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Rapid Generation and Control of Microporosity, Bimodal Pore Size Distribution, and Surface Area in Davankov-Type Hyper-Cross-Linked Resins

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ABSTRACT: Synthesis of Davankov-type hyper-cross-linked resin beads has been carried out using gel-type and permanently porous poly(divinylbenzene-*co*-vinylbenzyl chloride) (DVB−VBC) precursor resins without any external electrophile. Of the Lewis acids examined ($FeCl_3$, $AlCl_3$, $SnCl_4$), $FeCl_3$ was by far the most effective catalyst. Rather remarkably in the case of a gel-type 2 mol % DVB−VBC precursor, extensive microporosity was generated within only 15 min of initiating the cross-linking reaction, yielding a surface area (N_2 sorption/BET) of ~1200 $m^2\ g^{-1}$, which rose steadily to a maximum approaching 2000 $m^2\ g^{-1}$ after 18 h. In the case of porous DVB−VBC precursor resins, the presence of discrete pores in the precursor, accompanied by a micropore fraction on hyper-cross-linking, yields resins with a clearly bimodal distribution of pores. Manipulation of the Friedel−Crafts reaction variables and the structure of the precursor resin allows final resin products to be prepared with surface areas in the range ~300−2000 $m^2\ g^{-1}$.

Introduction

Suspension-polymerized styrene−divinylbenzene (St−DVB) copolymer beads are widely used in many fields, particularly in ion exchange, in size exclusion chromatography, as specific sorbents, and as catalyst or reagent supports. The morphologies of St−DVB resins are usually classified as "gel type" or "macroporous", and this can determine the suitability for various applications. The term "macroporous" was established many decades ago and, as introduced then, simply implied that the resin had permanent porosity; it did not necessarily imply the presence of any particular size of pores. To avoid confusion, in the present paper the term "porous" resin will be used to classify such precursor resins and the terms "macroporous", "mesoporous", and "microporous" will be used as defined by IUPAC.

In the dry state the porosity of gel-type resins is very small, corresponding only to the distance between chains. The corresponding dry state surface area is also very small, usually <5 $m^2\ g^{-1}$ (N_2 sorption, BET). On addition of a thermodynamically good solvent considerable porosity is established in these lightly cross-linked polymers (sometimes referred to as "solvent porosity") which can sometimes absorb many times their own weight of an appropriate solvent. Not surprisingly, therefore gel-type resins are usually employed in the presence of a good solvent. On the other hand, porous resins with their permanent pores can have very large surface area even in the dry state. Furthermore, the porosity of the polymer network usually changes only marginally on contacting a good solvent. Porous resins can therefore be applied in gas-phase or liquid-phase reactions even in the latter case with poor solvents. A number of excellent papers and reviews have been published on controlling the porosity of these materials.[1−5]

In 1969, a novel method for the synthesis of porous polystyrenic networks was introduced by Davankov and coworkers.[6] This consisted originally of extensive post-cross-linking of linear polystyrene chains by means of a Friedel−Crafts reaction producing various structural bridges between neighboring phenyl groups in a highly swollen state. However, the method has since been extended to the use of precursor resins as well.[6−8] The resulting hyper-cross-linked polystyrene materials are characterized by their very high microporosity and very high dry state surface area. They also display interesting swelling properties, despite the high degree of cross-linking. Moreover, the resins swell to similar degrees in both good and poor solvents for polystyrene,[8] in keeping with the argument that all solvents should return each dried network to its lowest energy state formed under the conditions of hyper-cross-linking.[9] These properties provide potential for applications as improved sorbents for organic vapors,[10] for recovery of organic compounds from water,[11−14] for toxic trace metal removal,[15,16] as ion-exchange resins,[17,18] and in preconcentration of hydrophilic aromatic compounds by reversed-phase HPLC.[19] Indeed, such materials are now available from a number of commercial sources.[20] Recently, new synthetic methods for porous polymers have been reported, including the modification of polystyrenic beads containing excess DVB (0.7−0.9 mole fraction) by Friedel−Crafts acylation,[21,22] the UV irradiation of benzoylated polystyrenes,[24] and the self-assembly of polymer nanospheres.[25]

In the main Davankov-type resins have been prepared by post-cross-linking of linear or lightly cross-linked gel-type polystyrenes using external electrophiles to introduce the new cross-links. However, Veverka and Jerabek[14] have shown that

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chloromethylated St−DVB resins are also excellent precursors for the synthesis of hyper-cross-linked resins where the $-CH_2Cl$ substituent in effect yields an internal electrophile to form the basis of the cross-link. In principle, however, if a porous resin were to be used as the precursor, then the product should contain the original pores as well as the new micropores generated during the extensive cross-linking process. Such a bimodal pore structure may facilitate the transport of substrates inside the polymer beads and offer improved performance in applications.

In fact, such an approach has already been reported by Veverka and Jerabek[26] although they have used commercially sourced chloromethylated St−DVB resins as the precursors where presumably the chloromethyl functionality was introduced by chemical derivatization. As a result, the composition of the precursors was not as well-defined as it might have been. Additionally, they have employed $SnCl_4$ as the Lewis acid, and as we shall see later this does not provide optimum cross-linking.

The objective of the work reported here therefore was to prepare compositionally well-defined gel-type and porous divinylbenzene−vinylbenzyl chloride (DVB−VBC) precursor resins and to hyper-cross-link these using a number of Lewis acid catalysts and reaction conditions. The main target was to generate resins with a bimodal distribution of pore sizes (micropores and macropores) with simultaneously optimized surface area, beyond that achievable by conventional one-pot suspension polymerization methodology.[1−5]

Experimental Section

Materials. Divinylbenzene (DVB 55% grade, balance being *m*- and *p*-ethylstyrene), vinyl benzyl chloride (VBC mixed *m*- and *p*-isomers), poly(diallyldimethylammonium chloride) (mol wt 100K−200K 20 wt % in water), isoamyl alcohol, azobis(isobutyronitrile) (AIBN), and the Lewis acids $FeCl_3$, $AlCl_3$, and $SnCl_4$ were from Aldrich Chemical Co. and were used as supplied. Gelatin, 1,2-dichloroethane, and toluene were received from Daejung Chemical Co. and were used as supplied.

Preparation of 2 mol % DVB−VBC Gel-Type and 20 mol % DVB−VBC Porous Precursor Resins (2% PVBC and 20% PVBC). These resins were prepared by conventional free radical suspension polymerization. Typically for the gel types the monomer phase comprised DVB (2.00 g), VBC (61.78 g), and AIBN (0.35 g). The aqueous phase consisted of distilled water (300 mL), poly(diallyldimethylammonium chloride) (15 g), and gelatin (1 g). The organic phase was suspended in the aqueous phase at 75 °C at a stirring speed of 450 rpm. After 8 h the polymer beads were collected, washed with water and acetone in a Soxhlet, and finally dried in a vacuum oven at 60 °C.

The porous species were prepared similarly. Typically the aqueous phase consisted of distilled water (600 mL), poly(diallyldimethylammonium chloride) (30 g), and gelatin (2 g). The corresponding monomer phase contained DVB (33.14 g), VBC (68.25 g), and AIBN (1.00 g) together with a mixture of toluene (25 mL) and isoamyl alcohol (75 mL) as the inert porogen.

Preparation of Hyper-Cross-Linked Resins. A typical procedure was as follows. The precursor resin beads (5 g) were swollen in 1,2-dichloroethane (DCE) (40 mL) for 2 h. The slurry was cooled to ∼4 °C in an ice bath, before the Friedel−Crafts catalyst, $FeCl_3$ (2 g), was added. After allowing 2 h to achieve a uniform dispersion of $FeCl_3$ throughout the precursor beads, the temperature was raised to 80 °C. After a given reaction time (see Results and Discussion) the mixture was quenched by addition of methanol. Catalyst fragments and solvent were washed out with methanol, a mixture of acetone and HCl (0.5 M × 2), and finally deionized water. The resulting polymeric beads were dried under vacuum at 80 °C.

Characterization of Resins. The dry state surface area and pore size distribution were evaluated using N_2 or Ar sorption porosimetry (Micromeritics automatic analyzer ASAP 2000C fitted with an optional high stability (1.33 mbar) pressure transducer). The swelling ratio (SW), defined as the ratio of the volume occupied by the resin when swollen in given solvent (usually toluene) to its volume in the dry state at room temperature, was determined using a small measuring cylinder. More accurate solvent imbibition data (mL g^{-1} dry resin) were obtained gravimetrically using the centrifuge method,[27] and the volume of solvent imbibed was deduced by assuming the normal bulk density data.

Elemental microanalytical data for each resin were obtained from a Perkin-Elmer Series II 2400 elemental microanalyzer. FTIR spectra were recorded using a Bomem MB102 spectrometer. The samples were scanned over the range 650−4000 cm^{-1}. The residual metal contents of the final hyper-cross-linked resins were measured by the inductively coupled plasma (ICP) technique using a Thermo Jarrell Ash Inc. Atomscan 25. Prior to these measurements, each resin sample was heated in a furnace for 3−4 h at 420 °C, and after cooling to room temperature the residues were dissolved in aqua regia.

Results and Discussion

Synthesis of Precursor Resins. Four 2 mol % DVB−VBC gel-type precursor resins (2% PVBC (0:1); (1:3); (1:1), and (3:1)) were prepared with mole ratios of comonomers St:VBC = 0:1, 1:3, 1:1, and 3:1, respectively, to provide a progressively reduced level of chloromethyl functionality in each resin. Likewise, four 20 mol % DVB−VBC porous precursor resins (20% PVBC (0:1); (1:3); (1:1), and (3:1)) were prepared using similar St:VBC feed ratios. In all cases good yields of beaded products were obtained. Typically, the chlorine contents of the resins were a little below the theoretical values (e.g., 2% PVBC (0:1) Cl = 22.2%; 20% PVBC (0:1), Cl = 13.8%) which we believe is due to minor hydrolysis of the VBC monomer. In fact, we have studied this effect in some detail and have shown that the pure *p*-VBC isomer is much more prone to hydrolysis than the mixed isomer grade *p*- and *m*-VBC and that consequently the latter is a far better feed material for good retention of $-CH_2Cl$ functionality.[28] Particle size distributions in the range 200−1400 μm were realized, and fractions with diameters 600−1000 μm were sieved and used in the hyper-cross-linking reactions. The swelling ratios of these precursor resins were ∼2 for the gel types and ∼1.4 for the porous species when toluene was used as the swelling solvent (Table 1).

Synthesis and Generic Properties of the Hyper-Cross-Linked Resins. The eight precursor resins, 2% PVBC (0:1); (1:3); (1:1), (3:1) and 20% PVBC (0:1); (1:3); (1:1) and (3:1), were converted in essentially quantitative yield to the corresponding hyper-cross-linked species. As expected, the surface areas of the products were generally substantially higher than their precursors with the maximum value approaching 2000 m^2 g^{-1} (see later). The internal morphologies of the beads before and after hyper-cross-linking were observed by scanning electron microscopy (SEM), and typical micrographs are shown in Figure 1. The gel-type precursors become visibly more highly porous after the Friedel−Crafts reaction; however, the porous precursors show no obvious morphological change at the resolution of the SEM used.

Confirmation of the high level of cross-linking achieved was obtained via the decline of the intensity of the 1270 cm^{-1} band ($-CH_2Cl$) in the FTIR spectra and the increasing complexity and intensity of the aromatic skeletal bands at 700−900 cm^{-1}. Most importantly, the significant fall in the elemental chlorine content of the resins (Table 2) is consistent with the conversion of $-CH_2Cl$ groups into methylene bridges. Overall, relative to the data for the precursor resins, the swelling ratio in toluene declined a little for the hyper-cross-linked resins prepared from both precursor types (Table 1) (see later for details).

Table 1. Effect of the Chloromethyl Group Content in Precursor Resin on the Surface Area of Derived Hyper-Cross-Linked Resins[a]

				hyper-cross-linked resin	
precursor resin	surface area (m^2/g)	swelling ratio	catalyst	surface area (m^2/g)	swelling ratio
2% PVBC (0:1)		1.85	$FeCl_3$	2090	1.69
			$AlCl_3$	1600	1.88
			$SnCl_4$	1130	1.72
2% PVBC (1:3)		2.01	$FeCl_3$	1706	1.52
			$AlCl_3$	1302	1.62
			$SnCl_4$	1020	1.51
2% PVBC (1:1)		2.22	$FeCl_3$	1056	2.21
			$AlCl_3$	208	1.76
			$SnCl_4$	8	1.78
2% PVBC (3:1)		2.27	$FeCl_3$	2	1.83
			$AlCl_3$		1.97
			$SnCl_4$		1.76
20% PVBC (0:1)	69	1.37	$FeCl_3$	1055	1.11
			$AlCl_3$	620	1.21
			$SnCl_4$	475	1.38
20% PVBC (1:3)	69	1.36	$FeCl_3$	902	1.20
			$AlCl_3$	646	1.19
			$SnCl_4$	616	1.18
20% PVBC (1:1)	79	1.14	$FeCl_3$	643	1.14
			$AlCl_3$	392	1.14
			$SnCl_4$	454	1.22
20% PVBC (3:1)	86	1.25	$FeCl_3$	474	1.35
			$AlCl_3$	441	1.39
			$SnCl_4$	330	1.42

[a] Solvent: 1,2-dichloroethane; reaction temperature: 80 °C; reaction time: 12 h.

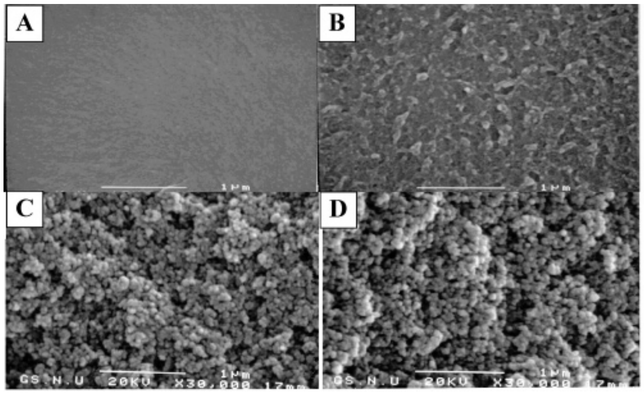


Figure 1. Internal morphology of polymer beads before and after Friedel−Crafts hyper-cross-linking: gel-type precursor resin (2% PVBC (0:1)) before (A) and after (B) modification; porous precursor resin (20% PVBC (0:1)) before (C) and after (D) modification.

Pore size distributions were measured via Ar adsorption porosimetry for micropores and N_2 adsorption for larger pores. Typical data obtained are shown in Figure 2. The nonporous gel-type precursors yield hyper-cross-linked resins with only a unimodal population of micropores, whereas as planned, the porous precursors yield resins with a bimodal pore size distribution. One fraction of pores corresponds to the large pores originally present in the precursor, and the second fraction is of the micropores formed on hyper-cross-linking. This result is similar but perhaps more definitive to that reported by Veverka and Jerabek.[26]

Table 2. Elemental Microanalytical and Surface Area Data of Cross-Linked Resins Derived from Gel-Type and Porous DVB−VBC Precursor Resins[a]

			elemental analysis (%)			surface area
catalyst (g)	temp (°C)	time (h)	C	H	Cl	(m^2/g)
precursor gel-type 2% PVBC (0:1)			72.0	6.2	22.2	2
$FeCl_3$(2)	70	12	86.5	6.8	3.9	1890
$AlCl_3$(2)	70	12	89.3	6.8	1.4	1330
$SnCl_4$(2)	70	12	81.1	6.5	11.3	60
$FeCl_3$(1)	70	12	86.7	6.9	3.8	1860
$AlCl_3$(1)	70	12	80.5	6.7	11.7	1
$SnCl_4$(1)	70	12	79.5	6.6	12.1	34
$FeCl_3$(2)	80	12	87.0	6.9	3.8	2090
$AlCl_3$(2)	80	12	89.8	7.1	0.9	1600
$SnCl_4$(2)	80	12	83.2	6.8	8.1	1130
precursor macroporous 20% PVBC (0:1)			77.6	7.2	13.8	60
$FeCl_3$(2)	80	15	88.2	7.7	2.4	1160
$FeCl_3$(2)	80	12	87.3	7.6	2.9	1130
$FeCl_3$(2)	80	9	87.5	7.5	2.8	1140
$FeCl_3$(2)	80	6	87.0	7.1	3.2	1120
$FeCl_3$(2)	80	3	86.6	7.6	2.9	1130
$FeCl_3$(1)	80	12	88.2	7.2	2.4	1160
$FeCl_3$(0.5)	80	12	88.1	7.4	2.2	1070
$FeCl_3$(0.25)	80	12	88.1	7.3	2.5	1030
$FeCl_3$(0.1)	80	12	87.2	7.3	4.0	880

[a] Solvent: 1,2-dichloroethane; reaction temperature: 80 °C.

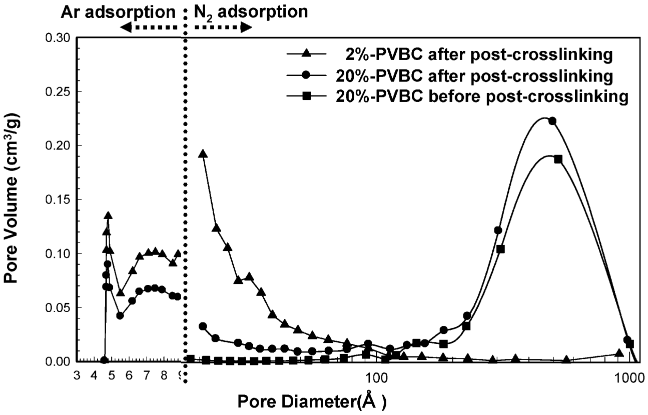


Figure 2. Pore size distributions of hyper-cross-linked gel-type resin (2% PVBC (0.1)) and porous precursor resin (20% PVBC (0:1)) and the hyper-cross-linked derivative therefrom ($FeCl_3$ catalyst).

Effect of Lewis Acid Catalyst. In principle, many Lewis acids might be used in the hyper-cross-linking reaction ($FeCl_3$, $AlCl_3$, $SnCl_4$, BF_3, etc.) and also protonic acids such as HF. Solid catalysts are preferred in terms of ease of handling, though in this work $FeCl_3$, $AlCl_3$, and $SnCl_4$ were investigated. The results are summarized in Tables 1 and 2. These data show that $FeCl_3$ is consistently the most active Lewis acid examined, as indicated by the elemental microanalytical data in Table 2 and the additional surface area in Table 1. The maximum surface areas achieved with each Lewis acid in the case of both the gel-type and porous precursor resins are summarized in Figure 3, where it is clear that the order of activity is $FeCl_3 > AlCl_3 > SnCl_4$ based on this criterion. It is not entirely clear why such significant differences arise between these species, but it may be that $AlCl_3$ has somewhat poorer solubility than the other two Lewis acids under the reaction conditions used and that the sheer bulk of $SnCl_4$ is limiting, particularly in the case of the second bridging alkylation step between pairs of aromatic rings (see later). $FeCl_3$ may therefore simply offer the best compromise between solubility and molecular size. Be that as it may, it is interesting that Veverka and Jerabek[26] have used $SnCl_4$ consistently throughout their studies, and it seems likely that this is one reason why the surface areas they have achieved using porous precursor resins are significantly lower than those that we now report.

In the case of precursor 20% PVBC (0:1) the effect of different levels of $FeCl_3$ was also investigated. Beyond a mass of 0.5 g in the reported procedure the final surface area achieved

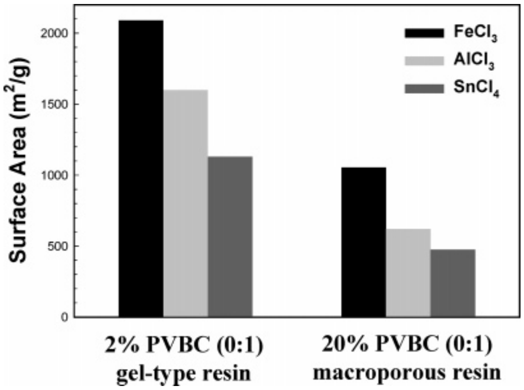


Figure 3. Effect of catalyst type on maximizing surface area of hyper-cross-linked resins.

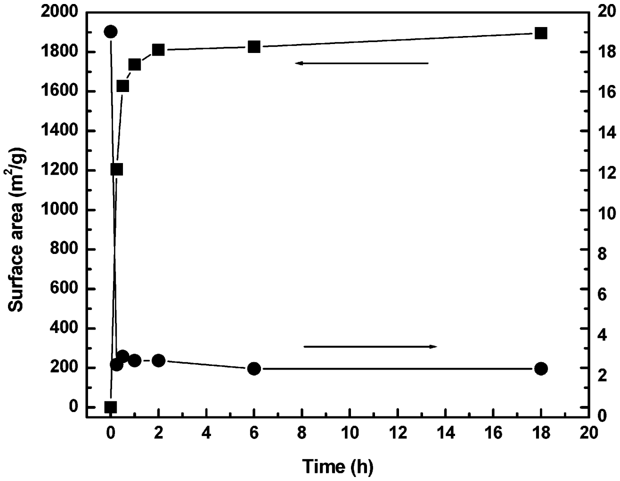


Figure 4. Changes in Cl content and surface area during hyper-cross-linking of gel-type 2% PVBC(0:1) precursor resin ($FeCl_3$ as catalyst).

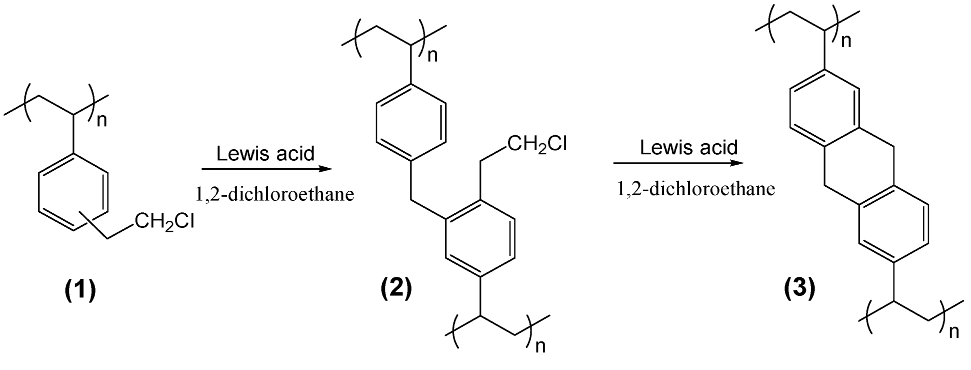
in the corresponding hyper-cross-linked resin did not change significantly (~2%). Typically the level of residual Fe detectable in the isolated resins was very low, ~10^{-3} g of Fe per g of polymer.

Effect of Reaction Time. The effect of the reaction time scale was investigated using gel-type precursor 2% PVBC (0:1) with $FeCl_3$ in DCE at 80 °C. A series of reactions were carried out as reported earlier, and the products were isolated and worked-up after periods ranging from 15 min to 18 h. The elemental chlorine contents and surface areas of the resultant resins are shown in Figure 4. Somewhat to our surprise, the chlorine content was found to fall dramatically within only 15 min of reaction, with the resin surface area rising simultaneously from ~0 to 1200 m^2 g^{-1}. Further reaction over 18 h results in measurable but minor additional loss of chlorine and a rise in surface area to >1800 m^2 g^{-1} after 2 h, with only a very small increase beyond this time. While efficient cross-linking and micropore generation with chloromethylated PS-DVB resins have been reported before,[14,26] the sheer speed and efficiency of the cross-linking are remarkable and seem likely to exceed those of a low molar mass model solution phase electrophilic aromatic substitution reaction.

One possible explanation for this efficiency resides in the "intramolecular" nature of the cross-linking process, and the fact that in the case of a gel-type precursor resin with ~98 mol % of segments carrying a reactive $-CH_2Cl$ group, the final level of cross-linking (based upon the loss of elemental chlorine) corresponds to most aromatic groups being triply alkylated. Indeed, the possibility of dihydroanthracene structures (**3**) (Scheme 1) forming has been proposed before along with solid state magic angle spinning (SS MAS) ^{13}C NMR evidence.[29,30] The second step in particular (i.e., **2** converting to **3**) may well be extremely favorable in that the aromatic group to be substituted is already doubly alkyl substituted and hence electron rich, but perhaps more importantly the cyclization reaction which ensues is stereochemically well set up to form the new six-membered ring. Indeed, this may well be the step that becomes less favorable in the case of the bulky $SnCl_4$ Lewis acid. This fact may also explain why (with $FeCl_3$) controlling the surface area of the derived resin by control of reaction time is rather difficult, in that once cross-linking starts, further reaction occurs rapidly via in effect a cooperative phenomenon.

Gel-Type vs Porous Resin Precursors. The data in Table 1 show clearly that providing good consumption of $-CH_2Cl$ groups and efficient cross-linking occurs using $FeCl_3$, the gel-type precursor (2% PVBC (0:1)) with essentially zero surface area readily yields hyper-cross-linked species with surface area as high as 2000 m^2 g^{-1}. Furthermore, the level of microporosity and surface area attained are consistently higher than those achieved using the porous precursor 20% PVBC (0:1). Nevertheless, the latter still yields species with surface area up to ~1200 m^2 g^{-1}. However, the comparison of data is perhaps not really fair since the $-CH_2Cl$ content of the gel-type resin 2% PVBC (0:1) in Table 1 is ~98 mol % of segments whereas the $-CH_2Cl$ content of the porous precursor 20% PVBC (0:1) is only ~80 mol % of segments. A more satisfactory comparison therefore would be between the latter and gel-type 2% PVBC (1:3) (Table 2), which has a similar $-CH_2Cl$ content. However, gel type 2% PVBC (1:3) still yields a hyper-cross-linked species with surface area ~1700 m^2 g^{-1} using $FeCl_3$ as the Lewis acid. It is clear therefore that even when matching the degree of functionality very closely in the two precursor types, the gel type still yields a hyper-cross-linked species with significantly higher surface area than that derived from the porous precursor. One possible explanation for this is that the initially higher and

Scheme 1. Hyper-Cross-Linking of DVB−VBC Precursor Resins via Generation of "Internal" Electrophile



more uniform swelling of the gel-type species in DCE might allow more efficient and uniform generation of the doubly bridged structures (**3**) shown in Scheme 1. This in turn might yield a more regular microporous structure than that formed from the porous precursor. It is also tempting to suggest that the porous precursor with 20 mol % DVB paradoxically might present inherent accessibility limitations, although the low residual chlorine contents in the derived hyper-cross-linked resins is not consistent with this argument.

Interestingly, if the DVB content of the precursor gel-type resin is increased to 5 and 8 mol %, with all other factors remaining the same, the surface area of the derived hyper-cross-linked resins does fall somewhat to ~1500 and ~1400 m^2 g^{-1}, perhaps suggesting that the DVB content of the precursor resin, whether gel-type or porous, in some way is the limiting factor.

Effect of $-CH_2Cl$ Content of Precursor Resins. In principle, to achieve on average one methylene bridge between each pair of aromatic groups in the resin would require only 50% of these to carry a $-CH_2Cl$ substituent. The precursor resins prepared with increasing levels of St as comonomer, 2% PVBC (0:1), (1:3), (1:1), (3:1) and 20% PVBC (0:1), (1:3), (1:1), (3:1), were prepared primarily to probe this issue. The data in Table 2 show the data for hyper-cross-linked resins obtained using both gel-type and porous precursors with progressively lower $-CH_2Cl$ content. In the case of the 2% PVBC gel-type precursors, surface area in excess of 1000 m^2 g^{-1} is indeed achievable with only ~50% of aromatic groups carrying a reactive $-CH_2Cl$ group; however, this is only so with $FeCl_3$ as the Lewis acid. With $AlCl_3$ and $SnCl_4$ it seems that the $-CH_2Cl$ content needs to ~75% or higher, and this is in agreement with the findings of the Veverka and Jerebek,[26] who used $SnCl_4$ with their precursors. These observations are also consistent with the data in Table 1 for gel-type precursor 2% PVBC (0:1). Those cross-linking reactions which fail to yield high surface area products in fact do so because the conversion of $-CH_2Cl$, as evidenced by the high residual chlorine content in the products, is low, and hence the level of methylene bridging is also low. When the latter falls below a critical level, it seems most likely that any pore structure that is formed is able to shrink or collapse during the isolation and drying processes resulting in resins with very low surface area. In any event the unique porosity characteristics of a hyper-cross-linked resin are not achieved.

In the case of the 20% PVBC porous precursors irrespective of the Lewis acid used, a content of $-CH_2Cl$ groups of ~80% or higher seems necessary to generate surface area >1000 m^2 g^{-1}. Interestingly, however, all the porous precursors yield resins from the Friedel−Crafts reactions having significantly enhanced surface area, and indeed there is reasonable correlation between the $-CH_2Cl$ content in the precursor and the surface area achieved on further cross-linking. Almost certainly the original rigid structures of these porous precursors prevent collapse of the resins on isolation and drying following the cross-linking reaction, and indeed these precursor compositions allow fairly sensitive control over the surface area of the final resins, all of which of course still retain the large pore fraction of the precursors.

Though we have not investigated in great detail, the type of porogen used in synthesizing the precursor porous resin may also be very important. Thus, for example, a precursor prepared with 12 mol % DVB and VBC comonomer with 2-ethylhexanol as porogen yielded a hyper-cross-linked resin with a maximum surface area of only ~900 m^2 g^{-1} when the porogen was used at 1:1 vol:vol relative to the comonomers and only ~725 m^2 g^{-1} with the same porogen used at 2:1 vol:vol relative to the comonomers. This factor may also be contributing to the limited surface area reported by Veverka and Jerabek,[26] where they appeared to have no knowledge (and presumably no control) over the nature and level of porogen used in the preparation of their precursor resins. It seems likely therefore that further work aimed at evaluating the role of the porogen in the precursor resin and its influence on the final hyper-cross-linked species would be very valuable.

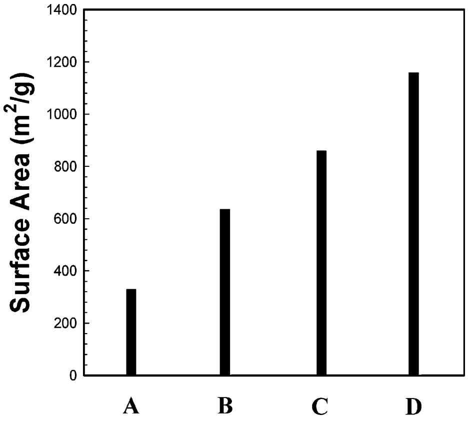


Figure 5. Effect of reaction solvent used during hyper-cross-linking of 20% PVB (0:1) porous precursor resin on the surface area of the final resin product ($FeCl_3$ as catalyst): A = chlorobenzene; B = hexane; C = DCE/hexane (50/50 v/v); D = DCE.

Effect of Hyper-Cross-Linking Reaction Solvent. Because the original hyper-cross-linking work was carried out using linear polystyrene, the choice of thermodynamically good solvents for the polymer (which were also compatible with the Friedel−Crafts chemistry) was a logical one for efficient reaction. Indeed, the use of highly swelling solvents such as DCE was continued when gel-type resin precursors were employed. Use of porous resin precursors, however, presents an opportunity to examine the effect of using a much wider range of solvents. The data in Figure 5 show how the surface area of hyper-cross-linked resins prepared from 20% PVBC (0:1) varies with the reaction solvent used in the cross-linking reaction. DCE yields a species with the highest surface area, but very interestingly hexane, which is essentially a precipitant for polystyrene, and which would not be expected to solvate the polymer matrix in the precursor resin, yields a resin with a very respectable surface area of >600 m^2 g^{-1}. Equally surprising, this value exceeds that of the resin prepared using chlorobenzene as the solvent. As far as we are able to tell, the solubility of $FeCl_3$ in these various solvents is not limiting and so offers no alternative explanation. Clearly, therefore, although we have shed some further light on the synthesis of these interesting resins, there remains further questions to be answered.

Swelling Characteristics of Hyper-Cross-Linked Resins. One of the most remarkable properties of hyper-cross-linked resins is of course their response to solvents and particularly their tendency to sorb high levels of highly polar protic solvents such as water. Not surprisingly, therefore, the species synthesized here behave likewise. However, in our study of the effect of the reaction time of the hyper-cross-linking of 2% PVBC (0:1) we had the opportunity to examine the response to various solvents by the resins prepared using the different reaction times. The data obtained are shown in Figure 6 for the precursor gel-type resin 2% PVBC (0:1). These are consistent with the known compatibility of polystyrene with gel-type resin 2% PVBC (0:1). These are consistent with the known compatibility of polystyrene with the various solvents. The uptake is greatest for tetrahydrofuran and extremely low for water. Also, the final

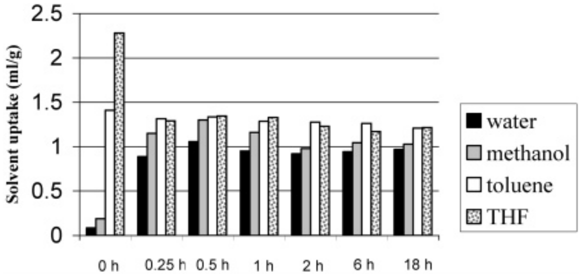


Figure 6. Solvent uptake data of resins isolated at various times (hour) during hyper-cross-linking of gel-type 2% PVBC(0:1) precursor resin ($FeCl_3$ as catalyst).

hyper-cross-linked resin obtained after 18 h shows the remarkable change in solvent sorption behavior characteristic of Davankov-type polystyrene-based resins. All solvents including the polar protic species such as water and methanol, despite being incompatible with polystyrene, are sorbed to almost the same level as tetrahydrofuran and toluene. There has been some debate in the literature regarding the mechanism of sorption of what would normally be regarded as thermodynamically incompatible species. It seems most likely that this arises because all solvents, irrespective of their thermodynamic compatibility with the matrix, return the dried network to its lowest energy state formed under the conditions of hyper-cross-linking. Davankov himself-has argued that this is in effect the relief of steric strain arising in the dry state.[8] In the present work, however, the key result is that the remarkable change in solvent sorption behavior is almost completely developed even in the resin isolated after only 15 min of reaction, confirming that all the properties of hyper-cross-linked resins are more or less developed on this extremely small time scale. Further reaction time does generate resins where the solvent sorption properties are further refined, but the additional changes are small. Resin isolated after 1 h shows behavior essentially identical to that of the species produced after 18 h. In terms of practical production therefore reaction times much in excess of 1 h seem unnecessary.

Conclusions

Use of gel-type and porous DVB−VBC resins as precursors to hyper-cross-linked Davankov-type resins offers a very convenient synthetic methodology. Resins with surface area up to ∼2000 $m^2\ g^{-1}$ are readily obtainable from gel-type precursors, and $FeCl_3$ is a much more effective Lewis acid catalyst than $AlCl_3$ and $SnCl_4$. Remarkably, the microporous structure is extremely well-developed after only 15 min reaction in DCE at 80 °C, and thereafter only minor refinements to the morphology take place. Use of porous precursors also allows facile preparation of high surface area resins (up to ∼1200 $m^2\ g^{-1}$) which in this case exhibit a well-defined bimodal pore size distribution with the originally present large pores (macropores in the present examples) of the precursor being joined by a major micropore fraction formed during hyper-cross-linking. With the porous precursors, adjustment of the $-CH_2Cl$ content using styrene as comonomer allows the synthesis of a group of resins with bimodal pore size distributions in which the total surface area can be tailored in the range ∼300−1200 $m^2\ g^{-1}$. The unique solvent sorption characteristics of hyper-cross-linked resins are generated as quickly as the micropore structure, and reaction times in excess of 1 h are unnecessary. The species with a bimodal pore size distribution are indeed extremely useful as enhanced sorbents showing not only faster kinetics than conventional sorbent resins but also larger working capacity, and we have already reported on their behavior.[31] We have also shown that a small level of hydrolysis of $-CH_2Cl$ groups during suspension polymerization to form the precursor resins generates a low level of intrinsic polarity in the resins. This leads to enhanced behavior in applications in solid-phase extraction, and again these preliminary results have now been published[28] and are disclosed in more detail.[32]

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