

High-density foams prepared with the styrene–divinylbenzene copolymer/heptane system

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(Received 9 June 1989; revised 14 November 1989; accepted 18 November 1989)

This report focuses on the production of $0.1\text{--}1.03\text{ g cm}^{-3}$ foams by taking an open, microcellular foam, saturating it with a radical-polymerizable monomer solution, polymerizing the monomers and removing the non-polymerizing diluent solvent. This study also contains information about the phase separation behaviour of divinylbenzene-crosslinked polystyrene from heptane, and about the expansion and retraction of crosslinked polystyrene. The influence of filler composition on the microstructure of the foams is presented. These two-component foams provide a new line of microporous materials, which may provide a simple alternative to the beads currently used in chromatography.

(Keywords: polymer; styrene; divinylbenzene; heptane; foam; microcellular; microstructure; gel; macroporous; swelling; contraction; phase behaviour; scanning electron microscopy; compression properties)

INTRODUCTION

Although physicists prefer the simplicity of modelling substances of uniform density, such as a gas, over more non-homogeneous materials, large shock-wave experiments are difficult to perform at high pressures. Polymeric foams have proven to be an adequate, if not ideal, substitute for gases. As the void regions (called cells) between mass units become smaller, the foam approximates a gas better. The two main objectives are to produce foams with: (1) very small cell sizes; and (2) densities ranging from that of air (0.0015 g cm^{-3}) to that of full-density polymer ($\sim 1\text{ g cm}^{-3}$). Efforts to produce very small cell sizes and low densities ($<0.01\text{ g cm}^{-3}$) have received considerable attention from us and others in recent years^{1–10}. This report focuses on the production of high-density ($0.1\text{--}1.03\text{ g cm}^{-3}$) foams.

The technique¹¹ that we chose for preparing foams with these higher densities involves taking an open, microcellular foam, saturating it with a radical-polymerizable monomer solution, polymerizing the monomers and removing the non-polymerizing solvent used to make the monomer solution. The technique seems so simple (Figure 1), but gave us considerable anxiety when we tried to make 0.3 g cm^{-3} foam using styrene (with 10% divinylbenzene) in heptane. Starting with a 0.1 g cm^{-3} foam prepared by an emulsion process³, we obtained a wide range ($\pm 20\%$) of foam densities from seemingly identical conditions. A slight change in the monomer concentration in the solution (from 0.37 to 0.42 g ml^{-1}) gave dramatic changes in the final foam density (from 0.27 to 0.56 g cm^{-3})! Since we were obviously operating under sensitive conditions, we evaluated the parameter space indicated in Figure 2. This extensive study yielded information about how to make reproducible high-density foams and insight into the phase separation behaviour of divinylbenzene-crosslinked polystyrene from heptane (useful in preparing macroporous or gel-type resin beads), as well as an explanation for the expansion

and retraction behaviour of the crosslinked polystyrene foam that occurred during the experiment.

EXPERIMENTAL

Right-cylindrical foam preforms (2.5 cm diameter by 2.5 cm high) were cut from 0.074 g cm^{-3} emulsion foam prepared from 90/10 styrene/divinylbenzene by an emulsion polymerization technique³. Monomer solutions were prepared from divinylbenzene (DVB), styrene, heptane and azobisisobutyronitrile (AIBN; an initiator). Both of the monomers were used without removing their inhibitors, as this was the final intended procedure. Since the DVB had more inhibitor, the amount of AIBN was scaled according to the formula $0.0018g_{\text{styrene}} + 0.0129g_{\text{DVB}}$. Details of the amounts of each component are given in Table 1. A foam preform was placed in a 125 ml wide-mouthed bottle (4.5 cm diameter by 8 cm tall) and covered with 100 ml of the appropriate solution. The bottle was placed in a bell jar and the foam was held beneath the surface with a stainless-steel rod. A vacuum was applied at room temperature to remove the entrapped air. The vacuum was released before the monomer solution began to boil, however. The vacuum/release cycle was repeated twice more before the jar was capped and heated overnight in a 60°C oven. The polymerized solid masses were removed from the jars by cracking the glass and carefully removing the fragments. Each sample was set on a piece of plate glass and placed in a $60\text{--}80^\circ\text{C}$ forced-air convection oven and dried for several days or weeks (as in the case of the very dense gel samples). Physical characteristics (appearance, texture, hardness, etc.) were made by visual inspection. The largest, crack-free, right-cylindrical preform possible was machined from each dried mass. Foam densities were determined from weight and volume measurements on the machined pieces. Cylinder diameter and final densities are given in Table 1. Compression analyses were determined on the right cylinders using an Instron with a

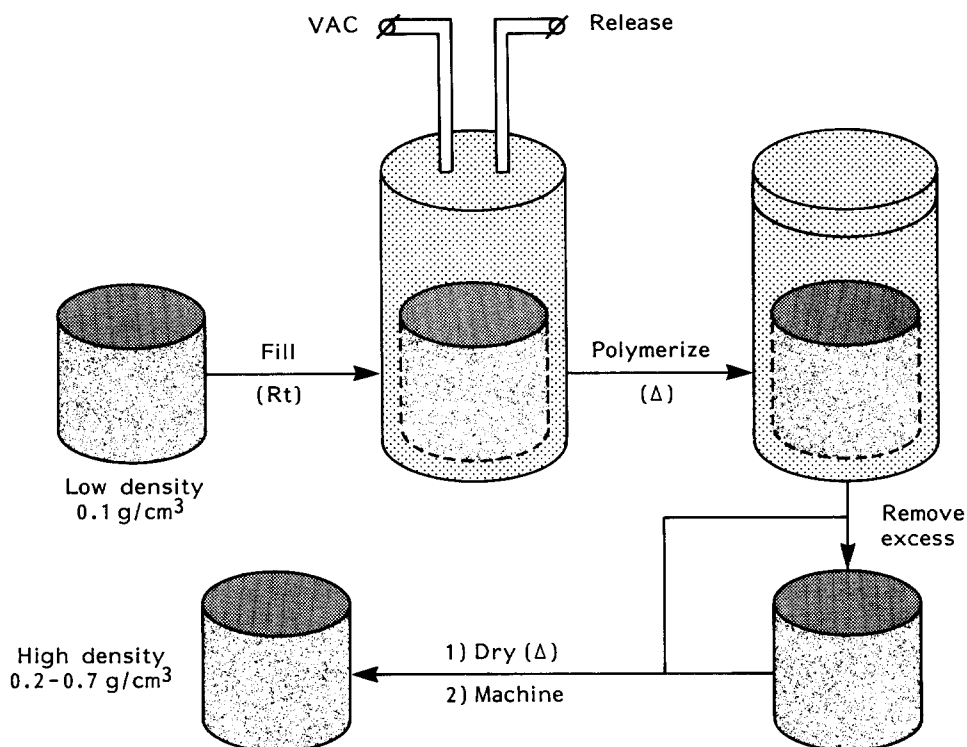


Figure 1 Procedure for preparing high-density foam. The low-viscosity filling solution contains polymerizable monomers

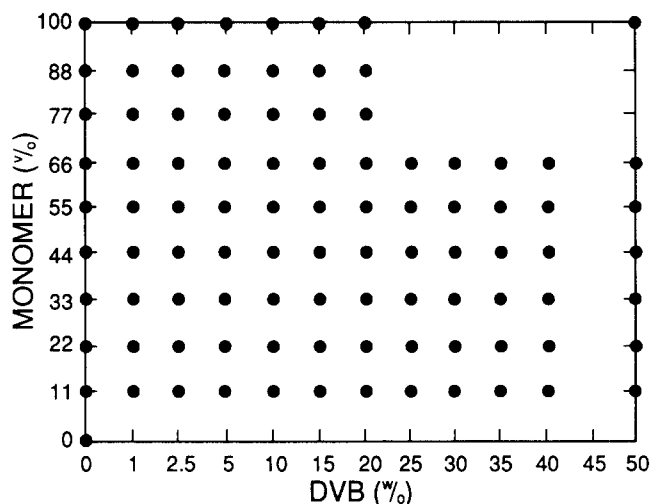


Figure 2 Parameter space evaluated. Remainder of volume per cent made up of heptane. The percentage of DVB is the percentage of 55–60% active material actually used. This terminology holds for all the figures

454 kg (1000 lb) or a 4540 kg (10 000 lb) load cell and a platen speed of $0.127 \text{ cm min}^{-1}$ ($0.05 \text{ inch min}^{-1}$). Elastic modulus, yield strength and scanning electron microscopy data were determined as previously reported^{3,12}. The physical properties are discussed in detail elsewhere¹³.

RESULTS

Bulk polymer properties and phase behaviour

Within the parameter space studied (0–100% monomer in solution and 0–50% divinylbenzene*), the bulk

* In this paper the percentage of DVB represents the percentage of 55–60% active material used and not the percentage of pure DVB present. Millar *et al.*¹⁴ reported that they used nominally 55% active DVB. It is not clear, but it seems most probable that they plotted their data in the same way that we did

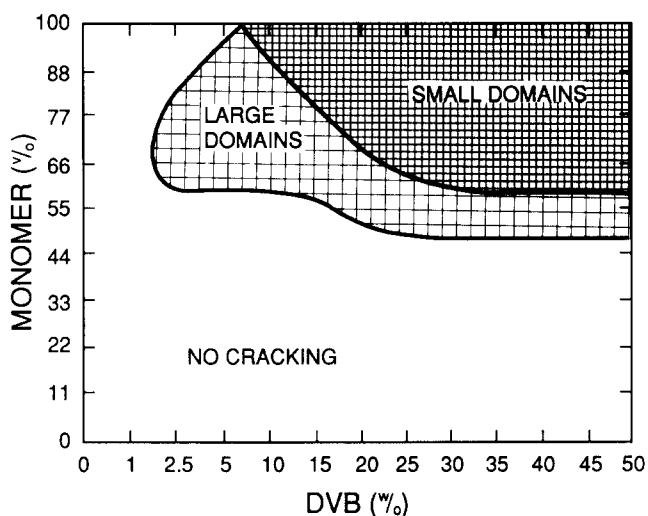


Figure 3 Stress cracking produced in bulk polymer when polymerized as a continuous cylinder. After drying and exterior to the foam preform. The sizes of the specimens are 3–5 cm diameter by 3–5 cm high

polymer (i.e. the polymer produced outside the foam preform) varied considerably. The following observations were made concerning this bulk polymer. The polymer only filled the solution space when the solvent (heptane) fraction was less than the volume fraction unoccupied by close-packed uniform spheres, i.e. 27%. Stress-cracked blocks of polymer were generally found when the monomer level exceeded 50% (Figure 3). The severity of cracking was more extensive at higher monomer and DVB levels; presumably much greater internal stresses were present. Under all conditions, the polymer was colourless, but ranged from clear or slightly cloudy to opaque. A more complete physical description of the polymer mass produced under each of the different conditions is presented in Figure 4. The gel-type polymer varied from a very soft to a hard clear plastic. The

Table 1 Formulations and properties of foams

Monomer (%) ^a	DVB (%) ^b	Filler type ^c	Density (g cm ⁻³)	Cylinder diameter ^d (cm)	Compression modulus		Yield strength (psi) ^f
					(MPa)	(ksi) ^e	
0.0	0.0	CNTL	0.07	2.03	19	2.8	94
11.0	0.0	P	0.09	2.03	19	2.7	136
11.0	2.5	G	0.10	2.03	38	5.6	181
11.0	5.0	MC	0.11	2.03	49	7.1	239
11.0	10.0	MC	0.12	1.65	43	6.2	222
11.0	20.0	MC	0.12	2.03	50	7.3	287
11.0	25.0	MC	0.13	2.03	64	9.2	315
11.0	30.0	MC	0.14	2.03	68	9.9	339
11.0	35.0	MC	0.14	1.59	69	10.0	362
11.0	50.0	MC	0.15	2.03	78	11.3	400
22.0	0.0	P	0.12	2.03		Damaged	
22.0	2.5	G	0.12	1.51		Damaged	
22.0	10.0	MC	0.19	2.02	111	16.1	501
22.0	20.0	MC	0.22	2.03	136	19.7	729
22.0	40.0	MC	0.22	2.03	168	24.4	879
22.0	50.0	MC	0.26	2.03	223	32.4	1168
33.0	0.0	P	0.20	1.52	102	14.7	327
33.0	1.0	G	0.24	2.03	174	25.3	794
33.0	2.5	G	0.17	2.03	108	15.6	537
33.0	5.0	MC	0.32	1.52	286	41.5	1490
33.0	10.0	MC	0.31	1.52	248	36.0	1316
33.0	20.0	MC	0.33	1.52	293	42.5	1605
33.0	40.0	MC	0.38	2.03	276	40.1	1548
44.0	0.0	P	0.38	2.03	220	31.9	1074
44.0	1.0	G	0.50	2.01	444	64.5	1658
44.0	2.5	G	0.52	2.01	461	66.8	1577
44.0	5.0	G	0.52	2.03	510	74.0	2423
44.0	10.0	MC	0.44	2.03	234	33.9	1067
44.0	15.0	MC	0.46	2.04	217	31.5	969
44.0	20.0	MC	0.45	2.03	178	25.8	812
44.0	25.0	MC	0.45	2.03	193	27.9	868
44.0	30.0	MC	0.49	2.03	216	31.3	1048
44.0	35.0	MC	0.49	2.04	224	32.4	912
44.0	40.0	MC	0.49	2.03	203	29.5	1044
44.0	50.0	MC	0.50	2.04	215	31.1	1114
55.0	0.0	P	0.46	2.03	478	69.3	1719
55.0	0.0	P	0.24	2.03	159	23.1	517
55.0	0.0	P	0.39	2.00	249	36.1	680
55.0	1.0	G	0.51	2.00	469	68.1	1896
55.0	1.0	G	0.33	2.00	209	30.2	844
55.0	2.5	G	0.67	1.59	830	120.4	2314
55.0	2.5	G	0.74	1.99	920	133.5	4571
55.0	2.5	G	0.70	1.99	756	109.6	2768
55.0	2.5	G	0.76	1.57	877	127.3	3970
55.0	5.0	G	0.91	1.97	1228	178.1	7791
55.0	10.0	BL	0.73	2.03	741	107.5	2859
55.0	15.0	MC	0.67	2.03	558	81.0	3138
55.0	20.0	MC	0.63	2.03	551	79.9	2700
55.0	25.0	MC	0.60	2.04	445	64.6	2084
55.0	30.0	MC	0.53	2.03	265	38.4	1281
55.0	40.0	MC	0.56	2.03	276	40.1	1736
55.0	50.0	MC	0.56	2.03	286	41.5	1386
60.5	2.5	G	0.68	1.58	748	108.5	2861
60.5	2.5	G	0.76	1.58	885	128.4	3692

Table 1 (cont.)

Monomer (%) ^a	DVB (%) ^b	Filler type ^c	Density (g cm ⁻³)	Cylinder diameter ^d (cm)	Compression modulus		Yield strength (psi) ^f
					(MPa)	(ksi) ^e	
66.0	0.0	P	0.33	1.52	186	27.0	548
66.0	0.0	P	0.28	2.03	140	20.3	611
66.0	1.0	G	0.63	1.99	652	94.5	2573
66.0	1.0	G	0.58	2.00	545	79.0	2063
66.0	2.5	G	0.41	2.01	377	54.7	1270
66.0	2.5	G	0.63	1.59	685	99.3	2468
66.0	2.5	G	0.27	2.00	156	22.7	702
66.0	5.0	G	0.70	2.02	814	118.0	3721
66.0	5.0	G	0.99	2.01	1322	191.7	7018
66.0	10.0	G	0.87	2.01	1198	173.7	7018
66.0	15.0	G	0.77	2.03	902	130.9	4647
66.0	25.0	MC	0.76	0.95	810	117.5	4156
66.0	25.0	MC	0.84	0.64	983	142.6	6133
66.0	30.0	MC	0.82	0.71	846	122.7	5567
66.0	40.0	G	0.85	1.01	1065	154.5	7533
66.0	50.0	G	0.65	0.75	596	86.5	2974
71.5	2.5	G	0.33	1.59	233	33.7	734
71.5	2.5	G	0.39	1.59	306	44.4	1081
77.0	0.0	P	0.46	2.04	381	55.2	1248
77.0	0.0	P	0.57	2.04	589	85.4	2626
77.0	1.0	G	0.64	2.01	611	88.7	2718
77.0	1.0	G	0.69	2.00	740	107.3	2834
77.0	2.5	G	0.41	1.59	327	47.5	1080
77.0	2.5	G	0.41	2.00	390	56.5	1164
77.0	2.5	G	0.50	1.59	451	65.4	1467
77.0	2.5	G	0.54	2.01	594	86.1	1970
77.0	5.0	G	0.82	1.97	1041	151.0	6774
77.0	10.0	G	0.84	2.02	1074	155.8	5742
77.0	20.0	G	0.77	1.26	1148	166.4	4743
82.5	2.5	G	0.55	1.59	583	84.6	2139
82.5	2.5	G	0.63	1.59	780	113.1	3143
88.0	0.0	P	0.77	2.03	1137	164.9	5709
88.0	1.0	G	0.86	2.02	1117	162.1	5324
88.0	2.5	G	0.84	2.02	1128	163.5	4629
88.0	5.0	G	0.77	2.01	1001	145.1	4539
88.0	10.0	G	0.77	2.01	1078	156.3	5707
100.0	0.0	P	0.87	2.03	1185	171.9	6867
100.0	1.0	G	0.83	2.02	1095	158.9	5125
100.0	2.5	G	1.03	1.21	1848	268.1	10723
100.0	5.0	G	1.02	1.40	1483	215.1	8503
100.0	10.0	G	0.81	1.01	1037	150.3	5234

^a Volume per cent of total filling solution^b Weight per cent of total monomers^c CNTL = control; P = popcorn; MC = macroporous; G = gel; BL = borderline between G and MC^d Diameter of right cylinder used to perform compression test^e 1 ksi \equiv 10³ lb/inch²^f 1 psi \equiv 1 lb/inch²

macroporous-type polymer, produced when DVB was present, varied from a very crumbly 'cottage cheese' to an opaque powder to a very hard opaque plastic. When DVB was absent, the opaque polymer was more like bits of popcorn[†]. Based on the experimental results obtained,

[†] Miller¹⁵ also reports this term for polymer made when DVB is present in trace amounts

we have drawn a phase separation diagram for this styrene-divinylbenzene/heptane system (Figure 5). This phase diagram is essentially the same as that reported previously by Millar *et al.*¹⁴ for the same styrene-divinylbenzene/heptane system. Our phase separation line tops out at a slightly lower percentage monomer level, which may result from the fact that our line is based on visual

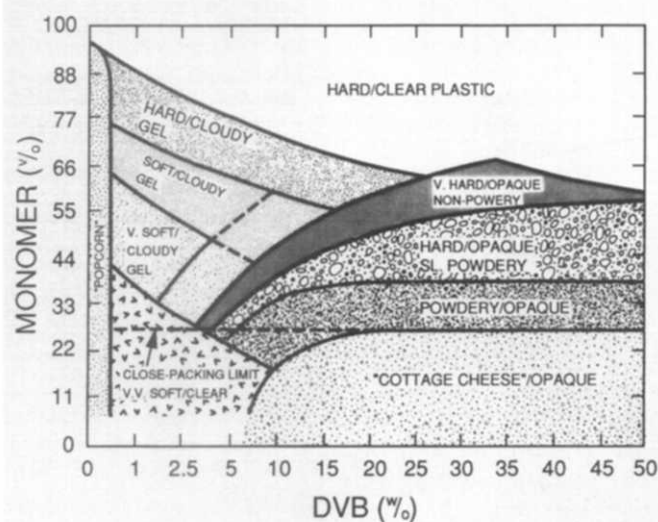


Figure 4 Physical character of bulk polymer. After drying and exterior to the foam preform. Soft gel regions identified before drying

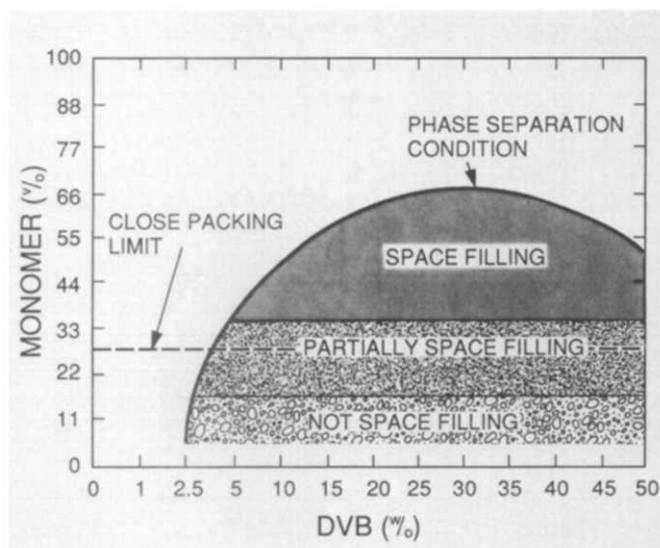


Figure 5 Phase separation diagram (at 60°C) for styrene-divinylbenzene/heptane system

observations whereas Millar *et al.*¹⁴ based theirs on toluene swelling data.

Foam response to internal polymerization

The filled foam is less sensitive to stress cracking than is the bulk polymer (compare Figure 6 with Figure 3). Indeed, we have prepared filled foams as large as 5 cm diameter by 30 cm long with 44% monomer and 35% DVB without cracks. Scale-up in volume is less critical with regard to cracking for the filled foam than it is for the bulk polymer mass alone*. We attribute this lower sensitivity to the strength and continuity provided by the foam preform. This is most evident within the 60–90% monomer/2.5–15% DVB conditions. In the bulk polymer,

* The reader is cautioned that the crack behaviour in Figure 3 and 6 are for moderately small specimens (3–5 cm diameter by 3–5 cm high). On scale-up to larger volumes, the crack domains broaden dramatically into the lower monomer levels! All attempts to make 0.5 g cm⁻³, right cylinders 25 cm diameter and 20 cm high have produced ruptured or highly bloated foams

the strength of the gel structure is not sufficient to overcome the stresses developed during polymerization and the gel mass cracks. The foam preform under the same conditions provides sufficient strength to overcome those stresses and thus yields a crack-free material.

During the saturating and polymerization process, we observed that the polymeric foam preform expanded (Figure 7). The initial swelling of 1.6–2 times in volume was expected for a lightly crosslinked material in a good polymer solvent, such as styrene. (The swelling was fortunately not rapid and the foam preform could be saturated before any significant swelling occurred.) Contrast the poor swelling by heptane (0% monomer) to the better swelling by the styrene/DVB cases shown in Figure 8. A subsequent swelling was not anticipated but, in retrospect, is understandable. We attribute this secondary swelling to the enormous swellability of low-molecular-weight polymer formed early in the polymerization of the monomers. This low-molecular-weight material will even be susceptible to some solvation by the normally poor solvent, heptane. At even the low levels of monomer studied (11%), there is sufficient good solvent for the initial swelling to occur. This low level is not sufficient, however, to generate enough polymer to create any significant secondary swelling. As the monomer level increases (up to 44–55 vol%), the secondary swelling increases as more polymer is produced. As the amount of non-polymerizing solvent becomes scarce (see 0% DVB data in Figure 8), the secondary swelling decreases. In general, increased crosslinking (higher DVB) retards this secondary swelling (see the negative dependence of swelling on DVB level (Figure 8)). In fact, above 33% monomer, the secondary swelling is controlled principally by the amount of crosslinking and not by the concentration of monomers in solution (Figure 9; compare this with the decrease in swellability of polystyrene as crosslinking with DVB increases¹⁶). Below 33% monomer, the amount of monomers is the principal controlling factor and, since its influence is dramatic, process control will be sensitive to slight changes in monomer concentration! The effects of monomer and crosslink levels show up somewhat differently (Figure 10) on the grid used for the phase diagram. Above curve A, the expansion is practically insensitive to monomer level

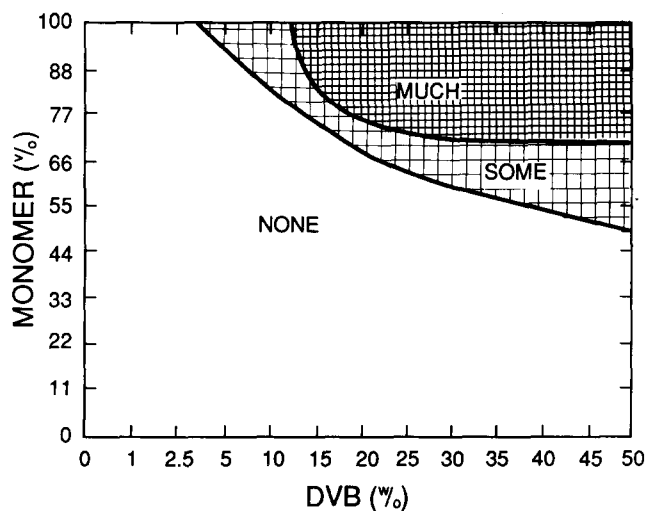


Figure 6 Stress cracking produced in foam preforms. After polymer filling and drying

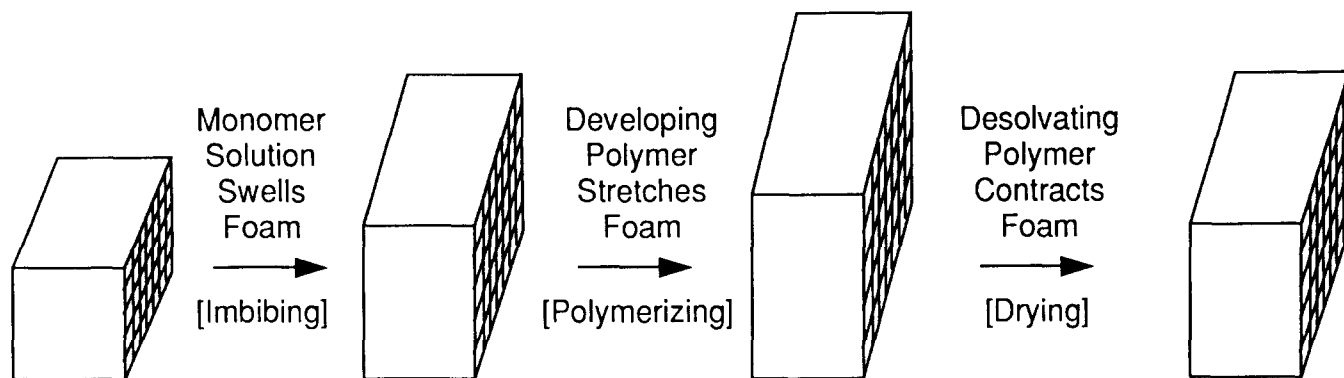


Figure 7 Dimensional behaviour of a foam preform when filled with a monomer solution that is subsequently polymerized and dried

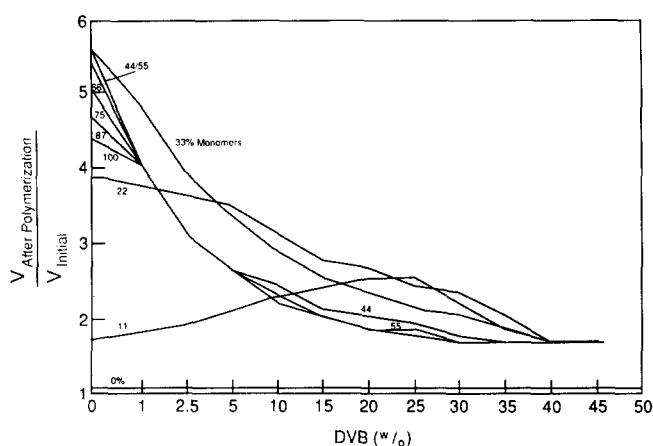


Figure 8 Dependence of foam preform volume increase on crosslinking level in the imbibing monomer solution. The number on each curve corresponds to the percentage of monomer in the filler solution

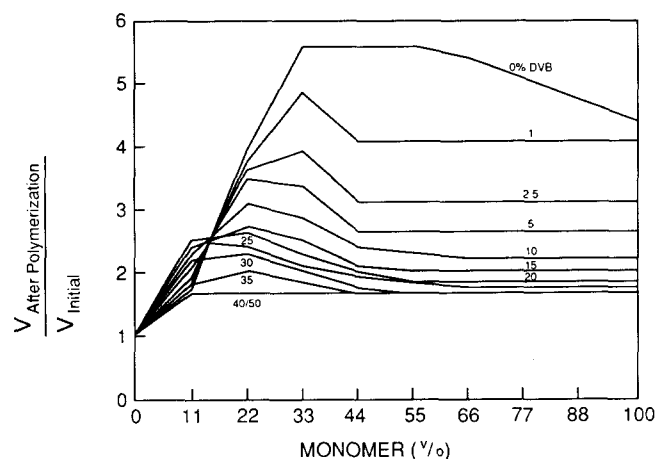


Figure 9 Dependence of foam preform volume increase on monomer level in the imbibing solution. The number on each curve corresponds to the percentage of DVB in the filler solution

at a given DVB level. Below curve B, changes in the monomer level dominate. Curve C represents the transition (inflection point) in the swelling of the foam preform from monomer dominance to crosslink dominance. Interestingly, this transition occurs around 37 vol% monomer for all crosslink levels, i.e. near the conditions that we found so difficult to control in our initial experiments. An important consequence of the secondary expansion phenomenon is the reduction in the density

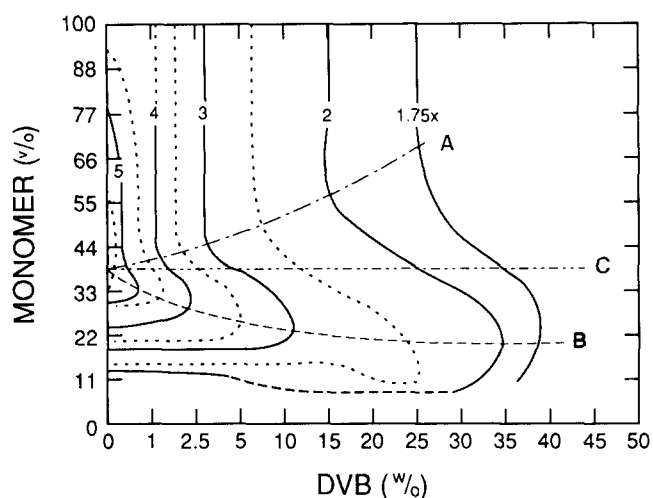


Figure 10 Volume expansion of foam preform during imbibing and polymerization. The contour lines are for constant x -fold volume expansion. See text for comments

of the filled preform. Since the monomers external to the preform are also polymerizing, they cannot flow into the swelling foam. Consequently, the mass added to the foam preform by the monomers is set by the amount of monomer that enters the preform before polymerization occurs. As the preform swells, the mass of the preform and its monomer filler do not change, but the volume they occupy increases and, thus, their combined density decreases.

The final density of the filled preform depends on the amount of monomer incorporated, the swelling of the preform and the contraction of the entire mass during drying. In the absence of any abnormal behaviour, one would anticipate a somewhat smooth contour surface for the parameter space involved. Such is not the case (Figure 11), although some 'smooth' behaviour is readily evident. Density clearly increases as the monomer level increases, although not as rapidly as might be expected because of the secondary swelling effect. There is a general lowering of the density as the crosslinking decreases. Again, this is attributable to the secondary swelling effect. In addition to these 'smooth' responses, there are three discontinuous ones (indicated by curves A, B and C in Figure 11). Curve C corresponds to the phase separation condition described in Figure 5. Crossing from gel- to macroporous-type polymer is generally accompanied by a decrease in density at constant monomer level. We attribute this to a greater contraction in the gel-type polymer than in the

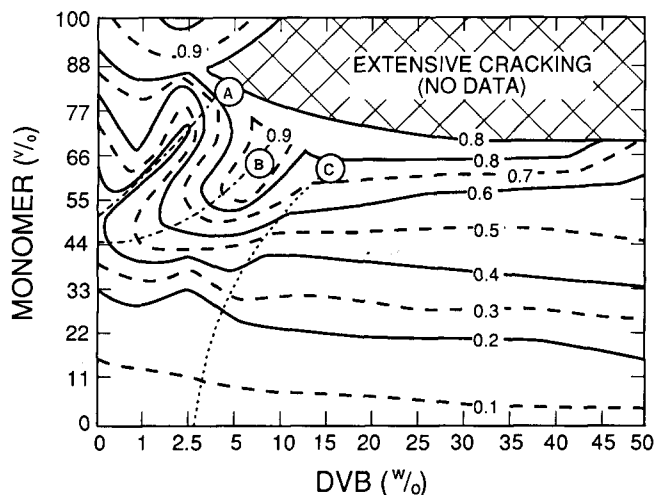


Figure 11 Dependence of filled-foam bulk density on monomer and crosslinking levels. Contour lines are 0.1 g cm^{-3} units. Curves A, B and C are described in the text

macroporous polymer of the same density. Certain compositions of gel polymers contract to a much greater extent than others. Curve B indicates the maximum-contraction compositions. In the region where the symbol B is located, the contraction is so great that the final foam is nearly equal to full density! For this to occur, the original foam preform must have collapsed, too. This behaviour demonstrates that tremendous retraction forces can occur in mildly ($\leq 10\%$) crosslinked networks when they are dried (presumably above their glass transition temperature). Certain other compositions of gel polymers do not contract much at all! Curve A indicates the minimum-contraction compositions. Under these conditions, the foam preform experienced normal solvent swelling and secondary swelling during polymerization, but the contraction forces in the gel-type polymer filler were insufficient to collapse the filled structure on drying. Thus a 0.33 g cm^{-3} final foam was obtained from a 0.074 g cm^{-3} foam preform and a 0.65 g cm^{-3} (71.5 vol%) monomer solution (Table 1 and Figure 11)! This line (A in Figure 11) represents the only significant perturbation in density due to the preform itself, because this is the only area where secondary swelling and drying contraction are both great and the swollen preform has sufficient strength to resist the contraction of the filler. In summary, monomer level in the filling solution establishes the baseline for the final density of a polymer-filled preform. Secondary swelling lowers the density inversely proportional to the swelling, while contraction during drying, especially when the filler is the gel-type polymer, raises the density. The polymeric foam preform influences the density in two ways: by how much it swells during the secondary swelling and by how well it resists contraction of the filling polymer during drying.

The microstructure of the foams prepared by back-loading is expected to vary with the concentration of the monomers and the type of non-solvating diluent*. Microstructures of filled foams prepared with various amounts

* For the purpose of discussion, we will present SEM microstructures that correspond to positions along the vertical 10% DVB line and along the horizontal 44% monomer line of Figure 4. Microstructures of many more of the compositions can be found elsewhere¹³ in a paper that covers the compressive modulus of these filled foams

of monomer and a constant 10% DVB level are shown in Figure 12. As expected from the space-filling observations external to the foam (Figure 5), foams filled with low monomer levels (11–22%) should only be partially filled (Figure 12a). Indeed, this is the case as the filler polymer coats the walls. Somewhat surprisingly, the 33% monomer level (Figure 12b) also gave predominantly coated foam walls even though the mass external to the foam would have indicated more uniform space filling. The coating, in each of these cases, is an integral part of the wall rather than a precipitate. The difference in the behaviour, i.e. internal and external to the foam preform, is best attributed to the fact that most of the monomers at low monomer levels diffuse into the foam walls in order to swell the foam. At a still higher monomer level (44%) and with the monomer composition still in the macroporous phase regime, the foam is completely and uniformly filled. The preform structure is still present in the 'composite foam' structure that can be seen by carefully inspecting the '44% M' photomicrograph in Figure 12c. At monomer levels above the phase separation level, the bulk polymer is of the gel type and is space filling, but inside the preform the polymer primarily coats the walls (Figures 12d–f). The high degree of space filling observed at the 66% monomer level (Figure 12e) presumably results from tremendous shrinkage (see above and Figure 11). The tendency of gel-type polymer to coat and of macroporous-type polymer to fill is also clearly visible from microstructures of foams filled with a 44% monomer solution, but with varying amounts of DVB (Figure 13). With no DVB present (Figure 13a), the uncrosslinked polymer produces wall coatings with occasional polymer globules. With a little DVB present (up to at least 5%; Figure 13b), the monomer composition is still in the gel regime (Figure 4) and still coats the walls, although some wispy webs are observed in the cells. With enough DVB (e.g. 10–50%; Figures 13c and 13d), macroporous material is formed and the cells of the preform are completely filled. Thus, not only does the type of polymer (gel or macroporous) depend on the solution parameters (monomer and crosslinking levels), but the deposition of this polymer on the cell walls also depends on these parameters.

DISCUSSION

The technique that we describe can be used to prepare foams with densities from 0.1 to 1.03 g cm^{-3} . Because of heat transfer problems during polymerization, there is a practical limit on the size of back-filled foams that can be prepared. For 5 cm diameter pieces, we have only been limited by the length of the tubes that our ovens can handle. Right-cylindrical parts measuring 10 cm in diameter have proven difficult to prepare. All attempts to make large 0.5 g cm^{-3} cylinders (25 cm diameter by 20 cm high and requiring 20 litres of monomer solution!) have resulted in ruptured or severely bloated preforms even at 50°C .

The phase diagram for the styrene-divinylbenzene/heptane system is given in Figure 14. From this diagram, the physical character of the polymer is seen to vary considerably with monomer composition and diluent. For example, the softness and the tendency of the gel-type polymer to shrink during drying are inversely related to the percentage of monomer and crosslinking (DVB). The hardness and amount of interaction (compactness) of the

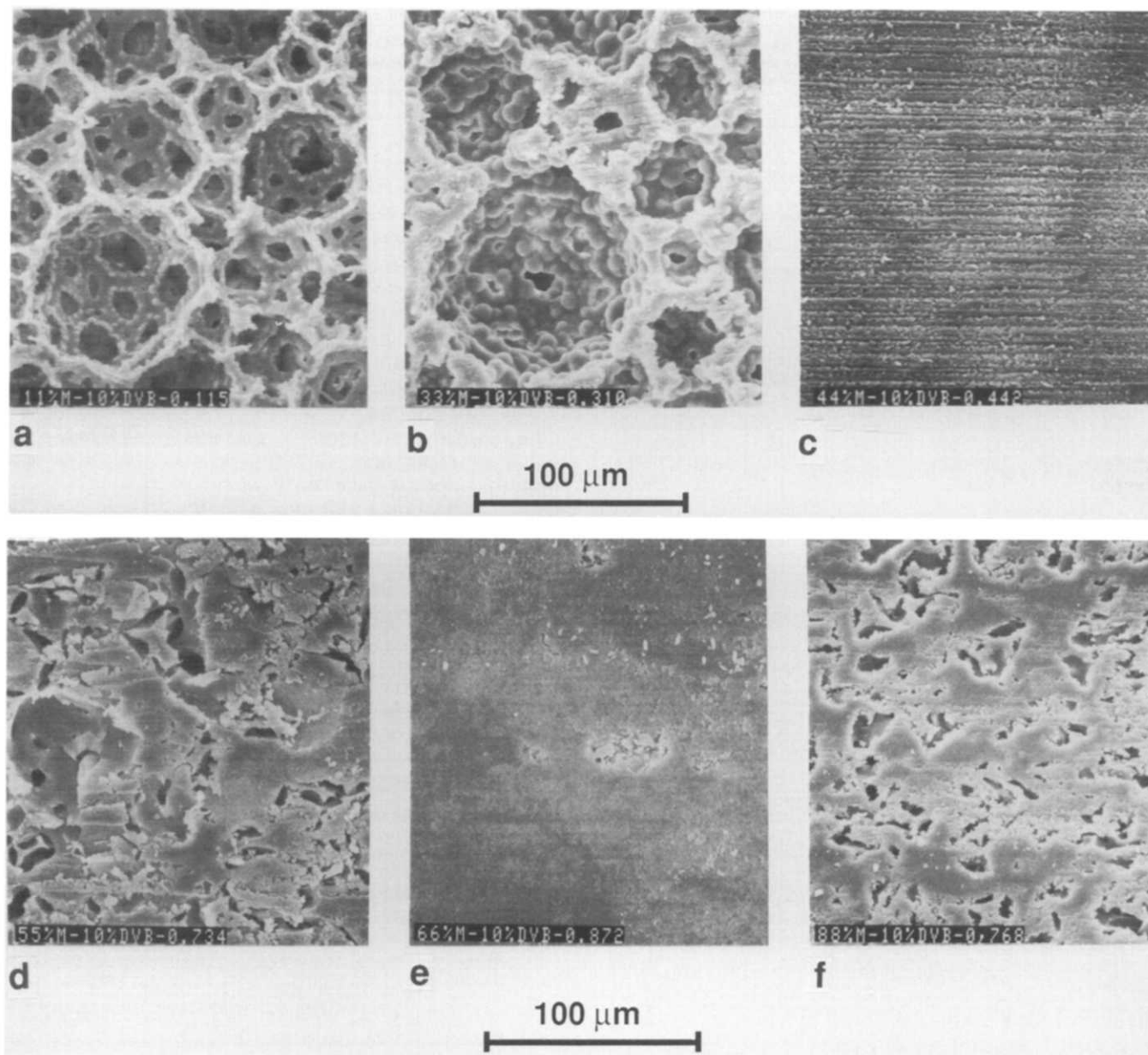


Figure 12 Influence of monomer level on the microstructure of foams prepared by back-loading a foam preform. Percentage of monomer is indicated for each photomicrograph followed by the percentage of DVB and the final foam density (g cm^{-3}): (a) 11% M-10% DVB-0.115; (b) 33% M-10% DVB-0.310; (c) 44% M-10% DVB-0.442; (d) 55% M-10% DVB-0.734; (e) 66% M-10% DVB-0.872; (f) 88% M-10% DVB-0.768

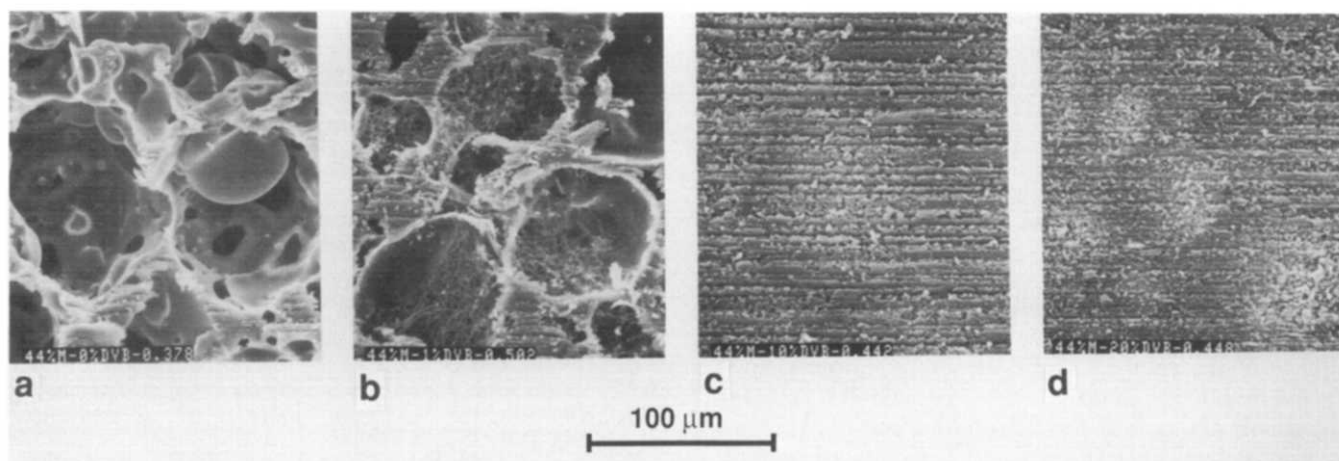


Figure 13 Influence of crosslinking level on the microstructure of foams prepared by back-loading a foam preform. Percentage of monomer is indicated for each photomicrograph followed by the percentage of DVB and the final foam density (g cm^{-3}): (a) 44% M-0% DVB-0.378; (b) 44% M-1% DVB-0.502; (c) 44% M-10% DVB-0.442; (d) 44% M-20% DVB-0.448

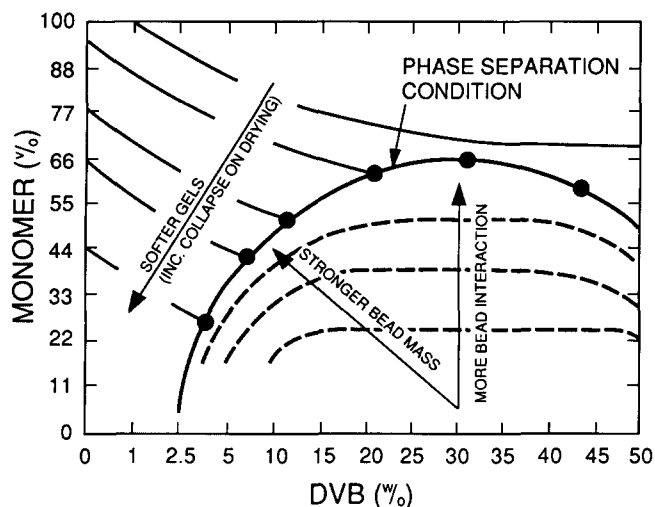


Figure 14 Phase separation diagram for styrene-divinylbenzene/heptane system at 60°C. DVB is only 55–60% active

macroporous polymer are also inversely related to the crosslinking (DVB), but are directly related to monomer levels. If a better solvent, such as toluene, is substituted for heptane, the conditions for phase separation are suppressed and gel-type conditions prevail at higher DVB and lower monomer levels than depicted for heptane (our observations and those in ref. 14). Since the DVB used in this experiment is only 55–60% active and the residual 40–45% contains at least some alkyl-substituted benzenes, the phase separation curve is slightly lower than would be found if the DVB were pure divinylbenzene. Practitioners should be sensitive to the fact that phase separations frequently occur when polymers are forming and that changes in solubility are often abrupt and very sensitive to solvent changes¹⁷.

Several items in the behaviour of the *in situ* polymerized polymer-foam system seem worthy of reiteration. The exceptionally large swelling of the foam preform when the DVB level is low is attributed to the tremendous swelling of the weakly crosslinked polymer that is being produced. Even at high monomer levels, the gel-type polymer does not fill the foam preform cells, but rather coats the walls. At low monomer levels (<33%) the macroporous polymer coats the walls, but fills the cells at higher monomer levels. At comparable monomer levels, the foam filled with gel-type polymer shrinks more than that filled with the macroporous-type polymer. Gel-type polymers with composition ranging from ~43% monomer (0% DVB) to ~70% monomer (10% DVB) have exceptionally strong contractive forces. Indeed, forces under the latter conditions are sufficient to collapse the polymer-filled foam preform to nearly full density. In contrast, gel-type polymer with composition ranging from ~50% monomer level and no DVB present to ~70% monomer with 2.5% DVB present have insufficient contractive forces to shrink the swollen preform once the monomers have polymerized. (We repeated the experiment in this region several times to ensure the validity of the results.) The polymer-forming system is quite complex, and thus the results are difficult to unravel. The seemingly anomalous density results are most likely tied to several facts: (1) styrene and divinylbenzene have different abilities to solvate the foam preform (styrene is

better) and polymerize with different reactivities¹⁸; and (2) the second vinyl group of DVB is not as reactive as the first¹⁸ and may even end up unreacted. The upward slope with increasing DVB and monomer levels may be related to the increased amounts of AIBN used (higher for DVB relative to the styrene—see 'Experimental') and/or to the fact that higher monomer level can solvate a polymer possessing a higher degree of crosslinking (DVB). Each of these conditions controls the nature of the polymer (separation and number of crosslinks, degree to which the two monomers segregate because of different reactivities, etc.) and hence the propensity of the polymer to contract when the solvent is removed¹⁸. Dusek¹⁹ has addressed the inhomogeneities introduced in crosslinked networks, specifically for styrene/DVB, during crosslinking copolymerization.

The two-component materials generated by back-filling provide an entirely new line of microporous materials. Generally classified as 'composite foams', the filler material can be almost anything. Elsewhere²⁰ we have described silica and resorcinol-formaldehyde fillers. When thin layers of polymer are deposited on the foam walls, this technology may provide a simple alternative to the beads currently used in chromatography.

ACKNOWLEDGEMENTS

The authors thank Jake Bartos for machining the samples, Jim Gray for the scanning electron microscopy, and Alice Nyitray and Dave Duchane for their editorial comments. Ted Gunn of the Atomic Weapons Establishment in England is thanked for his open discussions.

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