfonated adsorbent can be also used for separation of aliphatic carboxylic acids such as formic, butyric and malonic acid via ion-exclusion chromatography when eluted with 10 mM H_2SO_4 and 5 vol% acetonitrile [47].

However, the mechanism of retention on the packing materials remains to be examined in detail. In general, retention mechanisms on H-PS resins will vary with experimental conditions, especially with the mobile phase composition and the nature of adsorbates [48]. But Davonkov et al. pointed that the basic overlapping mechanisms of the H-PS resins involved π-interactions between π-systems of the polymeric matrix and adsorbates, dispersive solute/sorbent interactions and solute solvating effects [49].

Support of nanoparticle formation and hydrogen storage

Large numbers of nanocavities in H-PS materials can serve as nanoreactors in which various nanoparticles can form and grow. For instance, Davankov et al. [50] impregnated H-PS networks with either $Co_2(CO)_8$ in 2-propanol or the $[Co(DMF)_6]^{2+}$ $[Co(CO)_4]^{2-}$ complex in dimethylformamide, following by thermolysis at 200 °C, obtained the spherical Co nanoparticles of about 2 nm in mean diameter over a wide range of Co concentration, which is comparable to the average pore size of the polymeric support. Undoubtedly, formation of regulated Co nanoparticle is attributed to nanoscale cavities or pores inside H-PS materials. Also, Pt(II) complexes could be obtained via incorporated H-PS materials with tetrahydrofuran containing platinic acid. Following reduction of the complexes by H_2 results stable and robust Pt nanoparticles with a mean diameter of 1.3 nm. The metal/polymer nanocomposite exhibits high reaction selectivity in the catalytic oxidation of L-sorbose to 2-keto-L-gulonic acid, a vitamin C precursor [51]. However, the micropores limits the mass transport of reactant inside the metalated H-PS support and, consequently, catalytic activity. Recently, Davankov's research group used another H-PS resins with both micropores and macropores as a support to prepare the identical metal/polymer nanocomposite. They found that the catalytic activity of the same oxidation reaction had a 4.6-fold increase compared with the former system [52]. Without doubt, this substantial increase in catalytic activity is due to the presence of macropores, which facilitate L-sorbose transport.

Recently, application studies of H-PS materials are extended to the matrix for reversible hydrogen storage. Moreover, H-PS resins exhibit potential capacity of

Table 1 Hydrogen storage capacities of various H-PS materials [54]

Type of H-PS materials	Composition	BET surface area (m^2/g)[a]	H_2 capacity (wt.%)[b]
Amberlite XAD4	Poly(styrene-*co*-divinylbenzene)	1,060	0.8
Amberlite XAD16	Poly(styrene-*co*-divinylbenzene)	770	0.6
Hayesep N	Poly(divinylbenzene-*co*-ethylenedimethacrylate)	460	0.5
Hayesep B	Polydivinylbenzene modified with Polyethyleneimine	570	05
Hayesep S	Poly(divinylbenzene-*co*-4-vinylpyridine)	510	0.5
Wofatit Y77	Poly(styrene-*co*-divinylbenzene)	940	1.2
Lewatit EP63	Poly(styrene-*co*-divinylbenzene)	1,206	1.3
Lewatit VP OC 1064	Poly(styrene-*co*-divinylbenzene)	810	0.7
Hypersol-Macronet MN200	Hyper-cross-linked polystyrene	840	1.3
Hypersol-Macronet MN100	Amine functionalized hyper-cross-linked polystyrene	600	1.1
Hypersol-Macronet MN500	Sulfonated hyper-cross-linked polystyrene	370	0.7
H-PS from gel precursor[c]	Poly(vinylbenzyl chloride-*co*-divinylbenzene)	1,930	1.55
H-PS from macroporous precursor[c]	Poly(vinylbenzyl chloride-*co*-divinylbenzene)	1,300	1.2

[a] Measured using nitrogen adsorption/desorption

[b] Hydrogen storage capacity at a pressure of 0.12 MPa and 77.3 K

[c] H-PS prepared by Svec et al.

hydrogen storage. For example, the H-PS resins prepared by Cooper et al. [53] can adsorb 2.75 wt.% H_2 at 77 K and 10 bar, which represents the highest levels of hydrogen adsorption yet observed for an organic polymer. Svec and co-workers [54] evaluated the hydrogen adsorption capacity of H-PS resins and some commercially available adsorbents. Table 1 lists the hydrogen storage capacities of various H-PS materials. Apparently, the hydrogen storage capacities increase with the specific surface area rising. Although the storage capacity cannot meet the goal for 2010, H-PS resins provide the promising candidates for use in future hydrogen storage systems.

In conclusion, the synthetic techniques of H-PS networks are extremely versatile. It should therefore be possible to prepare new, high surface area microporous materials based on a very broad range of aromatic molecules. Furthermore, modification of synthetic polymers is a well-charted field, a number of reactions leading to a variety of different functionalities are currently being tested to determine their effect on hydrogen adsorption. The ease with which hydrogen adsorbing or other functional moieties can be attached to these polymers is one of their primary advantages. Hence, designing new pore structure and introducing new surface chemistry may be result in higher reversible hydrogen storage.

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