

The Preparation and Stability of Snake Cage Membranes

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Synopsis

Linear chains of poly(methacrylic acid) have been successfully trapped in different polymeric matrices of variable degree of reticulation. The length of the linear chains and the porosity of the cages are the two fundamental parameters which control the stability of the snake cage systems. The physical character of trapping in the membranes which are described in this paper is qualitatively demonstrated. The snake cage effect seems to be a very general principle of insolubilization. By this method, systems with specific exchange or absorption characteristics may be prepared.

INTRODUCTION

Among those resins and synthetic membranes which show specific exchange or absorption characteristics, the so-called snake cage systems have not been widely developed although their applications appear to be very large.

In the majority of cases, the active group (ion or electron exchanger, complexing or optically active) is bound chemically onto a polymer matrix by more or less complex reactions depending on the nature of the group. The resin can also be prepared by polymerization of the monomer in the presence of a reticulating agent.

In a snake cage resin, an active polymer A is imprisoned in a reticulated matrix of polymer B, simply by a physical effect of entanglement. The B matrix can sometimes carry active groups different from those of polymer A; if the two groups are of opposite charge, the insolubilization of the A chains is partly due to electrostatic linkages.

The fact that sufficiently stable snake cage systems can be prepared opens up in principle the possibility of synthesizing a wide range of exchanging and absorbing materials by a very general method: polymerizing an active monomer inside a reticulated or insoluble matrix, or forming a polymeric cage around preformed active polymers.

A number of investigators have prepared snake cage-type resins or membranes. The results are often contradictory and there is a lack of experimental informations. Some examples of snake cage systems are given hereafter.

Hatch and co-workers¹ obtained amphoteric polyelectrolytes on polymerizing acrylic acid inside commercial anion exchange resins. Trostyanskaya and co-workers² polymerized, at 70°C, the sodium salt of methacrylic or vinylsulfonic acid in sulfonated styrene-divinylbenzene (St-DVB) matrices; without producing any evidence, the authors attributed the increased capacity and the stability of these systems to a grafting reaction onto the polymer cage.

A St-DVB mixture can be polymerized inside sheets of poly(vinylidene fluoride)³ or polyethylene,⁴ and the reticulated polymer is then sulfonated. Snake cage systems can also be prepared by forming a cage around a preformed polymer. It has thus been possible to fix polynucleotide chains (poly U) in polyacrylamide gels. By repeated washing, 10–20% of the biopolymer are eliminated, the rest being unextractable.⁵

The commercial membranes (A.C.I., Asahi Chemical Industries) are prepared by dissolving a polystyrene in a St-DVB mixture which is copolymerized to give a cage system. The membranes so obtained are sulfonated or aminated.⁶

Gregor and co-workers⁷ prepared oleophilic ion-exchange systems by forming an easily activated St-DVB copolymer around linear chains of polyisobutylene (mol wt 8×10^4). The stability of the resulting resins is increased by ⁶⁰Co γ -irradiation which grafts to a certain extent the linear chains to the matrix.

Rabek⁸ has carried out a number of experiments, all of them with negative results; he formed a silica gel in the presence of polyacrylic acid (mol wt 10^6) and poly(vinylpyridine); he also imprisoned the same poly(acrylic acid) in phenol-formaldehyde matrices of varying porosity and swelling properties. In all cases, the polyacid and polybase could be almost completely extracted.

The preparation of stable snake cage membranes by polymerizing an active monomer in an inert matrix seems never to have been studied systematically. In the context of a general research project on the electrochemical properties of snake cage membranes,⁹ we carried out a systematic preliminary study of the preparation and stability of such systems. The constituents were chosen so that all effects other than those of physical entanglement of the polymer chains are reduced to a minimum.

EXPERIMENTAL

The steps for preparing snake cage membranes are as follows: (1) preparation of an inactive cage membrane with adequate mechanical and dimensional properties; (2) swelling of the membrane by an active monomer; (3) polymerization of the monomer; and (4) extraction of the polymer unbound to the matrix lattice.

The choice of matrix is very important as the active membrane must keep a sufficient mechanical stability during the different steps of its preparation and use. Furthermore, the matrix porosity must be easily changed.

Preparation of Inactive Matrices with Variable Porosity

Two matrix types (a and b) are obtained by polymerization of mixed monomers in Teflon moulds (inner diameter 30 mm, depth 0.5 mm) (Fig. 1). A matrix is also prepared by reticulation of a silicone polymer (c).

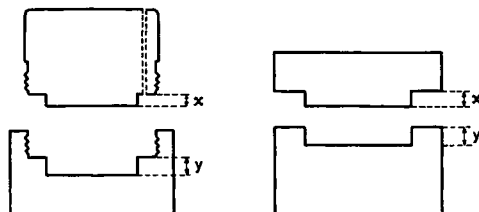


Fig. 1. Schematic diagram of Teflon moulds. $Y - X = 0.5$ mm.

*Styrene-*n*-Butylacrylate-Divinylbenzene Terpolymer (St-*n*-BA-DVB)*

St-DVB matrices do not possess adequate mechanical properties, but they can be improved by introduction in the monomeric mixture of an inner plasticizer such as *n*-butylacrylate. In order to keep the glass transition temperature (T_g) of the matrix under 25°C, the St and *n*-BA concentrations must be adjusted in function of the amount of the reticulating agent.

For example, a mixture of 60% St and 40% *n*-BA leads to the formation of a copolymer whose T_g is 23°C. Moreover, the T_g increases by about 4.5° C per 1% reticulation.

Polymerization takes place at 70°C in the presence of benzoyl peroxide (0.1%) and toluene (50% in volume). The porosity of this type of matrix can easily be controlled by the DVB content. Membranes with 3, 5, 7, and 9% DVB have been prepared.

Reticulated Polyacrylamide

In the presence of a redox system such as ammonium persulfate and tetramethylethylenediamine (TMED), a water solution of acrylamide and *N,N'*-methylenebisacrylamide forms a gel.

The permeability coefficient is independent of the proportion of the reticulating agent for a given polymeric concentration. Moreover, the diameter of the pores varies from 18 to 5 Å for a polymer concentration from 2.5% to 35%; 10, 20, 25, 30, and 35% acrylamide membranes are prepared by polymerization of the corresponding monomeric mixtures at 25°C. These mixtures contain 5% of reticulating agent, and the final concentration in catalyst is 0.5%. A filtered solution of acrylamide, *N,N'*-methylenebisacrylamide, and persulfate is poured in Teflon moulds, and then the desired quantity of TMED is added. The mixture is homogenized, and after a few minutes the gel is formed.

Reticulated Poly(dimethylsiloxane) (PDMS)

PDMS easily reticulates by action of 2,4-dichlorobenzoyl peroxide and is an excellent elastomer. Midland Silicones Ltd. has graciously supplied us with silicone gums such as Polysil 2432, Polysil 2449, and Perkadox P.D.S. 50. The latter is a dispersion in silicone fluid of 2,4-dichlorobenzoyl peroxide (50%). The mixture is introduced in the mould (inner diameter 130 mm, thickness 0.5 mm) formed by two cylindrical brass plates whose inner faces are covered with a Teflon sheet.

The whole system is cured at 115°C during 5 min under pressure and then during 24 hr at 250°C. The degree of reticulation is controlled by the quantity of peroxide for a given composition of the gum. The mechanical properties of such matrices are excellent: however, the presence of the trapped polymer decreases a little the mechanical stability.

Besides this silicone elastomer, rubber is also interesting for membrane preparation on account of its good mechanical properties and its chemical resistance to acids and bases.

Polymerization of Active Monomer Within the Matrix

Methacrylic acid, which may be easily titrated, is polymerized in the three cages described above using the following technique. Membranes are separated by Teflon sheets, placed on a support made of the same material, and dipped in the reactive mixture (Fig. 2b). The vessel is flushed by a stream of nitrogen (tube c). When the swelling equilibrium is reached, the membranes are separated from the solution by lifting the support attached to a magnetic rod d up by means of a solenoid; the whole system is fixed by slipping the magnetic bar f under the plate g. In the second apparatus (Fig. 2a), the membranes are disposed at the bottom of the vessel

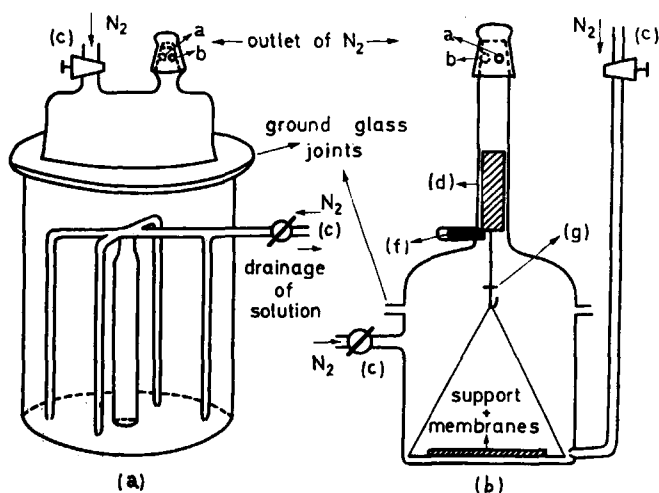


Fig. 2. Polymerization apparatus.

containing the solution to be polymerized. After equilibration, the solution is eliminated through the tube c. Hydrophobic membranes are equilibrated in a 15–30% AMA solution in dioxane or tetrahydrofuran; hydrophilic matrices are equilibrated in a 10% AMA solution in water.

The radical polymerization of AMA in membranes takes place at a rather low temperature (40°C) in order to get a polymer of high molecular weight and a low probability of grafting. The mean viscosimetric molecular weight of the poly(methacrylic acid) (APMA) from the outside-equilibrated solution is about 4×10^5 . This gives a rough idea of the length of the chains trapped in the matrix.

Stability of Snake Cage Membranes

St-n-BA-DVB Terpolymer plus APMA

After dissolving the polymer adsorbed on the membranes, these are extracted by water for a whole month in Soxhlet apparatus designed so that the membranes are always covered with water (Figs. 3 and 4). Table I summarizes experimental data such as the extracted APMA quantity and

TABLE I
Extraction Data

DVB, %	Extracted, meq/g	Capacity, meq/g	Extracted, %
3	1.75×10^{-2}	4.30	0.4
5	1.14×10^{-2}	3.92	0.3
7	0.96×10^{-2}	5.40	0.18
9	0.92×10^{-2}	5.46	0.17

the corresponding membrane capacity determined by titration; they are given in milliequivalents per gram of dried membrane.

The percentage of extracted polymer is low and decreases with the degree of reticulation of the matrix; the stability of such membranes is consequently very good. Their capacity is almost the same as that of similar commercial resins; a St-DVB copolymer completely monosulfonated must have a theoretical capacity of 5.43 meq/gr. Practically, the observed values are slightly lower. The swelling by water of these snake cage membranes varies from 8% to 19% and is low compared with the 45–50% for 10% DVB monosulfonated resins.

Reticulated Polyacrylamide plus APMA

The 10, 20, and 30% polyacrylamide membranes, whose water swelling changes from 52% to 59%, are characterized by an almost ideal stability. Less than 0.1% of the capacity of the different membranes is extracted; the capacity varies between 1 and 3.5 meq/gr according to the concentration of polyacrylamide in the matrices.

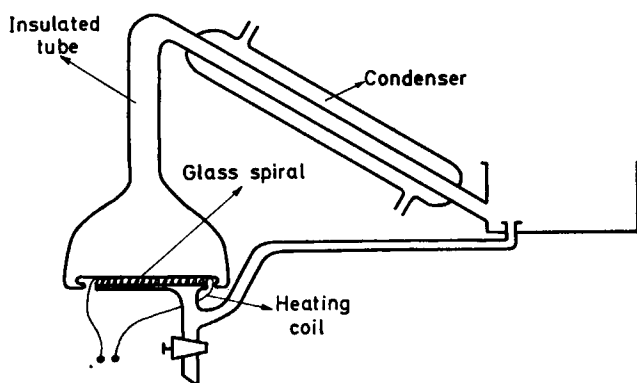


Fig. 3. Extraction apparatus.

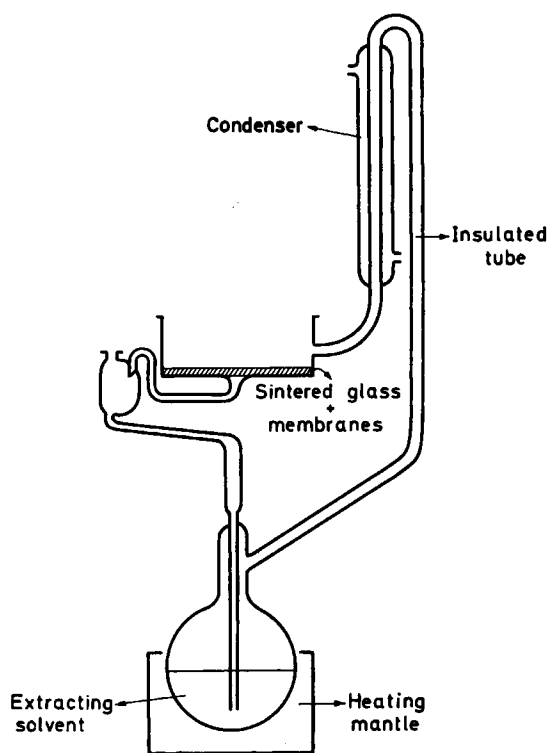


Fig. 4. Another extraction apparatus.

Reticulated Poly(dimethylsiloxane) plus APMA

The stability is also very good. The quantity of extracted polymer is about 0.5% of the capacity which is 1.2 meq/gr. The swelling by water reaches 45% for the extracted sample, whose degree of reticulation corresponds to an average molecular weight between bridges of 6,500¹ (stress-strain method).

The reticulation of this PDMS matrix and of St-DVB copolymers containing 2% DVB are comparable. The much higher swelling of the PDMS plus APMA membranes is due to their high elasticity. Considering the values of Table I and the highest value of their swelling, the stability of silicone membranes is as good as that of membranes built on hydrophobic matrices of St-*n*-BA-DVB.

Nature of Imprisonment

Some experiments were performed to see if the trapping of active polymer in the matrices is purely physical or if it is partially due to a chemical grafting.

St-n-BA-DVB Terpolymer plus APMA

If AMA is polymerized in the presence of a fraction of linear polymer corresponding to the matrix (St-*n*-BA), under conditions exactly the same as in intermembrane polymerization, the St-*n*-BA copolymer does not seem to be altered. Its viscosity in benzene is unchanged and it does not adsorb sodium hydroxide. It seems thus unlikely that APMA is trapped in these membranes by chemical bonds.

Reticulated Polyacrylamide plus APMA

The 10, 20, 25, 30, and 35% polyacrylamide membranes are equilibrated in a 10% aqueous solution of methacrylic acid. The quantity of monomer fixed to the membrane and expressed per gram of the whole system (dry membrane + absorbed monomer) is the theoretical maximum capacity.

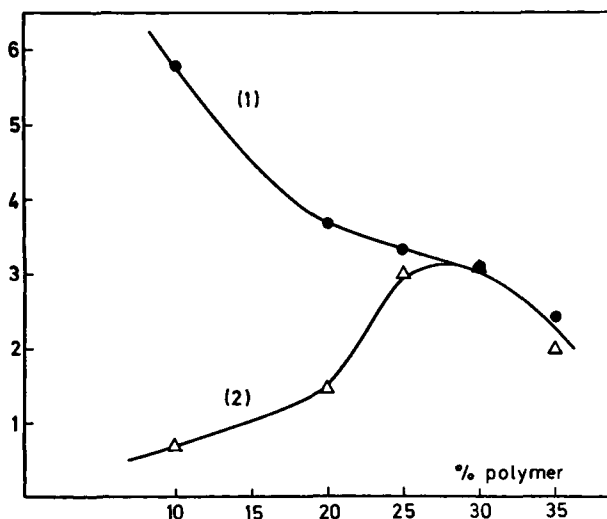


Fig. 5. Theoretical and experimental capacity of polyacrylamide + APMA membranes. Capacity (meq/g).

This value is plotted against the concentration of polyacrylamide in the membrane; it decreases regularly (Fig. 5, curve 1). Membranes equilibrated in the same way are simultaneously polymerized as described above. Then they are extracted with distilled water for a month. Their real capacity is determined and plotted against the polyacrylamide concentration (Fig. 5, curve 2). When this concentration is low in the cage, the greater part of the poly(methacrylic acid) is extracted; on the contrary, when it reaches about 25%, the whole quantity of the polymer is practically trapped. The experimental curve (curve 2) is characterized by a maximum; the membrane capacity is fixed by two factors varying inversely with increasing polyacrylamide concentration: (1) the quantity of absorbed monomer and (2) the efficiency of the cage effect. The former decreases whereas the latter increases. Comparison of the two curves shows clearly that such cage effects are chiefly and almost entirely responsible for the trapping of the polyacid in the matrix.

Poly(dimethylsiloxane) plus APMA

This membrane is destroyed with liberation of the active polymer by the following process: 4 g of membrane is heated in 80 cc dioxane at 70°C for 30 min; 7 cc concentrated HCl and then 11 cc water are added. The whole system is heated under reflux for several hours. After such treatment, the solid residue (white powder) and two immiscible liquid phases are collected; the lower phase contains APMA, which is identified by its IR spectrum. The IR spectrum of the solid residue is identical to that of the residue obtained by attack of the initial PDMS matrix, under the same conditions. These observations show again that the active polymer is physically trapped in the cage.

Furthermore, this polymer which has been recuperated has practically the same mean viscosimetric molecular weight as that of the compound resulting from simultaneous polymerization of the equilibrium solution. Chen and Friedlander¹⁰ have observed a molecular weight 3 to 4 times higher when styrene is polymerized radiochemically, not in solution but in a polyethylene sheet.

CONCLUSIONS

From these experiments, it appears that insolubilization of polymer chains by snake cage effect leads to satisfactorily stable systems, if the molecular weight of the active polymer is sufficiently high.

Porosity also plays an important role, as shown by the values of Table I and by comparison of curves 1 and 2 from Figure 5. The effect is determinant in the case of polyacrylamide cages which, as well as the active polymer, are hydrophilic. When the two polymer constituents have an opposed hydrophilic-hydrophobic character, the stability of the resulting material is enhanced. An extreme case is that of interpolymeric systems of high stability¹¹ one being hydrophilic and the other, hydrophobic, due to

the entanglement of two linear polymers. These interpolymers are in fact a particular application of the snake cage effect.

The physical character of trapping in the snake cage membranes described in this paper is qualitatively demonstrated. The large choice of adequate matrices is also illustrated.

The capacity of a snake cage system may be easily adjusted, whereas its swelling, function of the nature of the cage, its degree of reticulation, and the amount of active polymer may be controlled within certain limits.

In conclusion, the snake cage systems appear to have a great versatility.

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