One-Pot Synthesis of Branched Poly(styrene−divinylbenzene) Suspension Polymerized Resins

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Received June 25, 2002; Revised Manuscript Received October 2, 2002

ABSTRACT: Spherical particulate polymer resins have become ubiquitous support materials in both solid phase synthesis and in the heterogenizing of homogeneous catalysts. In the former case lightly cross-linked so-called gel-type species are favored whereas in the latter so-called macroporous species are finding increasing utility. Despite the success of these materials, mass transfer limitations can lead to poor performance, and in this context there is still a need for improvement in the morphology of these species. One potential advancement would be resins with a highly branched backbone architecture since such a molecular level structure would in principle generate a large proportion of functional groups near chain ends or at least on mobile chains anchored to the main matrix by a single linkage. In addition a high level of chain ends relative to that in conventional resins might lead to novel solvation characteristics. We now report a facile one-pot suspension polymerization which allows synthesis of both branched gel-type and branched macroporous resins. The procedure is an adaptation of our earlier reported methodology for producing soluble branched vinyl polymers and involves use of controlled levels of a free radical chain transfer agent which functions in effect to limit chain growth and in combination with a cross-linking comonomer leads essentially to branched backbone architectures. The system styrene/ divinylbenzene/ dodecanethiol has been probed in detail, and a range of experimental conditions have been identified which lead to branched gel-type and branched macroporous resins. The structure of these has been evaluated from solvent swelling data, dry state surface area measurements, and inverse size exclusion chromatographic data.

Introduction

Polystyrene (Ps)−divinylbenzene (DVB) based resins produced by suspension polymerization have evolved from being the workhorse materials of ion-exchange resins,[1] sulfonic acid resin catalysts,[2] and high surface area hydrophobic sorbents[3] to the pivotal supports used in most solid-phase synthesis nowadays. The precursor resins can be prepared with various morphologies[4−6] typified by the gel-type species so popular in solid-phase combinatorial and parallel organic synthesis[7,8] and the macroporous species used more widely as catalyst supports.[9−11] We have, however, previously probed the interface between these two morphological extremes and demonstrated that collapsible macroporous resins can be prepared with some of the favorable characteristics of both resin types.[12,13] Inevitably a given morphology imposes some limitations on a resin, the most important in the case of gel-type resins being the requirement to employ solvents which are thermodynamically compatible and hence which swell the gel matrix. In the case of macroporous resins a common limitation is that some functional groups within the highly cross-linked gel phase of the resin are inaccessible or impose some mass transport limitation on their exploitation. Another important restriction arising commonly with all resins is the maximum loading of a functional group on the resin matrix, expressed either as mmol g^{-1} dry resin, in the case of small scale users, or as mol L^{-1} of swollen resin in the case of large-scale users. Increasingly in the case of high throughput methodologies involving resin supports, the maximum loading of interest is the content of functional group on a single bead expressed as millimoles per bead. Increasing the loading per bead can be achieved by building terminally functionalized dendrimer structures within the bead via stepwise growth from functional group sites on the polymer backbone. Bradley and his group[14,15] have reported some excellent work in this context and demonstrated clearly the loading advantage that can be achieved. Constructing dendrimeric structures within a resin may also change the solvation characteristics of the final structure (advantageously or disadvantageously depending on conditions). In addition, however, the generation of dendrimeric linkers may also reduce the loading per gram of resin if the mass increase from the dendrimer framework “outweighs” the molar increase in terminal functional groups achieved. In terms of cost as well, dendrimer functionalized resins can bring an added penalty.

Considerable attention is currently being focused by the polymer chemistry community on the one-pot synthesis of hyperbranched polymers[16,18] as a cheaper and more convenient option to dendrimers. Furthermore, there is growing evidence that such macromolecular architectures give rise to physical properties (e.g., solubility, unusual rheological behavior, etc.) very similar to dendrimers. Recently, we reported on a facile, versatile, and cost-effective route to branched vinyl polymers using starting materials all of which are readily available and familiar to polymer chemists.[19,20] The strategy involves a conventional free radical polymerization of a vinyl monomer with a multifunctional vinyl comonomer. Normally such systems would generate a infinite cross-linked architecture, but by balancing the level of multifunctional comonomer with a free

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10.1021/ma0209794 CCC: \$22.00

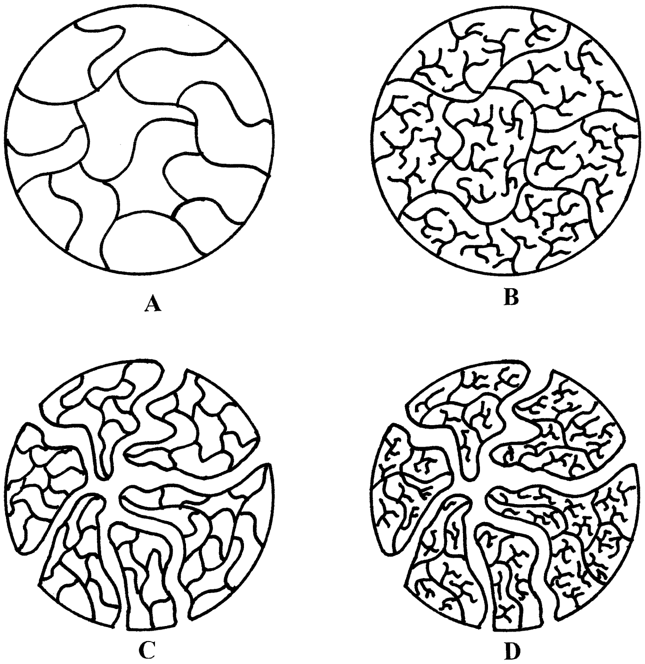

Figure 1. Schematic representations of (A) gel-type resin, (B) branched gel-type resin, (C) porous resin, and (D) branched porous resin.

radical transfer agent, high conversion to fully soluble branched polymer can be achieved.

The important experimental parameters in controlling the morphology of resins[4-6] are the level of cross-linker employed and the type and level of porogen or diluent used. Gel-type resins usually use low levels of cross-linker (≤5 mol %) and no porogen; macroporous resins typically employ 12−80 mol % cross-linker with ~50 vol % of a porogen in the organic phase. Porogens displaying good thermodynamic compatibility with the network being synthesized, combined with a high level of cross-linker, usually generate resins with high dry state surface area (100's $m^2\ g^{-1}$); porogens with low compatibility and with modest levels of cross-linker (~12−20 mol %) tend to yield resins with low dry state surface area (20−50 $m^2\ g^{-1}$). We hypothesized that we should be able to use our branching methodology and, by judicious manipulation of the cross-linker/chain transfer agent ratio, produce both gel-type and macroporous cross-linked resin with highly branched backbone architectures (Figure 1). Such species conveniently prepared in one pot would be highly cost-effective and have a very high proportion of free polymer chain ends relative to the proportion arising in conventional gel-type or macroporous resins. As a result, such a species might have unusual solvation properties and might offer advantages in terms of the efficiency of access to bound functional groups.

In this paper we report on our initial syntheses of branched resins and on our characterization data generated to demonstrate that branched architectures have indeed been achieved. Originally the term "macroporous" resin was coined by ion exchange scientists to distinguish rigid permanently porous resins from glassy nonporous ones that become gellike in the swollen state. "Macroporous" was not at that time meant to indicate any particular size of pore. For clarity hereafter resins with a discrete pore structure will be referred to as "porous" or "permanently porous", and the terms macroporous, mesoporous, and microporous will be utilized only in terms of the IUPAC definition i.e., micropores diameter <2 nm, mesopores 2−50 nm, and macropores >50 nm.

Experimental Section

Materials. Styrene (St) was used as supplied by the Fischer Co. Divinylbenzene (DVB) was used as supplied from the Aldrich Chemical Co. and was the ~80% technical grade quoted as an 80% mixture of 1,3- and 1,4-DVB isomers and 20% 1,3- and 1,4-ethylstyrene isomers. Dodecanethiol (DDT) was also from the Aldrich Chemical Co., while the azobis(isobutyronitrile) (AIBN) was used as supplied from the BDH Chemical Co. The porogens, toluene, and 2-ethylhexan-1-ol were each standard laboratory reagent grade. The stabilizer poly(vinyl alcohol) (PVOH) (98−99% hydrolyzed, $\bar{M}_w$ 85K−146K) was from Aldrich Chemical Co., as was the boric acid (99+%). The Cellosize (QP4400L) was from Hythe Chemicals, and the xanthan gum (Kelzan 90/GV/233) was a gift from Monsanto.

Suspension Polymerization Synthesis of Gel-Type Resins (G1−G10). The aqueous phase was prepared by dissolving PVOH (14 g) in distilled water (700 mL). This required gentle boiling for ~1 h. Once this solution cooled, a solution of boric acid (6 g) also in distilled water (175 mL) was added. A measured volume of this combined solution (225 mL) was then added to a 600 mL suspension polymerization reactor. Using resin G4-0 as an example, the organic phase comprised DVB (~80% grade) (1.2 g, ~4 wt % real DVB isomers), styrene (23.8 g, 95.2 wt %), and AIBN (0.25 g). This was suspended as droplets in the reactor by stirring at 350 rpm. The mixture was purged with N_2 and the temperature raised to 80 °C for 5 h. The resulting polymer beads were collected by filtration, the latter being aided if necessary by dilution with additional distilled water and decantation. After washing with water (500 mL) in the filter the beads were washed with methanol (100 mL) to harden them. They were then extracted in a Soxhlet overnight with acetone and finally deswelled and hardened by washing with methanol. This yielded a free-flowing particulate product that was vacuum-dried at 40 °C. The isolated yield of high-quality spherical particulate beads was 51%.

The other gel-type resins indicated in Table 1 were prepared similarly with the level of St, DVB, and DDT adjusted appropriately.

Suspension Polymerization Synthesis of Porous Resins (M.EH.20; M.T.20-80). The aqueous phase in this instance was prepared by adding preprepared solutions of xanthan gum (0.6 g in 150 mL of H_2O), Cellosize (0.08 g in 40 mL of H_2O), and boric acid (12 g in 500 mL of H_2O) to a flask and stirring thoroughly for 2 h. A measured volume of this mixture (225 mL) was then added to a 600 mL suspension polymerization reactor. Using resin M.EH.20-0 as an example, the monomer mixture comprised DVB (~80% grade) (3 g, ~ 20 wt % real DVB isomers), St (9.5 g, 76 wt %), to which was added 2-ethylhexan-1-ol (12.5 mL), and AIBN (0.125 g). The procedure was then as with the gel-type resins although the products beads were washed with both methanol and diethyl ether prior to extraction and drying. The yield of high quality beads was 67%.

The other (nominally) porous resins indicated in Table 2 were prepared similarly with the level of St, DVB, porogen (2-ethylhexan-1-ol or toluene), and DDT adjusted appropriately.

Characterization of Resin Morphology. *N_2 Sorption Porosimetry.* N_2 sorption isotherms were generated using a Micromeritics ASAP 2000 instrument. The packaged software was used to compute resin surface areas using a BET model. The data obtained are summarized in Table 2.

Hg Intrusion Porosimetry. Volume/pressure intrusion data up to 414 MPa were collected using a Micromeritics high-pressure porosimeter and the percent porosity of resins computed using the internal software. The data obtained are summarized in Table 2.

Table 1. Preparation of Branched Gel-Type Suspension Polymerized Ps-DVB Resins Using Various Levels of DDT Free Radical Chain Transfer Agent[a]

			resin parameters			
					solvent uptake (mL g^{-1})	
resin code	DVB (wt %)	DDT (wt %)	yield of beads (wt %)[b]	S content (wt %)	cylinder	centrifuge
G2-0	2	0	42		4.4[c]	2.6[c]
G3-0	3	0	47		2.9[c]	1.7[c]
G4-0	4	0	51		2.7[c]	1.5[c]
G5-0	5	0	88 (63)[e]		2.1[c] (2.2)[d]	1.3[c]
G5-1	5	1	~100		3.5[d]	
G5-2	5	2	~100		2.9[d]	
G5-3	5	3	88[f]		4.7[d]	
G5-4	5	4	71[f]		3.2[d]	
G5-5	5	5	91		4.7[d]	
G5-6	5	6	99		3.9[d]	
G5-7	5	7	62		6.2[d]	
G5-8	5	8	79		5.3[d]	
G5-9	5	9	81		5.5[d]	
G10-0	10	0	88	0	1.3[d]	
G10-5	10	5	~100	1.26	2.4[d]	
G10-10	10	10	74	1.87	5.6[d]	
G10-15	10	15	57	1.30	8.5[d]	

[a] See Experimental Section for further details. [b] Based on mass of St + DVB; particle diameter > 75 < 425μm. [c] Xylene. [d] Toluene. [e] Duplicate synthesis. [f] Beads rather aggregated.

Table 2. Preparation of Branched Porous Suspension Polymerized Ps-DVB Resins Using Various Levels of DDT Free Radical Chain Transfer Agent[a]

				resin parameters					
						dry state porosity		solvent uptake (mL g^{-1})[f]	
resin code	DVB (wt %)	DDT (wt %)	porogen[b]	yield of beads[c] (wt %)	S content (wt %)	surface area (m^2 g^{-1})[d]	%[e]	cylinder	centrifuge
M.EH.20-0	20	0	EH	67		74	46		
M.EH.20-5	20	5	EH	63	1.2	84	31		
M.EH.20-10	20	10	EH	53	2.4	23	21		
M.EH.20-15	20	15	EH	54	2.8	<5	14		
M.T.20-0	20	0	T	85		<5	-		
M.T.30-0	30	0	T	87		<5	-		
M.T.40-0	40	0	T	91		51	22	1.4	
M.T.40-2	40	2	T	87	trace	<5		1.3	
M.T.50-0	50	0	T	91		497	31	1.2	
M.T.50-2	50	2	T	86	trace	<5	-	1.4	
M.T.60-0	60	0	T	86		562	33	0.9	0.8
M.T.60-0.5	60	0.5	T	91	0.6	533	-	1.2	1.1
M.T.60-1	60	1	T	91	0.6	502	-	1.3	1.1
M.T.60-1.5	60	1.5	T	82	0.7	521	-	1.4	1.05
M.T.60-1.75	60	1.75	T	79	0.5	379	-	1.1	1.05
M.T.60-2	60	2	T	96	0.5	87	22	1.25	1.15
M.T.60-5	60	5	T	92	1.2	<5	14	1.3	1.15
M.T.60-10	60	10	T	90	2.1	<5	11	1.25	1.25
M.T.60-20	60	20	T	86	3.7	<5	8	1.7	1.3
M.T.80-0	80	0	T	88		756			
M.T.80-2	80	2	T	93	trace	609			
M.T.80-5	80	5	T	89	0.8	18			

[a] See Experimental Section for more details. [b] EH = 2-ethylhexan-l-ol; *T* = toluene; 1:1 v/v relative to comonomers. [c] Based on mass of St + DVB; particle diameter > 75 < 425μm. [d] N_2 sorption data BET model. [e] Hg intrusion data. [f] Xylene.

Solvent Uptake. *Volume Swelling Method.* A dry resin sample (1 mL = V_1) was added to a 5 mL measuring cylinder and the corresponding mass (grams) recorded. Xylene (or toluene) was then added in excess, any trapped bubbles removed by appropriate agitation, and the system left to equilibrate overnight. The final swollen volume of the beads was then noted. The increase in volume, $V_2 - V_1$, was adjusted per gram of dry resin. Note: this measurement is reasonably accurate with gel-type resins where significant swelling; i.e., volume increase occurs. With porous resins solvent uptake is more confined to pore filling, and if the actual volume change is small, this method is very much less accurate. The data obtained are summarized in Tables 1 and 2.

Centrifuge Method. This method is based on that described in the early literature.[21] A known weight of dry resin was placed in a small sinter stick, itself located in a metal centrifuge tube. The latter was then filled with xylene (or toluene) and the system left to equilibrate overnight. The excess solvent was poured out of the centrifuge tube, and then the sinter and contents were centrifuged at 3000 rpm for 3 min to remove the interstitial solvent from the beads. The exterior of the sinter stick was dried with tissue paper and reweighed. The mass increase per gram of dry resin was converted to a solvent uptake by assuming a value for the density of the solvent. The data obtained are summarized in Tables 1 and 2.

Inverse Size Exclusion Chromatography (ISEC). The swollen (tetrahydrofuran) state of resins was also probed by ISEC[22] in which each resin was used as a SEC stationary phase (4 mL swollen volume), and the elution volumes of standard solutes, C5−C30 alkanes, and polystyrenes of molecular weight 580−1 800 000 were recorded at a flow rate of 1 mL min^{-1} (Waters 510 hplc pump, differential refractometer detector RIDK 101, Laboratorni Pristroje). The interpretation of these data in terms of wet state surface area and pore volume each as a function of pore fraction (Tables 3 and 4) is discussed later.

Results and Discussion

Branched Gel-Type Resins. Resins G2-0 to G5-0 and G10-0 (Table 1) were prepared as controls in the

Table 3. THF Wet State Pore Volume/Pore Fraction Data for Macroporous Branched Resins Computed from a Cylindrical Model Analysis of Inverse Size Exclusion Chromatographic Data[a]

	pore vol (mL g^{-1})								
pore diameter (nm)	M.T. 60-0	M.T. 60-0.5	M.T. 60-1	M.T. 60-1.5	M.T.60-1.75	M.T. 60-2	M.T. 60-5	M.T. 60-10	M.T. 60-20
10.0	0.082	0.069	0.002	0.000	0.014	0.001	0.000	0.000	0.000
8.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
6.0	0.027	0.000	0.000	0.000	0.000	0.009	0.000	0.000	0.000
5.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
4.0	0.286	0.245	0.487	0.348	0.409	0.248	0.152	0.099	0.117
3.5	0.241	0.406	0.226	0.362	0.021	0.308	0.000	0.114	0.177
3.0	0.000	0.045	0.000	0.000	0.000	0.084	0.318	0.069	0.046
2.6	0.000	0.333	0.264	0.235	0.000	0.166	0.777	0.183	0.164
2.2	0.430	0.000	0.000	0.110	0.716	0.607	0.000	0.853	1.059
2.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
total pore vol (mL g^{-1})	1.066	1.098	0.977	1.055	1.160	1.422	1.247	1.318	1.503

[a] Elution volume data for polystyrene standards and C16 alkanes and larger.

Table 4. THF Wet State Surface Area/Pore Fraction Data for Macroporous Branched Resins Computed from a Cylindrical Pore Model Analysis of Inverse Size Exclusion Chromatographic Data[a]

	surface area (m^2 g^{-1})								
pore diameter (nm)	M.T. 60-0	M.T. 60-0.5	M.T. 60-1	M.T. 60-1.5	M.T.60-1.75	M.T. 60-2	M.T. 60-5	M.T. 60-10	M.T. 60-20
10.0	33	28	1	0	6	0	0	0	0
8.0	0	0	0	0	0	0	0	0	0
6.0	18	0	0	0	0	6	0	0	0
5.0	0	0	0	0	0	0	0	0	0
4.0	286	245	487	348	409	248	152	99	117
3.5	275	464	258	414	24	352	0	130	134
3.0	0	60	0	0	0	112	424	92	61
2.6	0	512	406	362	0	255	1195	282	252
2.2	781	0	0	200	1302	1104	0	1551	1926
2.0	0	0	0	0	0	0	0	0	0
total surface area (m^2 g^{-1})	1392	1308	1151	1322	1740	2076	1771	2152	2488

[a] Elution volume data for polystyrene standards and C_{16} alkanes and larger.

absence of DDT chain transfer agent. These are thus conventional gel-type species with the wt % of DVB, i.e., nominal degree of cross-linking, increasing progressively from 2 to 10%. Yields of quality spherical particulate beads ranged from ∼40 to 90% with most losses arising from aggregation and in workup and isolation. Resins G5-1 to G5-9 were all prepared with 5 wt % DVB/95 wt % St and with increasing levels of DDT chain transfer agent of 1−9 wt % (relative to the total mass of comonomers). The yields of quality beads varied from ∼60 to 100% with no particular systematic variation with the wt % DDT used. Thus, the presence of the free radical chain transfer is not detrimental in terms of achieving high conversion to polymer. We have found in parallel work involving solution polymerization of methyl methacrylate with divinyl comonomers such as ethylene dimethacrylate or DVB and also styrene with either of these two comonomers, in the presence of varying levels of DDT chain transfer agent, that cross-linking and macrogelation are inhibited, and primarily soluble branched copolymers are formed, providing the ratio of DDT to divinyl comonomer is ≥1.[19,20,23,24] In the present work therefore we argued that synthesis of St-DVB resins employing a DDT to DVB ratio <1 should produce overall a cross-linked product within which extensive branching would be prevalent. In the event resins which indeed overall are cross-linked, i.e., are totally insoluble (though swellable) in organic solvents, are obtained even when the DDT to DVB ratio reaches as high as ∼2. While this at first sight seems contradictory to the results of our solution polymerization studies,[23] in practice this is not so. In the latter work we have also shown that as the level of solvent employed is reduced, the ability to inhibit macrogelation simply by use of a chain transfer to difunctional comonomer of ≥1 becomes progressively reduced and is most difficult in the case of bulk polymerization. The present suspension polymerizations are of course in effect bulk polymerizations.

The series of gel-type resins G10-0 to G10-15 were similarly prepared with increasing levels of DDT and again moderate to good yields ∼60−100% of quality resin beads obtained. In this series confirmation of the incorporation of chain transfer residues, $CH_3(CH_2)_{11}S$-, into the resin matrix is provided by the elemental microanalytical data for S (Table 1).

Characterizing unambiguously that these two series of gel-type resins are indeed branched is very difficult because of their overall cross-linked nature. Indeed, characterizing the degree of branching in overall non-cross-linked polymers is also not straightforward and is still an active topic of research in itself. Some evidence with the present materials is provided by the swelling characteristics of the resins. The solvent (xylene) uptake for G2-0 to G5-0 falls progressively from 4.4 to 2.1 mL g^{-1}, and this is in keeping with the increase in level of cross-linking in this control series of conventional gel-type St-DVB resins. The swelling of G5-0 can therefore be taken as the baseline for the series G5-1 to G5-9. Though there is some scatter in the data arising with the inherent inaccuracy of the cylinder method (see Experimental Section) as the level of DDT employed rises, the solvent uptake capacity of this series of resins rises. Resins G5-7 to G5-10 indeed though prepared with 5 wt % DVB display levels of swelling greater than that of the control 2 wt % cross-linked species G2-0. Clearly therefore in terminating growing main chains prematurely, the chain transfer agent is effectively reducing the density of the cross-linked network and in doing so must be increasing the number of chain ends and generating an underlying branched architecture in the polymer backbone network; i.e., G5-11 to G5-9 are undoubtedly branched gel-type species (Figure 1b). If this picture is correct, one can predict that by employing a higher level of DVB with varying levels of DDT a series of gel-type resins should be produced which would show an even more dramatic shift in swelling behavior. This is indeed the case with the series G10-0 to G10-15. The control resin prepared with no chain transfer agent, G10-0, shows a toluene uptake of 1.3 mL g^{-1}. As the DDT level employed is increased stepwise to 15 wt %, the solvent uptake rises systematically to 8.5 mL g^{-1}. The latter represents a far greater swelling than that of a conventional 2% cross-linked St-DVB resin, and clearly G10-15 and the other members of this series must be highly branched.

Branched Porous Resins. Use of a thermodynamically poor porogen such as 2-ethylhexan-1-ol with relatively low levels of cross-linker (10−20 wt %) is known to yield Ps-DVB resins with modest surface area (∼50−100 m^2 g^{-1}) and with a broad pore size distribution including true macropores (i.e., diameter >50 nm[25]). In contrast, use of a thermodynamically good porogen such as toluene with relatively large levels of cross-linker (>50 wt %) is known to yield PS-DVB resins with a high surface area (>500 m^2 g^{-1}) and a large contribution from true micropores (i.e., diameter <2 nm). These guidelines were used in designing the targeted branched porous resins.

The first series M.EH.20-0 to M.EH.20-15 employed 20 wt % DVB and 2-ethylhexan-1-ol as the porogen. Yields of quality resin beads were moderate, ∼50−70% (Table 2), irrespective of the level of DDT chain transfer agent. Incorporation of the latter at correspondingly increasing levels is demonstrated by the increasing content of S in the product. In the absence of DDT the resin M.EH.20-0 displayed a dry state surface area of 74 m^2 g^{-1} (BET analysis of N_2 sorption isotherm) and a porosity (Hg intrusion data) of 46% much as anticipated. Increasing the level of DDT used causes a steady reduction in surface area down to <5 m^2 g^{-1} for 15 wt % of DDT and a corresponding fall in porosity to 14%. These represent very significant changes in the dry state porosity data with the chain breaking transfer reaction clearly reducing the overall density of the cross-linked matrix being formed while simultaneously generating additional chain ends and a branched architecture.

The same effects are seen with the resins prepared with toluene as the porogen, but in this case the morphological changes induced by the presence of the transfer reagent are much more dramatic. To appreciate these more easily, it is instructive to examine first the series of resins prepared with toluene as porogen, with no transfer agent and with increasing levels of DVB, i.e., M.T.20-0, M.T.30-0; M.T.40-0, M.T.50-0, M.T.60-0, and M.T.80-0 (Table 2). The dry state surface area data for this series of resins are shown in Figure 2. Clearly there is a remarkable change in morphology in moving from 40 to 50 wt % DVB. For DVB wt % ≥ 50 permanently porous resins are formed as a result of phase separation occurring during polymerization. The dry state surface area of this series increases systematically as the level of DVB employed is increased and reaches a maximum of ∼750 m^2 g^{-1} for 80 wt % DVB. This behavior agrees with previous reports in the literature.[4−6] Below 40 wt % DVB either no phase separation of the growing polymer matrix occurs, and a solvent expanded gel-type resin is formed, with essentially zero dry state surface area, or phase separation and pore formation does occur but on removal of the porogen the matrix is mechanically too weak and simply folds (reversibly?) on drying again, yielding a species displaying zero dry state surface area. The latter behavior has now been well characterized with very light cross-linked (<5 wt % DVB) resins prepared with a poor porogen, and these species have been designated as “reversibly collapsible” porous resins.[12,13]

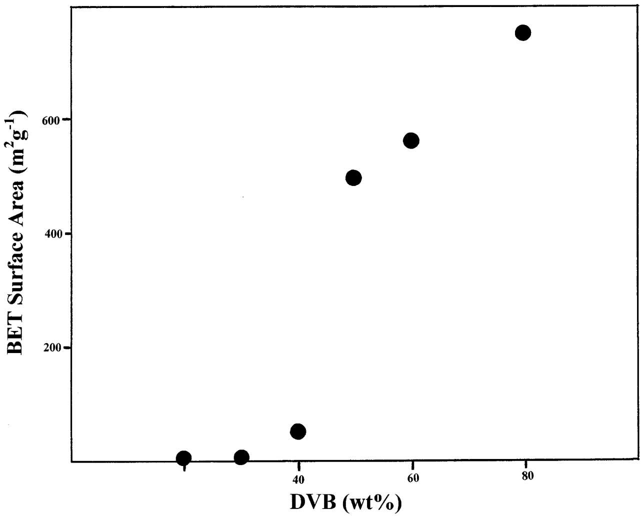

Figure 2. Dry state surface area as a function of mol % DVB in Ps-DVB resins prepared with toluene as a porogen.

Considering next the extensive series of resins M.T.60-0 to M.T.60-20 prepared with 60 wt % DVB, toluene as the porogen and increasing levels of DDT transfer agent. First there is again good evidence from the S% content for incorporation of residues of the DDT transfer agent into resins. Indeed, within experimental scatter there is a linear relationship across all the resins synthesized between the % S found in the product and the % DDT used in the suspension polymerization (Figure 3). Second, as the level of DDT used is increased to 1.5 wt % (i.e., resins M.T.60-0.5, -1, and -1.5) there is little effect on the dry state surface area of each resin which remains very high, >500 m^2 g^{-1} (Figure 4). However, further increase in DDT to 1.75 and 2% causes a catastrophic drop in the surface area of the resins to 87 m^2 g^{-1}, and at 5 wt % DDT the dry resin (M.T.60-5) is essentially nonporous with a surface area <5 m^2 g^{-1}. Further increase in DDT to 10 and 20 wt % likewise yields resins with essentially no dry state surface area. Hence, the pattern seen with the M.EH series of resins is repeated, but with much more dramatic changes induced in the resin morphology. Interestingly, a similar effect has been reported previously in the case of a ∼40% cross-linked resin prepared from glycidyl methacrylate and ethylene dimethacrylate in the presence of cyclohexanol porogen.[26] (We are grateful to one of our referees for drawing this work to our attention.) These workers were seeking methods of manipulating the pore structure of their resins that would avoid changing the level of cross-linker or type and level of porogen used. In doing so, they examined the influence of l-butanethiol. When the level of cyclohexanol was 60 vol % (of

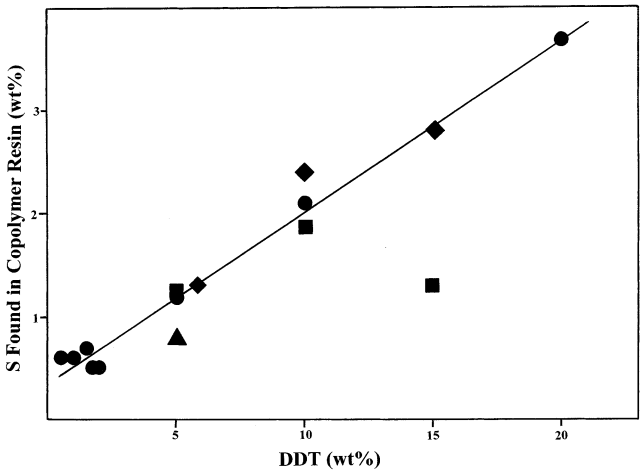

Figure 3. Correlation of % S found in Ps-DVB resins prepared in the presence of various levels of dodecanethiol (DDT) free radical transfer agent: (●) 60 wt % DVB/toluene porogen; (▲) 80 wt % DVB/toluene porogen; (◆) 20 wt % DVB/2-ethylhexan-1-ol porogen; (■) 10 wt % DVB gel type.

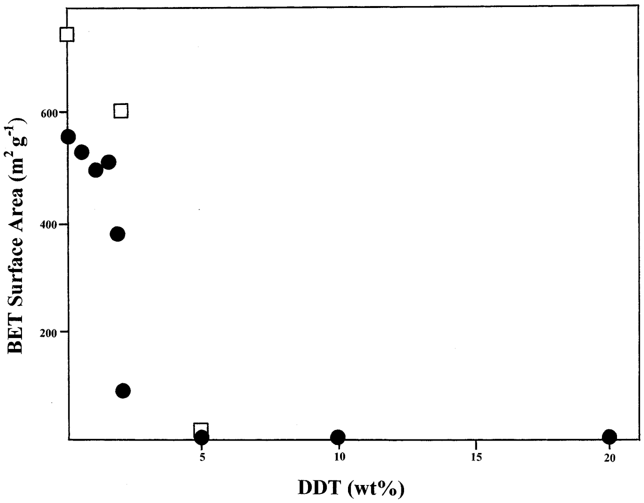

Figure 4. Dry state surface area as a function of level of dedecanethiol (DDT) used in the preparation of Ps-DVB resins: (●) 60 wt % DVB/toluene porogen; (□) 80 wt % DVB/toluene porogen.

the total organic phase), 0.8 vol % of butanethiol was sufficient to reduce the dry state surface area of the resin produced to <2 $m^2 g^{-1}$ from a value of ~80 $m^2 g^{-1}$ for an analogous resin prepared with no thiol present. Although this earlier work is restricted to much lower levels of chain transfer agent than we are reporting here, it seems clear that the resins produced must also have been branched, albeit to a lesser degree and perhaps not designed so to be.

It is clear in our own work that resins M.T.60-0 to M.T.60-1.75 are permanently porous with a high population of micropores and high surface area. Resins M.T.60-5 to M.T.60-20 are either solvent expanded gel types arising because phase separation has been eliminated in synthesizing these species or collapsed porous species arising because, despite phase separation still occurring, the density of the cross-linked network has been sufficiently reduced to allow reversible collapsing on drying. As we shall see later (ISEC data), characterization of these species in the wet (tetrahydrofuran) state in fact confirms them to be collapsible porous species. This change in morphology arises from the chain breaking transfer reaction induced by DDT and must simultaneously generate a surplus of chain ends and a highly branched architecture in the backbone polymer network. Overall therefore, resins M.T.60-0.5 to M.T.60-20 are all porous species with an increasing degree of backbone branching (Figure 1d) down the series and with the final three members being unable to sustain their porous morphology on drying.

The series of resins prepared with 80 wt % DVB and toluene as the porogen shows the same change in morphology as the 60 wt % DVB series. When the level of DDT used is increased from 2 to 5 wt %, there is a catastrophic fall in the dry state surface area with undoubtedly the generation of branched network structure. Parallel effects are seen with M.T.40-0 and M.T.40-2 and with M.T.50-0 and M.T.50-2 where in both cases use of 2 wt % DDT eliminates the dry state surface area in these resins.

Accumulation of further evidence from swelling data confirming the branched nature of these more highly cross-linked resins is more difficult, because these much more rigid species tend to sorb solvents by pore filling rather than by volume expansion. Nevertheless, using both the cylinder and centrifuge methods for evaluating solvent uptake, there is a consistent rise seen in the solvent inbibition for the series M.T.60 (Table 2) although the overall change observed is much less than is seen with the lightly cross-linked gel-type series (Table 1).

Inverse Size Exclusion (ISEC) Charaterization Studies. To establish a more detailed picture of the resin morphology in the solvent swollen state, the most extensive series of resins, M.T.60, were subjected to analysis by ISEC using tetrahydrofuran (THF) as the eluent. We have previously found this to be a uniquely invaluable tool in trying to characterize the internal structure of resins in the solvent wet state.[12] The interpretation of the probe molecule molecular weight vs elution volume data can be undertaken essentially using two possible models. The first assumes a permanent rigid pore structure which can be described most simply in terms of a cylindrical pore model. The second assumes that the probe molecules diffuse through a fairly uniform solvent swollen polymer gel network with no discrete pores, and mathematically this situation is conveniently treated using the Ogston model.[27] The problem arises with the ISEC elution data for small probe molecules since there is no unambiguous way of deciding whether these molecules migrate through very small permanent pores (e.g., micropores which survive or indeed fold in the dry state) or whether they diffuse through a swollen gel (which collapses in the dry state). Initially, therefore we have applied the cylindrical pore model to ISEC data for C16−C30 aliphatic hydrocarbons and polystyrenes of molecular weight 580−1 800 000 as probe molecules. We chose C16 as the lower limit of the probe molecules considered, corresponding to a size of ~2 nm, because we feel that features of lower dimension than this are more likely to be associated with a swollen gel phase, rather than with a permanent pore structure. The pore size distribution data obtained, expressed as pore volume for pore diameters 2−10 nm (no pores >10 nm were detected) per gram of resin, are shown in Table 3. The corresponding surface areas for individual pore fractions are shown in Table 4.

Considering the pore volume data first, it is interesting that the total volumes for M.T.60-0 to M.T.60-1.75 are close to 1 mL g^{-1}, which is what might be expected

Table 5. Chain Density/Gel Volume Data for Macroporous Branched Resins Computed from Analysis of Inverse Size Exclusion Chromatographic Data Using a Combination of the Cylindrical Pore Model and the Ogston Model[a]

polymer chain concn (nm nm^{-3})	gel vol (mL g^{-1})								
	M.T. 60-0	M.T. 60-0.5	M.T. 60-1	M.T. 60-1.5	M.T.60-1.75	M.T. 60-2	M.T. 60-5	M.T. 60-10	M.T. 60-20
0.1	0.000	0.000	0.015	0.000	0.000	0.000	0.000	0.000	0.000
0.2	0.000	0.000	0.031	0.022	0.016	0.034	0.163	0.000	0.000
0.4	0.157	0.162	0.000	0.001	0.000	0.002	0.000	0.385	0.502
0.8	0.009	0.000	0.018	0.277	0.632	0.821	1.092	0.170	0.000
1.5	0.400	0.415	0.344	0.000	0.026	0.198	0.000	0.885	0.922
2.0	0.847	0.196	0.889	0.823	0.683	0.000	0.267	0.063	0.582
column[b] vol balance (cm^3)	4.109	3.820	4.151	3.985	4.060	3.834	3.778	3.868	4.419

[a] Elution volume data for polystyrene standards and all alkanes down to C5. [b] Computed column volume balance from gel volume data − true volume being 4.04 cm^3.

for a rigid (nonswellable) permanently porous highly cross-linked Ps-DVB resin prepared with a toluene porogen:comonomer ratio of 1:1 v/v. The total pore volumes for the series M.T.60-2 to M.T.60-20 are significantly higher than 1 mL g^{-1}, consistent with the view that these resins generate additional accessible volume by swelling in solvents like THF. This is also consistent with the idea that the nominal degree of cross-linking of these species (≡60% DVB) is considerably reduced by the formation of branched structures as a result of the activity of the radical chain transfer agent, DDT. The data for total surface area in Table 4 reveal a related pattern, with the resins M.T.60-2 to M.T.60-20 showing effective surface area (in the wet state) much higher than the earlier members of the series, again consistent with the level of cross-linking being reduced and heavily branched architectures replacing these. It is important also to recall the surface area data derived from N_2 sorption BET analysis of the dry samples (Table 2), which for M.T.60-0 to M.T.60-1.75 are ~ 500 m^2 g^{-1}. For these resins it is tempting to suggest that the surface area arising in pores of diameter 3.5−4.0 nm in the THF wet state is associated largely with the permanent pore structure surviving on drying and that the surface area arising in pores of smaller diameter is associated either with pores which are collapsed in the dry state and which re-emerge in the THF wet state or with a swollen polymer gel phase. For resins M.T.60-5 to M.T.60-20 which show no dry state surface area the large majority of the THF wet state surface area must be associated either with small pores <3 nm diameter collapsed in the dry state and reemerging on solvation by THF or with a swollen polymer gel phase. In any event this behavior is totally consistent again with resins M.T.60-5 to M.T.60-20 being highly branched in their architecture.

If the wet state porosity characteristics nominally associated with collapsible pores in the size range 2−3 nm are in practice a reflection of a component of the swollen polymer gel phase, then the ISEC data can be reinterpreted using the cylindrical pore model for features 3 nm and larger and the Ogston model for the remaining data arising from a gel-phase feature. Using ISEC data for all probe molecules down to C5 hydrocarbon and applying the above models in the indicated ranges, the gel-phase data in Table 5 were computed. In terms of the mechanism of formation of the morphological features in these resins then it is important to recall that true pores (permanent or collapsible) arise when a discrete phase separation of a cross-linked polymer network occurs[4−6] whereas “gel porosity” arises simply from uniform solvation of a three-dimensional network of polymer chains, and no phase separation phenomenon arises in synthesizing these resins. With resins M.T.60-0 to M.T.60-1.75 chain transfer is not excessive; some branching does occur, but phase separation takes place similarly in all of these resins generating in due course permanent pores ~3.5−4.0 nm in diameter. For resin M.T.60-2 the level of chain transfer and branching becomes critical, and though phase separation and pore formation occur, the structure folds significantly on drying, yielding a partially collapsed resin with a much reduced dry state surface area (Table 2). Once resolvated in THF, however, this resin shows a pore volume/pore fraction distribution (Table 3) and a wet state surface area/pore fraction distribution (Table 4) very similar to the earlier members of this series of resins. With resins M.T.60-5 to M.T. 60-20 chain transfer and backbone branching becomes very significant, and despite phase separation occurring, the level of cross-linking is too low or the microgel particles too lightly fused[5] to prevent total collapse of the pore structure on drying (Table 2). However, once again in the THF swollen state the latent pore structure is reestablished, indicated most clearly by the data in Table 4 where a population of pores with a diameter 4−35 nm is demonstrated, this population being the same as that responsible for the dry state porosity and surface area in the non-collapsible porous resins earlier in the series.

Overall, the chain concentration data from the Ogston Model in Table 5 indicate a gradual decrease in the polymer chain density (i.e., a shift in gel volume fraction to lower chain concentration) for the whole series M.T.60-0 to M.T.60-20 as the level of chain transfer agent used is increased. This is in accord with a gradual reduction in the density of the cross-linked network and the increasing generation of chain ends and branched backbone architectures within these resins.

Conclusions and Future Work

By carrying out standard free radical suspension copolymerizations of styrene with divinylbenzene (DVB) in the presence of appropriate levels of a chain transfer agent dodecanethiol (DDT), it has been possible to synthesize in one-pot procedures a range of branched gel-type resins and similarly a range of branched porous resins. In the case of the gel-type species DVB contents in the range 1−10 wt % have been explored with corresponding DDT levels of 1−15 wt %. Thus, for example, a resin prepared with 10 wt % DVB and 15 wt %% DDT absorbs 8.5 mL of toluene per dry gram of resin, nearly twice the amount of a conventional gel-type resin prepared using 2 wt % DVB and ~6 times the amount of a conventional 10 wt % DVB resin. This reflects the much reduced density of the cross-linked network formed with chain transfer agent and the corresponding increase in the level of chain ends and branching in the matrix. In the case of porous resins the inclusion of chain transfer agent in the syntheses again results in a lowering of the density of each cross-linked network, the latter being reflected most obviously in a fall in the dry state surface area of these species as the level of transfer agent is increased. For example, in the case of a resin prepared with 60 wt % DVB and a 1/1 (vol/vol) ratio of toluene as a porogen, the dry state surface area falls from $\sim$550 m^2 g^{-1} in the absence of transfer agent to <5 m^2 g^{-1} for levels of transfer agent of 5 wt % and higher. Wet state porosity data from ISEC, however, suggest that these latter species are still porous but are collapsed in the dry state. Reducing the density of the cross-linked network in these porous species also increases the number of chain ends and branching in the polymer matrix.

To date, the evidence for branching has been gleaned from morphology studies, and molecular structural data are needed to confirm this picture. Soluble branched polymers produced using a similar methodology, but with excess of chain transfer agent, have been shown by solution ^{1}H NMR spectroscopy to be branched, and some qualitative data on the level of unreacted pendant double bonds have also been obtained.[23] In principle, similar molecular structural characterization of branched resins is also possible using solid-state magic angle spinning ^{13}C NMR spectroscopy. However, our own experience with this technique has shown this not be straightforward, and careful single pulse excitation (SPE) studies will be required to minimize purely instrumental effects.[28−30] In addition, evaluating unambiguously the number of chain ends will require some analytical handle specifically on or near chain ends.

Interest and exploitation of the novel resins we have reported will expand only if these species prove to provide advantages (particularly in solid phase synthesis) over conventional resins. The increased level of chain ends and branches in these species should provide accessibility and mass transfer advantages, and we are currently pursuing studies toward this end via functional variants of the resins we have reported here.

References and Notes

(1) Helfferich, F. *Ion Exchange*; McGraw-Hill: New York, 1962.
(2) Widdecke, H. In *Syntheses and Separations Using Functional Polymers*; Sherrington, D. C., Hodge, P., Eds.; J. Wiley and Sons: Chichester, 1988; Chapter 4, p 149.
(3) Millar, J. R. *J. Polym. Sci., Polym. Symp.* **1980**, *68*, 167.
(4) Albright, R. L. *React. Polym.* **1986**, *4*, 55.
(5) Sherrington, D. C. *Chem. Commun.* **1998**, 2275.
(6) Okay, O. *Prog. Polym. Sci.* **2000**, *25*, 711.
(7) Jung, G., Ed. *Combinatorial Peptide and Non-peptide Libraries;* VCH Pubs.: Weinheim, Germany, 1996.
(8) Czarnik, A. W.; De Witt, S. H. *A Practical Guide to Combinatorial Chemistry;* American Chemical Society: Washington, DC, 1997.
(9) Ley, S. V.; Baxendale, I. R.; Bream, R. N.; Jackson, P. S.; Leach, A. G.; Longbottom, D. A.; Nesi, M.; Scott, J. S.; Storer, I.; Taylor, S. J. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3815.
(10) Sherrington, D. C. In *Chemistry of Waste Minimisation;* Clark, J. H., Ed.; Blackie Publishers: Glasgow, UK, 1995; Chapter 6, p 141.
(11) Ermert, P. In *Solid-supported Combinatorial and Parallel Synthesis of Small-Molecular-Weight Compound Libraries;* Obrecht, D., Villagordo, J. M., Eds.; Pergamon: Oxford, UK, Chapter 1.6, p 44.
(12) Howdle, S. M.; Jerabek, K.; Leocorbo, V.; Marr, P. C.; Sherrington, D. C. *Polym. Commun.* **2000**, *41*, 7273.
(13) Hradil, J.; Svec, F. *Angew Makromol. Chem.* **1985**, *130*, 81.
(14) Fromont, C.; Bradley, M. *Chem. Commun.* **2000**, 1283.
(15) Basso, A.; Evans, B.; Pegg, N.; Bradley, M. *Tetrahedron Lett.* **2000**, *41*, 3763.
(16) Sunder, A.; Heinemann, J.; Frey, H. *Chem. Eur. J.* **2001**, *26*, 1233.
(17) Voit, B. *J. Polym. Sci., Part A*: *Polym. Chem.* **2000**, *38*, 2505.
(18) Jikei, M.; Kakimoto, M.-A. *Prog. Polym. Sci.* **2001**, *26*, 1233.
(19) O'Brien, N.; McKee, A.; Sherrington D. C.; Slark A. T.; Titterton, A. *Polym. Commun.* **2000**, *41*, 6027.
(20) Costello, P. A.; Slark, A. T.; Sherrington, D. C.; Titterton, A. *Polymer* **2002**, *43*, 245.
(21) Pepper, K. W.; Reichenberg, D.; Hale, D. K. *J. Chem. Soc.* **1952**, 3129.
(22) Jerabek, K. In *Cross Evaluation Strategies in Size Exclusion Chromatography*; Postekka, M., Dubin, P. L., Eds.; ACS Symp. Ser. No. 635; American Chemical Society: Washington, DC, p 211.
(23) Isaure, F. Ph.D. Thesis, University of Strathclyde, Glasgow, UK, 2002, in preparation.
(24) Dangoulème, V. Master of Philosophy Thesis, University of Strathclyde, Glasgow, UK, 2002.
(25) Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierroti, R. A.; Rouquérol, J.; Siemieniewska, T. *Pure Appl. Chem.* **1985**, *57*, 603.
(26) Smigol, V.; Svec, F. *J. Appl. Polym. Sci.* **1993**, *48*, 2033.
(27) Ogston, G. *Faraday Soc.* **1958**, *54*, 1754.
(28) Law, R. V.; Sherrington, D. C.; Snape, C. E.; Ando, I.; Korosu, H. *Ind. Eng. Chem. Res.* **1995**, *34*, 2740.
(29) Law, R. V.; Sherrington, D. C.; Snape, C. E.; Ando, I.; Korosu, H. *Macromolecules* **1996**, *29*, 6284.
(30) Law, R. V.; Sherrington, D. C.; Snape, C. E. *Macromolecules* **1997**, *30*, 2868.

MA0209794