

Preparation of Macroporous Styrene – Divinyl Benzene Copolymers

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Abstract

Suspension polymerization technique is used for the preparation of macroporous Styrene – Divinylbenzene (S-DVB) copolymer beads with different mole percent of divinylbenzene content in the presence of different contents and types of diluents which gives the porosity to the copolymer. It was found that increasing the percent of DVB with fixing the amount of toluene diluent (72%) results in a decrease in toluene regain (T. R.) values with increasing the degree of porosity. Increasing the percent of diluent with fixing the amount of DVB (16%) results in an increase in (T. R.) values with a decrease in the degree of porosity. Changing the type of diluent also has an effect on the physical properties of the prepared copolymer. Addition of polystyrene with toluene results in an increase in the degree of porosity. The other physical properties of the copolymer, apparent density and void fraction are also measured.

These copolymers are used as the base for the preparation of porous cation exchangers (by sulfonation) and anion exchangers (by chloromethylation and amination) under controlled experimental conditions. The physical properties of the prepared ion exchangers were also measured, with total exchange capacity (T. E. C.) and the rate of ion exchange ($t_{1/2}$).

Keywords: Styrene – Divinylbenzene (S-DVB) copolymer, Macroporous, Crosslinking, Toluene regain (T. R.), Total exchange capacity (T. E. C.).

تحضير مبادلات الأيونات السالبة المسامية

الخلاصة

لغاية الآن تستخدم كوبوليمرات الستايرين – ثنائي فاينيل بنزين المسامية بسبب مقاومتها الكيميائية العالية كمادة بادئة في تحضير المبادلات الأيونية. في هذا البحث تم دراسة مواصفات كوبوليمرات الستايرين – ثنائي فاينيل بنزين المسامية المحضرة بتكنيك بلمرة العوالق بوجود التلويين وكذلك دراسة مواصفات المبادلات الأيونية المحضرة من هذه الكوبوليمرات. تم إدخال مجموعة كلوريد المثلث (المحضرة من تفاعل البارافورمالدهايد وكلوريد المثلث) بوجود حامض لويس (كلوريد الألومنيوم اللامائي) على كوبوليمرات الستايرين – ثنائي فاينيل بنزين المسامية في الميثانول كوسط للتفاعل. حضرت مبادلات الأيونات السالبة الضعيفة والقوية القاعدية من خلال إدخال مجاميع الأمين على كوبوليمرات الستايرين – ثنائي فاينيل بنزين الحاملة لمجاميع كلوريد المثلث باستخدام الأمينات (الأولية، الثانوية)، والثالثية على التوالي. كانت السعة التبادلية الكلية لمبادلات الأيونات السالبة القاعدية القوية المحضرة (3.6 – 3.8 ملي مول/ غم رزن جاف)، حيث تعتمد هذه القيمة على درجة التشابك، وجود العامل المخفف، وكفاءة عملية إدخال مجموعة كلوريد المثلث.

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Introduction:

Most ion exchange bead materials are manufactured by suspension polymerization process using Styrene (S) and divinylbenzene (DVB). Ion exchange resins can be manufactured into one of two physical structures, gel or macroporous. Macroporous S-DVB copolymer materials are prepared by free-radical crosslinking copolymerization of S and DVB monomers in the presence of an inert diluent⁽¹⁾. In this process, the droplets of monomers in which the initiator was dissolved can diffuse through the suspension solution formed by dissolving cellulose (or one of its derivatives) or starch in water. This mixture was then heated under controlled temperature with homogenous mixing for a period of time at which translucent copolymer beads were formed and called gel type. They have no permanent porosity but swell to varying degrees in many organic solvents. They are often referred to as microporous, because the spaces between the crosslinks occupied by the swelling solvent are considered as small pores⁽²⁾. If special methods are used to carry out the polymerization of styrene and divinylbenzene, resins of higher porosity can be manufactured. The chemical structure of these porous resins is identical to that of the gel type, but the polymer matrix contains a large number of macropores. They therefore have a far greater surface area than the gel type, which contains only micropores⁽³⁾.

Macroporous resins are obtained when the polymerization is carried out with 5-60% DVB and in the presence of diluents, otherwise

referred to as pyrogens⁽²⁾. Higher DVB content gives the bead additional strength, but the additional crosslinking can hinder kinetics by making the bead too resistant to the shrinking and swelling necessary during normal operation⁽⁴⁾. The diluent, which is a solvent, a nonsolvent, or a linear polymer, is included in the reaction system as a pore forming agent, and plays an important role in the design of the pore structure of these crosslinked materials^(5, 6). During the polymerization, phase separation occurs i.e., the volume of the diluent phase (pore volume) in the network increases as the concentration of the crosslinker (DVB) or that of the diluent increases, or as the solvating power of the diluent decreases. After extraction of the diluent and drying process, the copolymers swollen in good solvents such as toluene may lead to a partial or total collapse of the pores^(7, 8, 9 & 10). Permanent pores or holes of various sizes are created; the voids (pores) of sizes 10 Å up to 1 µm are formed in the glassy state⁽²⁾.

Macroporous resins are made by mixing the monomers with heptane, or polyalcohols which expand the resin. The substance does not itself polymerize and, thus although it acts as a solvent for the monomers, it can cause the polymer to precipitate from the liquid. Channels are formed inside the beads, producing an artificially high porosity. Resins containing such channels are described as macroporous, whereas other resins with natural porosity are known as gel resins. Macroporous resins can have high degree of crosslinking than gel resins to strengthen the matrix and

compensate for voids left by the added solvents. The porosity and mechanical strength of the resin can be modified by varying the degree of crosslinking or the amount of the solvent added. They are highly resistant to osmotic shock⁽¹¹⁾.

Experimental:

The S-DVB copolymer beads were prepared by suspension polymerization technique. The initiator (Benzoyl peroxide) was dissolved in the monomers (S and DVB) and the diluents. This mixture was added to the suspension solution formed by dissolving one of cellulose derivatives or starch in deionized water in the reactor. The reactor is a 1 L Buchi jacketed glass fitted with a mechanical stirrer, nitrogen inlet, condenser, and temperature and pressure indicators. The reaction mixture was heated to 75°C and was allowed to proceed at this temperature for 6 hours and at 90 °C for 18 hours under nitrogen atmosphere with constant stirring at 300 rpm. After that, the copolymer beads were filtered and washed with dilute HCl solution and enough quantity of hot water and extracted with acetone, then dried at 150 °C and sieved. In order to measure the toluene regain, the copolymer beads were swollen to equilibrium in toluene for at least one week. Then, they were washed first with acetone and finally with pure methanol.

The pore size distribution of copolymer beads were determined by mercury intrusion porosimetry micrometrics on a Micrometrics 9320 model porosimeter. The total porosity, defined as the cumulative volume of the pores in one gram of the copolymer, was estimated from

the intruded mercury volumes of the pores larger than 3 nm radius.

Results and discussion:

As mentioned in the introduction, the aim of this work is to prepare a porous S-DVB copolymer (with high percent of crosslinking agent, DVB) which is important in the preparation of ion exchangers with good properties. The ion exchangers will have high exchange capacity for ions, and higher stability against chemical and physical changes compared to gel-type one^(2, 11, 12 & 13). The preparation of the copolymer can be regarded as the main controlling step for the properties of the ion exchanger in that it is the backbone for the functional groups.

Different experiments were conducted in order to prepare macroporous S-DVB copolymer beads with different mol percent of DVB in the presence of different diluents. The initial volume fraction of the monomer in the organic phase was taken to be constant throughout the present study, and the percent of DVB and types and contents of diluents were varied.

The DVB and the diluent will have the main effect on the final form of the ion exchanger bead and its internal structure. The crosslinking agent (DVB) will play an important role in the rigidity and the outstanding mechanical, thermal and chemical stability, and also the resistance to oxidizing conditions that tend to de-crosslink the polymer. When the percent of DVB increases, the rigidity of the copolymer will increase in the presence of the diluents which play an important role in the dispersion of polymer chains during the formation of the nuclei that forms the beads.

From studying the values of the toluene regain (T. R.), table 1, it can be seen that copolymers (1, 2, & 3) which has different mol percent of DVB and constant quantity of diluent (72% toluene) show that the (T. R.) values decrease with increasing the percent of the crosslinking agent. This may be due to the higher reactivity of DVB molecules which will cause its polymerization in the early stages of the polymerization process forming the gel that forms the beads and after that the crosslinking of the beads will increase which will render the swelling of the copolymer in toluene while measuring the (T. R.). The swelling of the copolymer beads is correlated with the porosity of the copolymer and the diameter of the pores in that the porosity increases on increasing the DVB content (in the presence of diluent) of the monomer mixture⁽¹³⁾. This can be noticed in Table (1).

The amount of crosslinking of the bead has an impact on the moisture content of the bead and the moisture content in turn has an impact on the selectivity. A bead with higher moisture content has a higher porosity and the active groups are spaced further apart from each other. Table (1) also shows that voids and the apparent density increase with increasing DVB content. Porous resins have lower capacity because the beads contain less exchange sites. The pores can take up to 10 to 30% of the polymer. This reduces the ion exchange capacity proportionately⁽¹⁴⁾. Table (1) shows that the total exchange capacity decreases on increasing the DVB content of the resin.

Porous type resins will have higher exchange rate for ions, and

especially in the case of the resins with a high crosslinkage⁽³⁾. The sponge like structure allows the active portion of the bead to contain a high level of DVB crosslinking without affecting the exchange kinetics⁽⁴⁾. Also increasing the DVB content yields smaller bead size which presents shorter diffusion path to active sites in the interior of the bead. This can be noticed in Table (1) when measuring the ($t_{1/2}$) values, in that the rate of exchange of ions becomes faster on increasing the DVB content.

Types of diluents will play an important role in giving the form and porosity of copolymer beads as mentioned in the introduction. The behavior of the diluent (toluene) depends on its quantity. Higher percent of diluent will cause an increase in the nuclei dispersion process in between them and the pore volume will increase⁽¹⁾. This is noticed in copolymers (1, 2 & 3); Table 2, when the percent of diluent (toluene) is increased with fixing the percent of DVB (16%), the (T. R.) values because decrease. This may be, as mentioned the literature, in that increasing the concentration of diluent results in increasing the pore volume. When are measured (T. R.) values, the copolymer beads are swollen in toluene and this may lead to a partial or total collapse of the pores which gives lower values of (T. R.). In contrast to that, permanent pores or holes of various sizes are created which will lead to the increase in the degree of porosity which can be noticed in Table (2).

Increasing the percent of diluent results in decreasing the apparent density values and the voids between the beads because of dispersion of the forces that form the bead. Some

results have been published in literature showing that when the pore volume increases, the capacity will increase in turn⁽¹⁵⁾. This is what is found in our experiments in Table 2, because of the increase in the pore volume, the (T. E. C.) values increase with decreasing the rate of exchange, (i. e.) slower.

Table 3 (copolymers 1 & 2), shows that changing the type of diluent (from methylethyl ketone to cyclohexanol in the presence of *n*-butanol), results in a decrease in (T. R.) values and this may be due to cyclohexanol which is a poor solvent for styrene and divinylbenzene in the early stages of polymerization and can be regarded as inert non-solvating diluent which leads to small pore volume, then lower (T. R.) values.

The increase in the degree of porosity means increasing the number of surviving pores after the extraction of the solvent. The apparent density and the voids between the beads increases with a decrease in the (T. E. C.) values and the resin beads have higher exchange rate. When comparing copolymers (2 & 3), it can be seen that increasing the percent of DVB from 24 to 30 (with fixing the percent and type of diluent) results in a decrease in (T. R.) values with a small increase in the degree of porosity. The apparent density increases and the voids between the beads also increase while the (T. E. C.) values decrease but the rate of exchange becomes faster. These findings are in accordance with that in Table (1), when the DVB content increases.

Table 4, for copolymer 1 (using 72% toluene as diluent alone), copolymer 2 (with the addition of 3% polystyrene), and copolymer 3

(increasing the concentration of polystyrene to 10%), shows a decrease in (T. R.) values and an increase in the degree of porosity. These results are in accordance with the findings of the authors in reference⁽²⁾ in that the pore volume increases with increasing the concentration of polystyrene in toluene. The apparent density increases and the voids between the beads decrease, while the (T. E. C.) values decrease with the increase in the rate of exchange.

From above one can conclude that it is possible to prepare porous copolymers throughout the use of different amounts of crosslinking agent and different types and concentrations of diluents.

References:

1. Erbay, E., Okay O., Polymer Bulletin, 41, 379, 1998.
2. Guyot, A., Synthesis and Separation using Functional Polymers, John Wiley & Sons Ltd. 1988, edit. D. C. Sherrington and P. Hodge, 1-42
3. Diaion, Manual of ion exchange resins and synthetic adsorbent, Mitsubishi Chemical Corporation, 1995.
4. DeSilva, F., Essentials of Ion Exchange, 25 Annual WQA Conference, March 17, 1999
5. Okay, O., Guran, C., J Appl Polym Sci, 46, 401, 1992.
6. Okay, O., Guran, C., J Appl Polym Sci, 46, 421, 1992.
7. Galina, H., Kolarz, BN., Wiczorek, PP., and Wojczynska, M., Br Polym J, 17, 215, 1985.
8. Okay, O., J Appl Polym Sci 32, 5533, 1986.
9. Poinescu, I., Vlad, C., Carpov, A., and Ionid, A., Angew

- Macromol Chem., 156, 105, 1988.
10. Cheng, CM., Vanderhoff, CW., and El-Aasser, MS., J Poly Sci Polym Chem Ed, 30, 245, 1992.
 11. Blaxal, K., Structures of Ion Exchange Resins and Ion Exchange Principles, Manual of Purolite Company, Ion Exchange Resins, 1995.
 12. Seidl, J., Malinskt, J., Dusek, K., and Heitz, W., Advan. Polym. Sci., 5, 1136, 1967.
 13. Millar, J., Smith, D., Marr, W., and Kressman, T., J. Chem. Soc., 218, 1963.
 14. Okay, O., J Appl Polym Sci 74, 2181, 1999.
 15. Ahmed, M., Malik, M. A., Pervez, S., and Raffiq, M., European Polymer Journal, 40, 1609, 20

Table (1)
Effect of increasing percent of crosslinking agent (DVB) on the physical
properties of the copolymer Diluent (toluene 72%)

Copolymer No.	Crosslinking Agent (DVB) %	Toluene Regain (T. R.) gm/gm	Degree of Porosity gm/cm ²	Apparent Density gm/cm ³	Void Fraction ml/gm	Total Exchange Capacity mmol/gm	t _{1/2} Sec.
1	12.7	3	0.24	0.61	0.28	2.7	1.31
2	16	2.5	0.25	0.68	0.28	2.37	0.98
3	20	2.2	0.27	0.76	0.3	2.30	0.88

Table (2)
Effect of increasing percent of diluent (toluene) on the physical properties of
the copolymer Crosslinking agent (16% DVB)

Copolymer No.	Diluent %	Toluene Regain (T. R.) gm/gm	Degree of Porosity gm/cm ²	Apparent Density gm/cm ³	Void Fraction ml/gm	Total Exchange Capacity mmol/gm	t _{1/2} Sec.
1	50	0.81	0.28	0.80	0.31	2.14	0.38
2	60	1.53	0.26	0.75	0.30	2.26	0.41
3	72	2.5	0.25	0.68	0.28	2.37	0.43

Table (3)
Effect of type of diluent and increasing percent of crosslinking agent on the
physical properties of the copolymer

Copolymer No.	Crosslinking Agent (DVB) %	Diluent 72%	Toluene Regain (T. R.) gm/gm	Degree of Porosity gm/cm ²	Apparent Density gm/cm ³	Void Fraction ml/gm	Total Exchange Capacity mmol/gm	t _{1/2} Sec.
1	24	Methylethyl ketone + n-Butanol	1.54	0.20	0.30	0.39	1.89	0.88
2	24	Cyclohexanol + n-Butanol	0.97	0.36	0.67	0.40	1.80	0.72
3	30	Cyclohexanol + n-Butanol	0.86	0.38	0.71	0.43	1.67	0.61

Table (4)
Effect of type of diluent on the physical properties of the copolymer
Toluene diluent (72%) and crosslinking agent (20% DVB)

Copolymer No.	Diluent	Toluene Regain (T. R.) gm/gm	Degree of Porosity gm/cm ²	Apparent Density gm/cm ³	Void Fraction ml/gm	Total Exchange Capacity mmol/gm	t _{1/2} Sec.
1	Toluene	2.2	0.27	0.75	0.30	2.37	1.32
2	Toluene + 3% polystyrene	2.15	0.29	0.77	0.29	2.33	1.04
3	Toluene + 10% polystyrene	1.91	0.33	0.80	0.27	2.32	0.83