

# Reticulated Versus Crenelated Surfaces on Macroporous Polystyrene–Divinylbenzene Membranes

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## Synopsis

Reticulated polystyrene–divinylbenzene (PSt–DVB) copolymer membranes or thin sheets were prepared using two different methods. The first method employed a nonsolvating diluent which dissolves the monomer but precipitates the polymer. This resulted in skinned membranes with the skin being nonporous, being either crenelated or smooth. The second method used paraffin wax as the inert phase. The wax was precipitated by cooling, followed by polymerization of the styrene. The wax was then solvent extracted. This resulted in a reticulated structure both on the surface and in the interior of the membrane. The resulting products from the two methods were compared using scanning electron microscopy. The objective of this study was to prepare a skinless, macroporous, crosslinked polystyrene, as polymer I for the preparation of novel interpenetrating polymer network (IPN) materials.

## INTRODUCTION

Macroporous or reticulated polymers contain a connected pore structure on a microscopic or submicroscopic level. Usually, the polymer is densely cross-linked to prevent collapse of the structure. Such polymers form a useful starting material for polymer blends and interpenetrating polymer networks (IPNs).

The sequential IPNs constitute a related family of materials. Using suspension polymerization techniques, for example, Solt<sup>1</sup> and Hatch<sup>2–5</sup> made anionic/cationic IPN ion exchange materials. One polymer was negatively charged and the other, positively charged.

It was later found that a much better ion exchange resin could be made if one began with a macroporous or reticulated form. These resins have been synthesized by Kolarz,<sup>6</sup> Bolto,<sup>7</sup> Barrett and Clemens,<sup>8,9</sup> and others.<sup>10,11</sup> An excellent series of papers describing the synthesis and characterization of these materials was presented by Miller et al.<sup>12–15</sup> Applications have included ion exchange,<sup>16</sup> desalination,<sup>17,18</sup> decoloring sugar,<sup>8</sup> chromatographic separations,<sup>19</sup> and removal of dissolved solvents from aqueous solutions.<sup>20</sup>

It must be emphasized that all of these materials have been made by suspension polymerization. It is the purpose of this work to synthesize a macroporous membrane by bulk polymerization. Such a membrane could serve as a beginning material for a piezodialysis membrane, in IPN form, containing negative and positive charges in different regions of space and having two co-continuous or co-connected phases. This work is a direct continuation of Hargest et al.'s study on piezodialysis membranes.<sup>21</sup>

Macroporosity can be defined in the same manner as used in the field of sorbents and catalysts. However, the definitions given here are based on the for-

mation mechanisms of Kun and Kunin<sup>22</sup> shown in Table I.<sup>23</sup> These mechanisms will be discussed in detail later. Briefly, macroporosity is defined<sup>23</sup> as pores between early formed microspheres and their agglomerations, where the pore diameters exceed 500 Å. Microporosity, on the other hand, is defined as pores present among the nuclei within the microspheres. For the materials of concern here, the effect of the macropores will overshadow the effect of the micropores, and therefore the latter will not be discussed in this article. Kun and Kunin<sup>22</sup> differentiated these macroporous materials from gel-type microporous materials by calling the former macroreticular materials.

According to Seidl,<sup>24</sup> three basic methods exist to form macroporous polymers based on polystyrene (PSt) and divinylbenzene (DVB) copolymers: (1) addition of a solvating diluent, (2) addition of a nonsolvating diluent, and (3) addition of a linear polymer. In the first method, the monomer is mixed with a diluent in which the monomer is soluble and the polymer, when formed, remains swollen. Such a diluent is toluene. In the second method, the monomer is mixed with a diluent in which the monomer is soluble, but the polymer is not, e.g., alkanes. The third method entails addition of a linear polymer to the monomer mixture which is removed after polymerization. Polymers which have been used for this include PSt, acrylics, polyesters, and poly(vinyl acetate).<sup>24</sup> To a considerable extent, the pore size depends on the domain size of the removed polymer component.

In this investigation, some of the samples were made via the second method given above, using a range of DVB concentrations and a number of different alkanes as diluents. More importantly, preliminary work was done on a variation of method three. In this case, the inert material used was paraffin wax instead of a linear polymer. The wax precipitates out first on cooling a hot monomer solution, then the PSt-DVB copolymer polymerizes around it, and finally the wax is extracted leaving a reticulated polymer.

The main problem in the use of alkanes relates to the formation of a skin on the polymer surface which is not macroporous. The judicious use of wax resulted in skinless products more suitable for piezodialysis membranes or other materials requiring true void continuity.

The skinned and skinless macroreticulated copolymers were studied using scanning electron microscopy (SEM). The present copolymers were also compared to the commercial resin Amberlite and to a Millipore Filter, both of which exhibit a macroporous or reticulated structure.

## MECHANISM OF FORMATION

The mechanism of formation of macroporous materials using nonsolvation diluent method (method 2, above) is described in the greatest detail by Kun and Kunin.<sup>25</sup> The mechanism is similar to that reported by Bobalek et al.,<sup>26</sup> except

TABLE I  
Schematic Representation of Kun and Kunin's<sup>21</sup> Mechanism of Pore Formation

	Agglomeration of polymer chains		
	Nuclei	Microspheres	Beads
Dimensions, Å	50-200 (estimation)	600-5000 (electron microscopy)	10 <sup>6</sup> -10 <sup>7</sup> (micrometer)

that in their case the diluent was more monomer.<sup>27</sup> The mechanism basically contains three steps characterized by (1) building of the microspheres, (2) agglomeration of the microspheres, and (3) fixation of the agglomerates within the membrane.

According to the above authors, the first step of the polymerization develops as follows: The first few molecules synthesized are linear or branched polymer with pendent vinyl groups. Almost immediately, however, polymerization yields soluble, intramolecularly crosslinked microgels and branched species to form "nuclei." These continue to grow to form microspheres, and at a certain conversion of monomer to polymer, the polymer goes through gelation and microsineresis.<sup>28-31</sup> It is important that the polymer forms microgels first and then precipitates. The phase separation conditions are a function of crosslink concentration, volume percent of diluent, solvating properties of the diluent,<sup>31</sup> and reaction temperature.<sup>23</sup> During this step the microspheres begin to be bound together.

In the second step the polymerization continues, and more microspheres are bound together. At this point the macroporous structure begins to be formed, although the characteristics of the pores are dependent on step 1.<sup>25</sup> The last step involves the final fixation of the macroreticular structure. When the diluent is removed by evaporation, the small amount of remaining monomer is forced into the polymer and polymerized on further heating.

Kun and Kunin<sup>25</sup> state that each submicroscopic droplet of organic solution in the suspension acts like an individual bulk polymerization. Therefore, it would seem logical to assume that the same mechanisms would apply to a bulk polymerization as to a suspension polymerization. This sets the stage for the following experiments.

## EXPERIMENTAL

The styrene monomer (St), DVB (55.0% effective), and benzoin were obtained from the Fisher Scientific Co. Styrene monomer was washed prior to use with 5 wt % NaOH aqueous solution to remove the inhibitor, washed with deionized water, and dried using anhydrous calcium sulfate (Drierite). All of the alkanes were obtained from Fisher or from the Aldrich Chemical companies and were used as received, as was the DVB and benzoin. The kerosene was obtained from the Fritch Oil Co. and was used without further purification. The paraffin wax used was a commercial product made by the Gulf Oil Corp. under the trade name Gulfwax.

The membranes were synthesized in the following manner: The required amount of St and DVB were mixed with 0.4% benzoin. Then the specific alkane was mixed into the solution. Table II shows the amount of alkane added to 5.0 g monomer solution, which was calculated to result in a final product containing 50% PSt-DVB polymer and 50% air space by volume. The monomer mixture was injected into glass plate molds separated by a 7-mil polyethylene gasket and polymerized via UV light for four days. The polymer was removed by soaking in deionized water between 2 and 24 hr. Finally, the samples were dried overnight under vacuum at approximately 105°C.

The wax samples were synthesized in essentially the same way, but with significant differences. First, in order to induce the wax to go into solution, the

TABLE II  
Amounts of Diluent Used for 5 g Styrene to Obtain a 50/50 Volume Fraction of Pores to Final Polymer<sup>a</sup>

Inert solvent	Solvent density	Weight % to obtain 50/50 product	Mass inert per 5.00 g monomer solution
Pentane	0.6262	37.4	2.99
Hexane	0.6603	38.6	3.14
Heptane	0.6376	37.8	3.04
Octane	0.7025	40.1	3.35
Decane	0.7300	41.0	3.47
Dodecane	0.7487	41.6	3.56
Kerosene	0.82	43.9	3.91
Paraffin wax	0.89	45.9	4.24

<sup>a</sup> Density of styrene = 0.9060 g/cm<sup>3</sup>; density of polystyrene = 1.05 g/cm<sup>3</sup>.

monomer was kept at 65°C while the wax was added and dissolved. Second, the hot monomer solution containing the wax was poured onto one glass plate at room temperature, and the second plate was set on top of it. (Hot glass plates were also attempted in order to facilitate injection of the hot sample, but this small change in procedure resulted in skinning.) After polymerization, the wax was extracted by soaking the samples in hexane for 48 hr. They were then refluxed from three to six times for 30 min each first in hexane and then in a 50/50 mixture of hexane and toluene.

In order to determine the time to phase separation, the time at which the sample changed from transparent to opaque white was observed. This experiment was done to determine the relationship between phase separation and carbon chain length of diluent. Therefore, the samples contained a constant 10% DVB concentration, and octane, decane, or dodecane served as the inert diluent.

The samples were prepared for scanning electron microscopy (SEM) by first drying them overnight under vacuum. The internal structures were examined by immersing the samples in liquid nitrogen and then fracturing them. The surface structures were examined on intact samples.

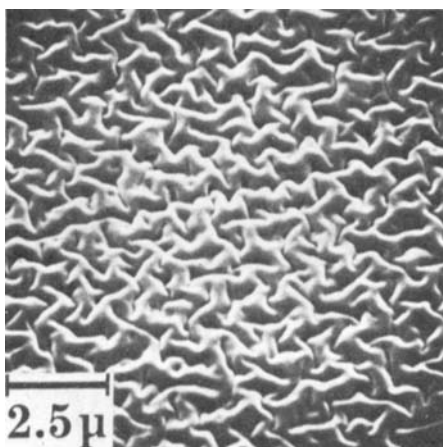
The copolymers were plated with gold using a Polaron E5100, Series II sputter coater for 75 sec. The samples were examined and photographed using a Etec Corp. Autoscan SEM.

## RESULTS

The membranes or thin sheets that were obtained using the alkane liquids all had macroporous interiors and a nonporous skin which was either crenelated, smooth, or somewhere in between. A typical crenelated surface is presented in Figure 1. The valleys, or bottoms, of the crenels are not pores that penetrate the skin but are just folds in it. The crenelated skin is a continuous nonporous barrier between the outside and interior of the membrane.

The smooth surfaces, not shown, were planar, showing very few irregularities up to a magnification of 20,000×.

Figure 2 is a map showing the type of surface as a function of the weight percent of DVB and the alkane used. The surfaces which are classified as "transition"



OCTANE, 10% DVB

Fig. 1. SEM photograph of typical crenelated PSt-DVB surface. The inert diluent used was octane, and the amount of DVB used was 10%.

typically had both smooth and crenelated regions or a combination of both in the same area.

All of the interiors of the membranes were porous and were made up of small, connected microspheres except the copolymers made with octane and decane with 3% DVB. The latter two membranes had an interior similar in appearance to Swiss cheese. For convenience, the interiors containing microspheres can be broken up into three types of porosity based on size of the microspheres: (1) small, (2) transition, and (3) large.

Figure 3 shows the three types of porosity and three sizes of microspheres obtained. Figure 3(a), designated as "small," is made up of small pores and microspheres with diameters between 0.06 and 0.2  $\mu\text{m}$ . Figure 3(b), designated as "transition," shows microspheres with diameters between 0.13 and 0.31  $\mu\text{m}$ . Finally, Figure 3(c), designated as "large," shows a sample with large pores whose diameters ranging from 0.5 to 3  $\mu\text{m}$  and microspheres having diameters between 0.3 and 0.5  $\mu\text{m}$ .

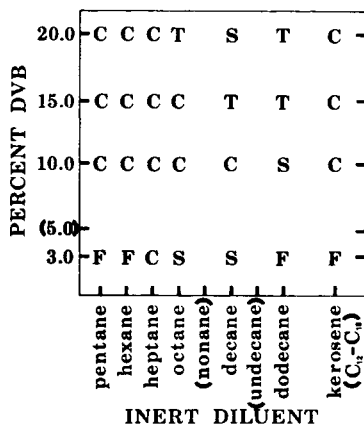


Fig. 2. Map of PSt-DVB copolymers showing the type of surface formed as function of percent DVB and inert diluent chain length: F, failed; C, crenelated; T, transition; S, smooth.

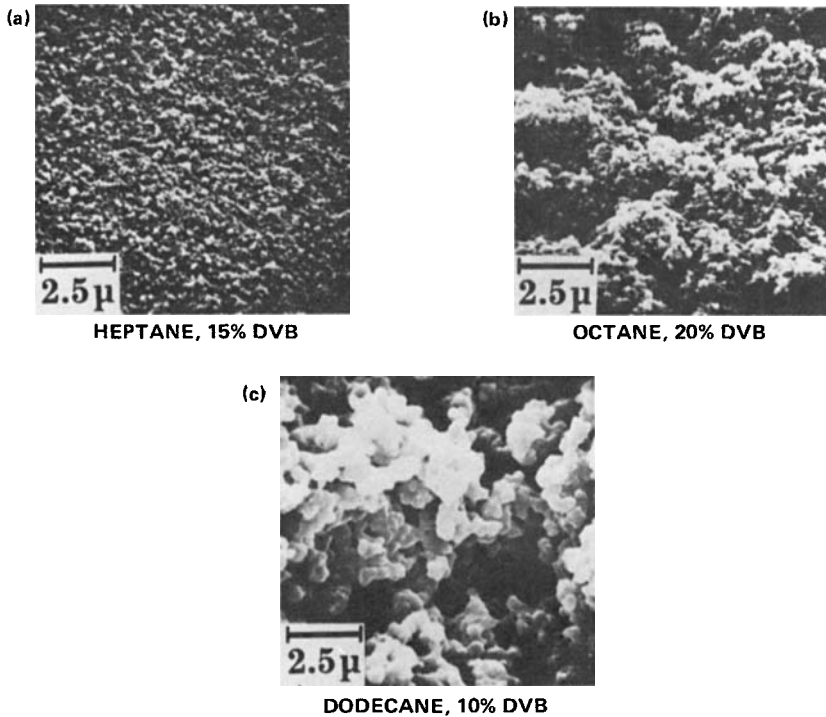


Fig. 3. SEM photographs of the three typical kinds of porosity: (a) classified as small, (b) classified as transition, and (c) classified as large. They were made with heptane, octane, and dodecane, respectively.

Figure 4 is a map showing these three types of porosity as a function of the weight percent of DVB and the alkane used. For the alkanes studied (but not the wax), the higher alkanes and higher levels of DVB produced larger pores.

The samples shown in Figures 2 and 4 that “failed” did not work in a number

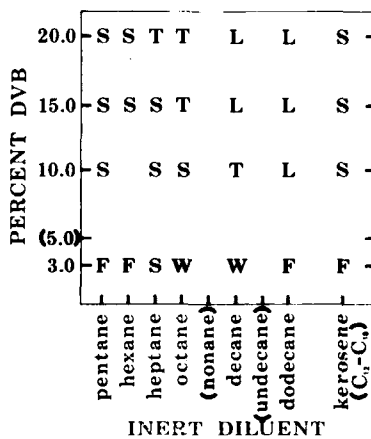


Fig. 4. Map of the PST-DVB copolymers showing the type of interiors after fracture as function of percent DVB and inert diluent chain length: F, failed; S, small pores; T, transition; L, large pores; W, Swiss cheese.

of different ways. Copolymers with 3% DVB made using pentane and hexane as the diluent formed a polymer coating on the glass plates, but the interior contained no polymer. Those made with dodecane and 3% DVB did not hold together upon separation of the glass plates, suggesting a discontinuous polymer phase. The 3% DVB sample made with kerosene could not be removed from the glass plates to be examined.

An analysis of the literature shows that 3% DVB is at the bottom of the range of crosslinking levels necessary to produce a reticulated structure (see Discussion section). Again, the polymer must first form microgels first and then precipitate to form a reticulated structure.

### Time to Phase Separate

The results of the experiments to determine the amount of time required to phase separate are shown in Table III. The decane and dodecane samples changed from a transparent material to an opaque white abruptly. The octane samples remained transparent throughout the polymerization and did not become opaque until the diluent was removed.

### Wax As a Diluent

The surface of the membranes made using paraffin wax are shown in Figure 5. Copolymers containing 15 and 10% DVB are shown in Figures 5(a) and 5(c), respectively. These figures show the surfaces themselves to be reticulated, unlike the skinned copolymers illustrated in Figure 1. However, membranes made using 3 and 20% DVB resulted in surfaces with skins.

Shown in Figure 5(b) is a surface resulting from the use of hot glass plates. This surface exemplifies all of the membranes made using hot glass plates, regardless of the DVB concentration. These surfaces appear to be similar to the crenelated surfaces obtained using the nonsolvating diluents. The internal structure also contained some microspheres like those found in the previous samples.

The internal structures of the membranes made using wax are shown in Figure 6. These interiors are typical for all concentrations of DVB. The pore diameters for this material range from the order of microns to as large as 0.02 mm.

### Commercial Materials

Figure 7 shows photographs of two commercial macroreticulated materials which were studied for comparative purposes. The first material is Amberlite XE-305 made by the Rohm and Haas Co. [see Fig. 7(a)]. This figure shows both

TABLE III  
Time to Phase Separation for 50/50 Styrene-DVB/Alkane Solutions during Polymerization

Inert diluent	Time to phase separation, hr
Dodecane	6
Decane	11, 13
Octane	24 (clear)

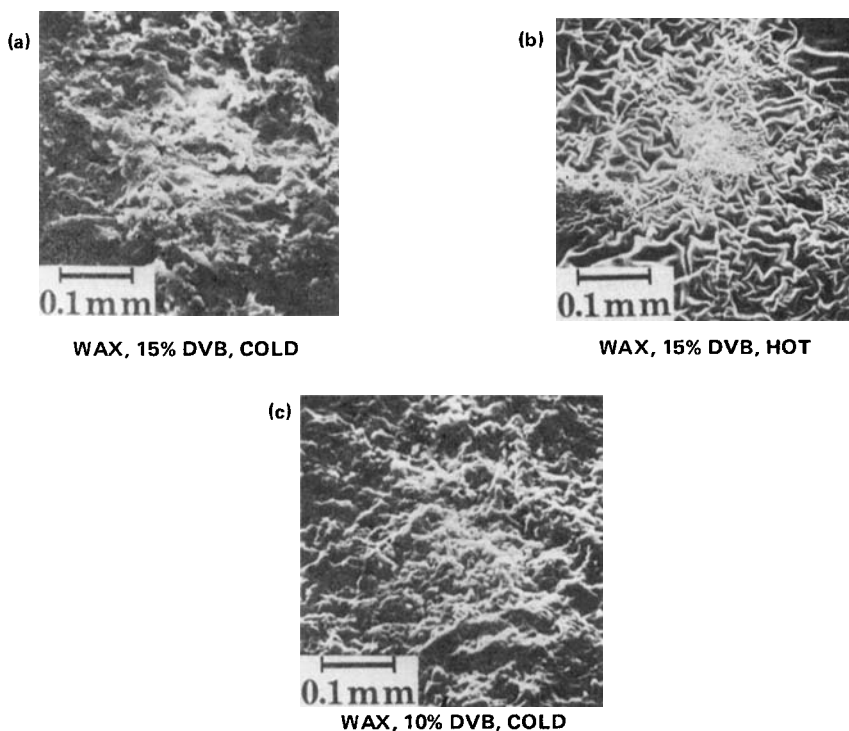


Fig. 5. SEM photographs of PSt-DVB surfaces made with wax: (a) and (c) are reticulated and were made with cold glass plates with 15 and 10% DVB, respectively; (b) was made with hot glass plates and is not porous.

the exterior and interior of a polymer bead, the exterior being on the left and the interior on the right. Amberlite XE-305 is listed<sup>32</sup> as having a volume fraction of pores equal to 0.5–0.6.

Figure 7(b) shows the surface of a Millipore filter made by the Millipore Co. This filter is type HA and has a given pore size of  $0.45\ \mu\text{m}$ . The surface and internal structure of this material appear to be exactly alike when viewed under the SEM. This material is made of cellulose, with some nitrates and acetates.<sup>33</sup>

## DISCUSSION

The present work carries many of the findings for suspension polymerizations of reticulated PSt-DVB copolymers made with nonsolvating diluents into the realm of bulk polymerizations in thin film form. Also, the work is extended to include the use of wax to form reticulated surfaces.

Czarczynska and Trochimczuk<sup>34</sup> give the lower limit of DVB concentration of 3% for the formation of reticulated structures. Below this concentration, the structure collapses upon itself.<sup>34</sup> Below 3% DVB there are no microspheres at all, but just thin, connected, bubblelike structures similar to soap suds. This would support their claim that this structure would collapse. Also in examining the samples in the SEM, the samples were deformed by the electron beam, showing their fragility.



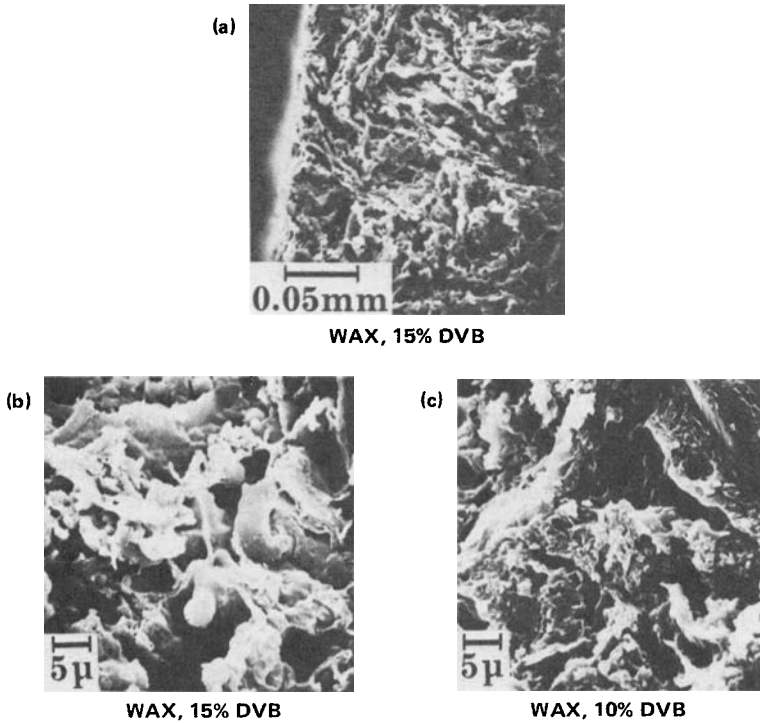


Fig. 6. SEM photographs of the interior of PSt-DVB copolymers made with wax: (a) and (b) were made with 15% DVB, and (c) was made with 10% DVB.

Millar et al.<sup>15</sup> and Seidl<sup>24</sup> also stated there is a critical concentration of DVB below which macropores will not form, depending both on the volume fraction of monomer in the initial solution as well as the DVB concentration. According to Figure 2 of Millar's work<sup>15</sup> and the volume fraction of monomer used, the critical DVB concentration for the present materials is about 10% DVB.

Since some of the present 3% DVB materials did yield a reticulated structure, differences between bulk and suspension polymerization need to be considered. For example, stirring may have caused the collapse of Millar's low crosslinked samples.

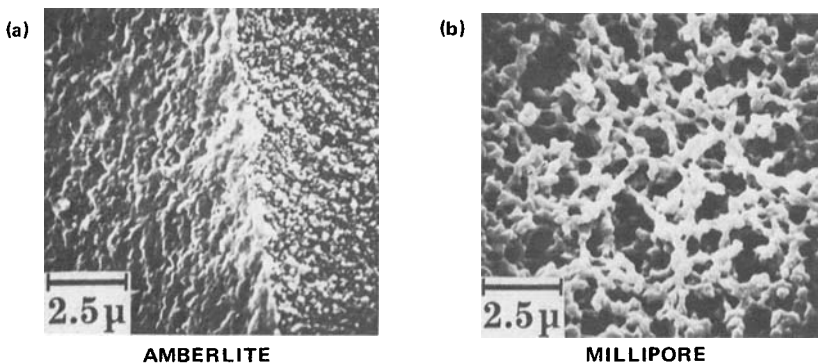


Fig. 7. SEM photographs of the commercial products (a) Amberlite made by Rohm and Haas and (b) a Millipore filter made by The Millipore Co.

The upper limit used for the DVB concentration was 20% DVB. Kolarz<sup>35</sup> stated this as being the upper limit above which the copolymer becomes too weak mechanically. It is commonly known that pore size increases with an increase in DVB concentration. This fact is clearly shown in the case of heptane and in octane (Fig. 4). Gózdź and Kolarz state that the longer the aliphatic chain of a diluent, the larger the pores.<sup>36</sup> This is shown to be true along any constant concentration of DVB (above 3%). Further, Gózdź and Kolarz<sup>36</sup> also state that the critical concentration of polymer should decrease as the precipitating properties of the diluent increase, confirmed by Table III.

The change in solubility with the molecular weight of the diluent arises from the difference between two opposing forces.<sup>37</sup> The first of these is the heat of mixing as illustrated by the solubility parameters. For the solvents and PSt-DVB copolymer the values of these parameters<sup>38</sup> are pentane, 7.05; hexane, 7.3; heptane, 7.45; octane, 7.55; decane, 7.75; dodecane, 7.9; kerosene, 8.0, estimated; and PSt-DVB copolymer, 9.1. The change in solubility parameter with molecular weight of diluent suggests that increasing the molecular weight, in this case, tends to increase mutual solubility.

Secondly, as the alkane chain length increases, the entropic contribution to mixing drops rapidly, favoring precipitation from high-molecular-weight diluents. Precipitation seems to be governed by entropic considerations, as the stronger of the two thermodynamic forces. Earlier precipitation (but after gelation in any case) allows for a coarser domain structure because the network is more mobile and deformable.

### Skinned Materials

The main problem inherent in the materials synthesized via the nonsolvating diluent method is the formation of a skin. In order for the final membrane or thin film to be truly porous, or for use as a starting material for piezodialysis membranes, theory dictates that both phases be continuous.<sup>39</sup> If phase I has a skin on it, then phase II cannot be continuous.

A possible mechanism for the formation of the skin begins with the macroporous formation mechanism of Kun and Kunin.<sup>22</sup> It has been shown that DVB polymerizes faster than the styrene. The resulting copolymer is therefore heterogeneous, with the first formed polymer being more densely crosslinked than later polymerized material.<sup>40</sup>

Because of shrinkage during polymerization, a thin gap forms between the glass plates and the polymer. This gap becomes filled with the diluent and a dilute monomer mixture, now containing but a small concentration of DVB. If the DVB concentration and the remaining monomer concentration fall below the critical concentration depicted by Millar et al.,<sup>15</sup> this may result in a crenelated rather than reticulated skin. Another factor which may play an important role is surface phenomena occurring at the glass plate and organic solution interface.

The mechanism of skin formation in suspension-polymerized products has not been explored. Of course, a water-polymer interface exists in that case. It should be pointed out that core shell-type effects present in latexes will result in a shell of solvent and remaining monomer mix in a late stage of a suspension polymerization.

### Wax As a Diluent

The samples made using wax as the diluent were formed via a variation of the known method of using a linear polymer. The mechanism of formation for this method is different than the one for a nonsolvating diluent. In this case, the wax precipitates out first, apparently coating the glass plates with wax. Apparently, a continuous phase of crystalline wax is formed, which extends from one glass plate to the other. The monomer then polymerizes around the wax.

After the completion of the reaction, the wax is extracted. The wax and polymer samples before extraction are as smooth as the smooth skinned samples, but as the wax is extracted, the surface develops pores.

### Commercial Products

As a final analogy, the present materials were compared to two commercial products. Amberlite, a PSt-DVB copolymer synthesized via suspension polymerization, closely resembles the present materials made with low to moderate concentrations of DVB and from five to eight carbons in the alkane chain of the diluent. It too is not a homogeneous, macroreticular material throughout but has a nonporous skin. The interiors of the Amberlite and the present materials are similar.

A Millipore filter was also examined. It was macroreticulated, both on the surface and in the interior, and was examined for comparative purposes.

The macroreticulated membranes made with paraffin wax lie between these two commercial products. Even though these samples are not as homogeneous as the Millipore filter, they are macroreticulated on the surface as well as the interior.

### CONCLUSIONS

The membranes resulting from using wax and 10 or 15% DVB were the only materials that can be considered to be totally macroreticulated. All the other materials had a nonporous skin, be it smooth or crenelated, and were not acceptable as the basis for piezodialysis membranes or other materials containing continuous pores.

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