Preparation of Anion-Exchange Resin from Styrene-Divinylbenzene Copolymer Obtained by Concentrated Emulsion Polymerization Method

Ali Ghaderi[1,2], Mojtaba Abbasian[1], Sohrab Rahmani[1], Hassan Namazi[2] , Habibollah Baharvand[3] and Ali Akbar Entezami[1*]

(1) Laboratory of Polymer, Faculty of Chemistry, University of Tabriz, Tabriz, Iran
(2) Laboratory of Denderimers and Natural Polymers, Faculty of Chemistry, University of Tabriz, Tabriz, Iran
(3) Department of Polymer Science, Iran Polymer and Petrochemical Institute, P.O.BOX: 14965/115, Tehran, Iran

A B S T R A C T

Concentrated emulsion polymerization was used for the synthesizing of cross-linked polystyrene-divinylbenzene (PS-DVB) containing 10% (X-10) and 16% (X-16) DVB with pore size less than 10 μm. For application of these resins as columns' filler in ion-exchange chromatography; chloromethylation and then amination processes were performed via aqueous trimethylamine. The chloromethylation reactions was done by 1,4-bis(chloromethoxy) butane in dichloromethane and in the presence of stannic chloride as catalyst at 0°C. The exchange capacities of anion exchange resins X-16 (C_E=3.5 meq/g) and X-10 (C_E=3.8 meq/g) was determined by titration procedure. The structure of PS-DVB was investigated by scanning electron microscope (SEM) technique. The SEM images showed that the porous structure of PS-DVB resin was approximately maintained intact after chloromethylation and amination reactions. TGA and FTIR techniques were used to investigate the thermogravimetric analysis and structures of obtained resins, respectively.

(*) To whom correspondence to be addressed.
E-mail: aentezami@tabrizu.ac.ir

INTRODUCTION

Concentrated emulsion polymerization has been used to make precursors for preparation of homopolymer latexes, copolymers and tough polymers [1-4]. They have also been employed to prepare conductive polymers, composites, composite membranes, micro sponge molecular reservoirs and polymer supported quaternary onium salts, polymer supported palladium complexes and quaternary onium salts polymer-supported enzymes [5, 6].

In contrast to the conventional emulsion, concentrated emulsion has a large volume fraction of dispersed phase, greater than 0.74 and as large as 0.99 [7-9]. It has a paste-like appearance and behaviour. When the volume fraction of continuous phase is sufficiently small, the dispersed phase is composed of polyhedrall cells separated by thin films of continuous phase.

The concentrated emulsions are prepared by dropwise addition of the dispersed phase to a small amount of a continuous phase containing a surfactant. As well known experimental observations have indicated that the phase in which the surfactant is soluble constitutes the continuous phase of an emulsion. The adsorption of surfactant on the interface between the two media of the emulsion is responsible for its kinetic stability [10,11].

The concentrated emulsion have attracted our attention as a possible pathway for a number reasons: (i) The ordered organization of surfactant molecules at the two media may organize the monomers in its vicinity and thus accelerated the rate of conversion, (ii) The presence of the surfactant layer, causes the reduction of mobility inside the cell, and could generate the earlier gel effect, which finally leads to the delay in the bimolecular termination reaction. Hence, the molecular weight is expected to be higher if the polymerization occurs in a concentrated emulsion than in the bulk.
(iii) The polymerized system maintains the structure of the emulsion precursor.
(iv) A better control of the size of latexes can be made by controlling the size of the cells of concentrated emulsion, using suitable surfactants, ionic strengths, and pHs. Hence the splitting of a bulk system into a large number of small, independent cells may have favorable effects. In addition, a concentrated emulsion can be polymerized to generate either latexes, or a porous medium or a composite [12,13].

Cross-linked styrene (St)-divinylbenzene (DVB) copolymer with chloromethyl substituents (-CH$_2$Cl) have a wide range of applications in the preparation of ion-exchange resins, and the supports for catalyst, gel permeation, gas chromatography and other because they contain reactive functional groups (-CH$_2$Cl). The easy chloromethylation of polystyrene copolymer (14, 15) as well as the high reactivity of the resulting

benzylic positions allow the introduction of a large number of functional groups and explain the widespread use of the polymers (16). The aim of this work was the preparation of anion-exchange resin which is used in the colums in column chromatography through concentrated emulsion polymerization technique. The so-called columns are applicable for separation of different compounds such as: inorganic cations and anions, amino acids, proteins, peptides, phenols, amines, organic acids, and bases [17-20].

Also, this work represents the preparation of anion-exchange resin from styrene-divinylbenzene copolymer which obtained by concentrated emulsion polymerization method. In the further steps, the copolymer was converted to the anion exchange resin containing one type ion exchange site with high sorptive capacity (compared with commercial anion exchange capacity) by amination reaction. The prepared resin had capability to eliminate the anions in water and purifying it.

EXPERIMENTAL
Materials
The following chemicals were used: styrene (Merck, as monomer), divinylbenzene (Merck, as cross-linking agent), nonionic surfactant, AIBN (2, 2'-azobisisobutyronitrile)(Fluka) and cumene hydroperoxide (Aldrich, as initiator), paraformaldehyde (Merck), 1,4-butandiol (Merck), stannic chloride (Merck, as catalyst for chloromethylation step), dichloromethane (Merck), acetone (Merck), trimethylamine (Fluka, assay 45% in water, as amination agent).
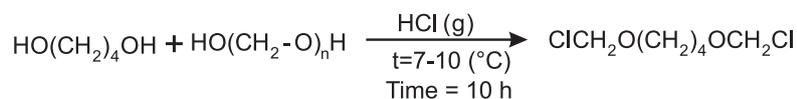
Instrumentation
FTIR spectra were recorded using Shimadzu FTIR-8101 M. Differential scanning calorimetry (DSC) analyses were performed on a Mettler 4000 TA thermal analytical system.

Methods
Preparation of PS-DVB copolymer by concentrated emulsion method
A 250 mL three-necked round bottom flask was equiped with a magnetic stirrer and thermometer. To prepare of inverse emulsion of water in monomer

$$HO(CH_2)_4OH + HO(CH_2\text{-}O)_nH \xrightarrow[\substack{t=7\text{-}10\,(°C) \\ Time = 10\ h}]{HCl\,(g)} ClCH_2O(CH_2)_4OCH_2Cl$$

Scheme I. Synthesis of 1,4-bis(chloromethoxy)butane.

solution, the flask in firstly charge with styrene, divinylbenzene, emulsifier and initiator. Then, double-distilled water was added to this solution dropwise, while stirring in this way. The concentrated emulsion containing 84% dispersed phase had been prepared. The above emulsion was transferred into glass tubes by means of vacuum. The packed tubes were closed and polymerization was performed in the oven for 48 h at 50°C. Then the water phase or dispersed phase of the PS-DVB was removed in the oven during the four steps:

    1) 10 h at 70°C
    2) 10 h at 80°C
    3) 10 h at 105°C
    4) 10 h at 140°C

Degree conversion in polymerization process was allowed to reach the value of 10%. By this procedure the PS-DVB copolymers with 10, 16 and 30 DVB weight-percent were produced.

Preparation of 1,4-bis (chloromethoxy) butane
Paraformaldehyde (20 g) and 1,4-butadiol (30g) were mixed together in a flask. The mixture cooled to about 7°C in a cold water bath and hydrogen chloride gas

was passed into the flask for 7 h. The mixture was then chilled to 0°C overnight during which it is separated into two layers. The upper layer was collected, washed, dried with magnesium sulphate and vacuum distilled to yield 29 g of 1,4-bis (chloromethoxy) butane (Scheme I).

Chloromethylation of PS-DVB (16%) copolymer
To a stirring suspension of cross-linked polystyrene (16% DVB) (1.04 g, 0.01 mol), and the 1,4-bis(chloromethoxy) butane (3.75 g, 0.02 mol) in dichloromethane (20 mL) was slowly added stannic chloride (0.05 mL, 0.00425 mol) at 0°C. The reaction mixture was stirred at room temperature overnight for 18-19 h. The mixture was then cooled at 0°C and treated with hydrochloric acid (15 mL, 1 N). The polymer beads were recovered by filtration with water-dioxane, dioxane, methanol and dichloromethane. The beads dried overnight in vacuum at room temperature. The resulting beads were analyzed for chlorine content. The chloromethylation analysis of PS-DVB (10%) copolymer beads was performed by this method and the chloromethylation yield was 71.8% (Scheme II).
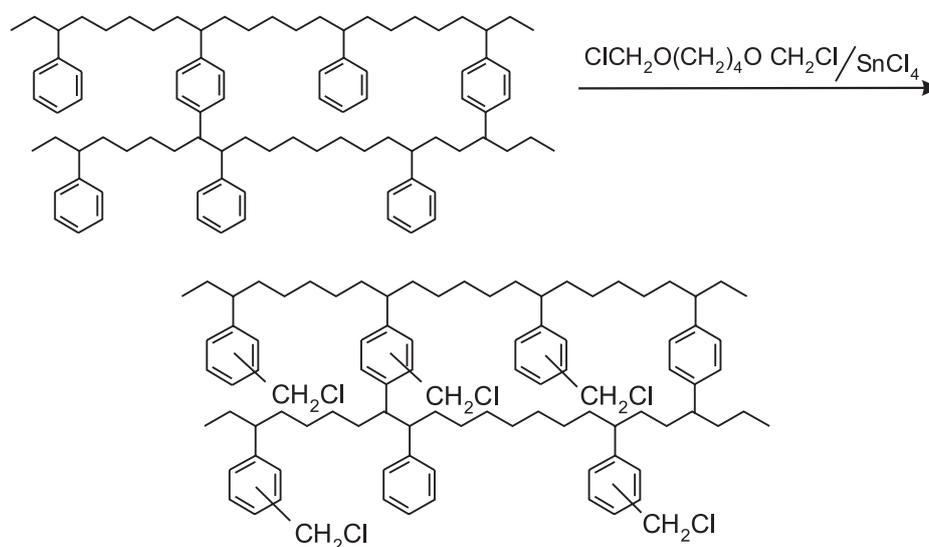
Scheme II. Chloromethylation of PS-DVB copolymers.
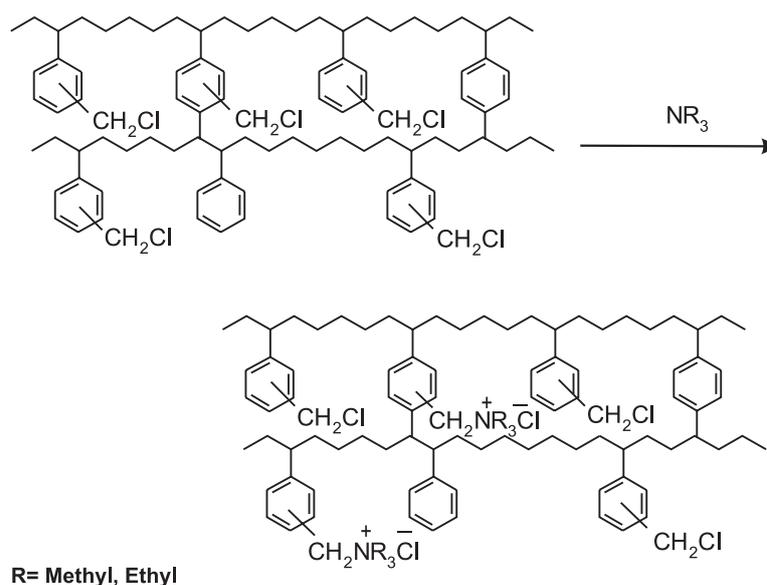
Scheme III. Amination of chloromethylated PS-DVB copolymer.

Amination of chloromethylated PS-DVB (16%) copolymer

A 100 mL one-necked round botton flask was filled with a magnetic stirrer. Then the flask was charged with 0.255 g chloromethylated PS-DVB (16%) copolymer, 30 mL acetone, and 2 mL of 45% aqueous trimethylamine. The mixture was allowed to react overnight at room temperature by stirring about 20 h. It was diluted with deionized water, filtered, and the beads were washed with ethanol and then deionized water. Also the amination step of chloromethylated PS-DVB (10%) copolymer was performed at the same way (Scheme III).

Amination of chloromethylated PS-DVB (10%) copolymer

A 10 mL pressure reactor was filled with 0.42 g of chloromethylated styrene-divinylbenzene (10%) copolymer, 0.096 g of dimethylamine, 0.072 g of sodium hydroxide, and 0.1 g of sodium chloride. The mixture is stirred and heated to 90°C for 5 h. The mixture is then cooled, and the contents of the reactor were emptied. The resin is analyzed according to standard methods used for determining ion-exchange capacities.

Calculation of anion exchange capacity

At first, Two samples of wet anion exchange resins (w_1 and w_2) weighted. First sample (w_1) dries at 100°C for 12 h and weighted again (w_1'). Second sample (w_2) was added to a 30 mL solution of sodium hydroxide (0.1 N) in a 100 mL round bottomed flask with a magnetic stirring bar. The mixture was stirred for 2 h at room temperature, then the mixture was filtered and washed well with water until the washing become neutral with phenolphthalein TS. The sample (w_2) was transfer into a 30 mL solution of sodium chloride (0.1 N) containing 3 drops of phenolphthalein regent (indicator) and stirred for 2 h at room temperature. The mixture titrates with 0.1 N hydrochloric acid until the white mixture is formed and calculates the ion exchange capacity by the formula as follow:

$$X = (w_1' \times w_2)/(w_1) = w_2' \tag{1}$$

$$(N \times V)_{HCl} = a \tag{2}$$

$$C_E = a/w_2' \tag{3}$$

w_1 = weight of wet resin

w_1' = weight of dry resin

w_2 = weight of wet resin in experimental sample
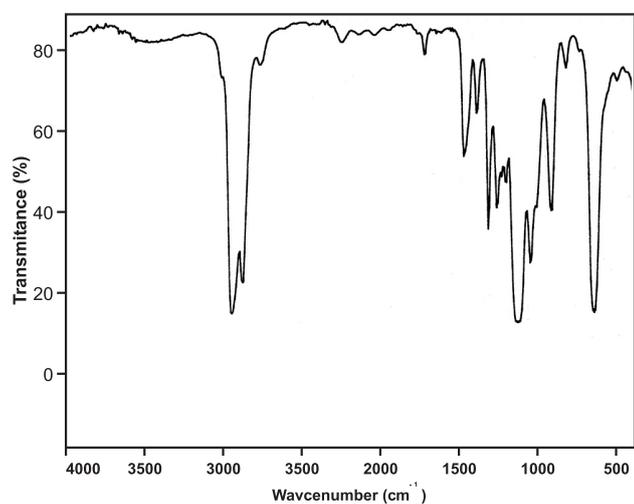
w_2' = weight of dry resin in experimental sample

a = mmol of chlorine in the dry resin in experimental sample (w_2')

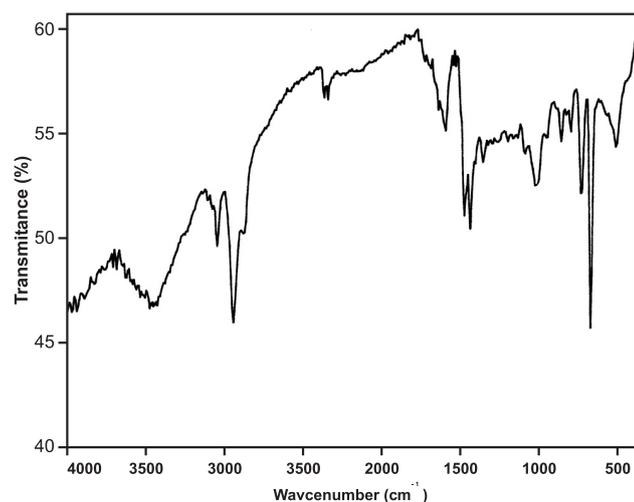C_E = Exchange capacity of anion exchange resins on

the base of [Cl$^-$]/[dry resin] (meq/g).

RESULT AND DISCUSSION

Figure 1 shows the FTIR spectrum of 1,4-bis (chloromethoxy) butane (a) and chloromethylated PS-DVB (10%) copolymer aminated with dimethylamine (b), respectively [21-26]. The absorption bonds of C-Cl, C-O, - CH_2, and aliphatic C-H were observed at 646, 1132, 1479, and 2851 cm^{-1}, respectively (Figure 1 a). Also the absorption bonds attributed to compound (b) were observed at 703,

1458, 1520, 2930, 3030 and 3447 cm^{-1} which were corresponding to C-Cl, CH_3, - CH_2, aliphatic - CH, aromatic – CH, and – NH, respectively.

Figure 2 showed the scanning electron micrographs (SEM) of chloromethylated PS-DVB (16%) copolymer (a) and aminated compound with trimethylamine (b), respectively.

As could bee seen in Figure (2 a), chloromethylated PS-DVB had high porous surface. Also, the X-16 anion exchange resin had the porous surface along with the holes irregularly distributed (Figure 2 b).

Thermogravimetric analysis (TGA) graphs of chloromethylated PS-DVB (16%) copolymer (a), X-16 anion exchange resin (b), and X-10 anion exchange resin (c) which both (b and c) aminated with trimethylamine had been showed in Figure 3. As
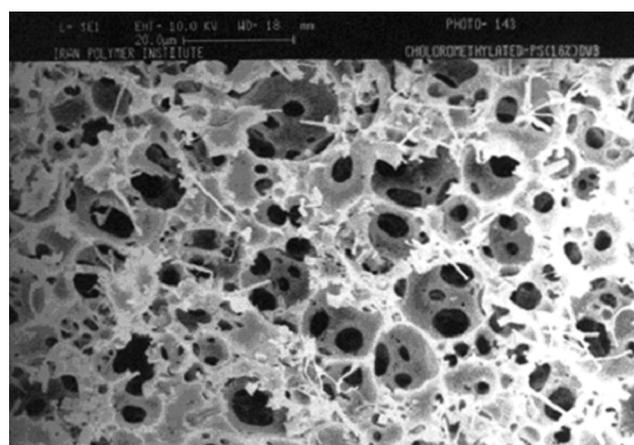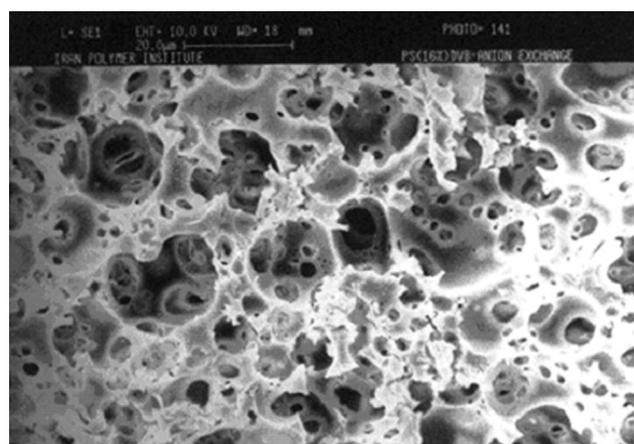

(a)

(b)

Figure 1. FTIR spectrums of (a) 1,4-bis(chloro-methoxy) butane and (b) chloromethylated PS-DVB (10%) copolymer which aminated with dimethylamine

(a)

(b)

Figure 2. Scanning electron micrograph (SEM) of (a) chloromethylated PS-DVB copolymer (16%) and (b) X-16 anion-exchange resin (magnification x500).
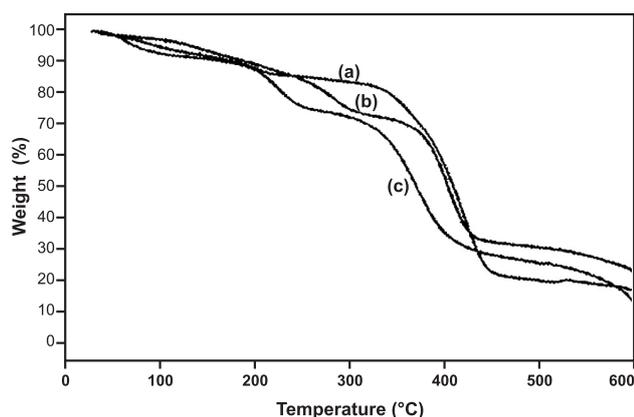
Figure 3. TGA Graphs of (a) chloromethylated PS-DVB (16%) copolymer, (b) X-16 anion-exchange resin, and (c) X-10 anion-exchange resin.

showed in Figure (3 a), at 110°C the chloromethylated PS-DVB (16%) copolymer gave a weight loss ca. 8%, which was attributed to dehydration of hydrophilic copolymer surface. At 300°C an overall weight loss of 23% showed which was attributed to isolation of chloromethyl and quaternary groups. This resin exhibited thermal stability up-to 350°C. After this temperature, degradation of resin was occurred.

As showed if Figure 3c, at 90°C the X-10 anion-exchange resin gave a weight loss of 7% which was attributed to dehydration of the hydrophilic resin surface. At 280°C an overall weight loss 25% showed which was attributed to isolation of chloromethyl and quaternary ammonium groups. This resin exhibited thermal stability up-to 300°C. After 300°C the degradation of resin was occurred.

The chloromethylation yield of PS-DVB copolymer beads were obtained from equations 4, 5, and 6 presented at Table 1.

$$Y = M_{Cl} \times 100 / M_M = 23.12\% \qquad (4)$$

$$Z = 23.12 \times 10^{-2} / 35.5 = 6.5 \text{ mmol} \qquad (5)$$

$$R = A \times 100 / 6.5 \qquad (6)$$

Y = Percent of chlorine in copolymer when the all of benzene rings in copolymer became chloromethylated

Z = mmol of chlorine when chloromethylation is 100%

M_{Cl} = Molecular weight of chlorine

M_M = Molecular weight of chloromethylated styrene

Table 1. The yield of chloromethylation reaction.

PS-DVB copolymer	X-10	X-16
Chloromethylation yield (%)	71.8	70

monomer

A = Content of chlorine in copolymer obtained from gravimetric analysis

R = Percent of chloromethylation of copolymer

As showed at Table 1, with increasing the DVB weight-percent, the yield of chloromethylation reaction decreased. This is according to increasing at steric congestion due to increasing DVB content.

We have determined the exchange capacity of anion exchange resins by titration procedure. The anion-exchange capacity of X-16 anion exchange resin (C_E=3.5 meq/g) which compared with X-10 anion exchange resin (C_E=3.8 meq/g) is lower because of its higher steric congestion. This fact led to the lower chloromethylation and amination yield. The obtained exchange capacity of these resins can be compared with the commercial anions exchange resins (CE= 4-4.5 meq/g) [27].

CONCLUSIONS

In this work, anion-exchange resins copolymer (styrene-divinylbenzene) was obtained by concentrated emulsion polymerization method. The influences of chloromethylation and amination reactions on internal morphology of styrene-divinylbenzene copolymers and anion exchange resins were demonstrated. The amount of DVB affected on degree of the thermal stability and anion exchange capacity of resins. The obtained exchange capacities of X-10 and X-16 are 3.8 and 3.5 meq/g, respectively. DSC, TGA, SEM and FTIR Spectroscopy techniqes were used to investigate the structure of the resins.

ACKNOWLEDGMENTS

Symbols and Abbreviation

PS-DVB: Poly styrene-divinylbenzene
SEM: Scanning electron micrographs
TGA: Thermogravimetric analysis
meq/g: Miliequivalent per gram
C_E: Exchange capacity
THF: Tetrahydrofuran
DSC: Differential scanning calorimetry

REFERENCES

1. Lissant K., The geometry of high-internal-phase-ratio emulsions, *J. Colloiod. Interface. Sci.*, **22**, 462 - 468, 1966.

2. Lissant K., Mayhan K., A study of medium and high internal phase ratio water/polymer emulsions, *J. Colloiod. Interface. Sci*, **42**, 201-208, 1972.

3. Lissant K., Peace B., Wu S., Mayhan K., Structure of high-internal-phase-ratio emulsions, *J. Colloiod. Interface. Sci*, **47**, 416- 423, 1974.

4. Princen H., Aronson M., Moser J., Highly concentrated emulsions. II. Real systems. The effect of film thickness and contact angle on the volume fraction in creamed emulsions, *J. Colloiod. Interface. Sci,* **75**, 246-270, 1980.

5. Princen H., Rheology of foams and highly concentrated emulsions: I. Elastic properties and yield stress of a cylindrical model system, *J. Colloiod. Interface. Sci*, **91**, 160-175, 1983.

6. Princen H., Kiss A., Rheology of foams and highly concentrated emulsions: III. Static shear modulus, *J. Colloiod. Interface. Sci*, **112**, 427-437, 1986.

7. Princen H., Rheology of foams and highly concentrated emulsions. II. experimental study of the yield stress and wall effects for concentrated oil-in-water emulsions, *J. Colloiod. Interface. Sci*, **105**, 150-171, 1985.

8. Bhakta A., Ruckenstein E., Drainage of a Standing Foam, *Langmuir*, **11**, 1486-1492, 1995.

9. Bhakta A., Ruckenstein E., Foams and concentrated emulsions: Dynamics and phase behavior, *Langmuir*, **11**, 4642-4652, 1995.

10. Webster A., Cates M., Osmotic stabilization of concentrated emulsion and foames, *Langmuir*, **17**, 595-608, 2001.

11. Van Aken G., Vliet T., Flow-induced coalescence in protein-stabilized highly concentrated emulsion: role of shear-resisting connections between the droplets, *Langmuir*, **18**, 7364-7370, 2002.

12. Pal R., Relative viscosity of non-newtonian concentrated emulsions of noncolloidal droplets, *Ind. Eng. Chem. Res*, **39**, 4933-4943, 2000.

13. Hebraud P., Lequeux F., Palierne J., Role of permeation in linear viscoelastic response concentrated emulsions, *Langmuir*, **16**, 8296-8299, 2000.

14. Van Aken G., Flow-induced coalescence in protein-stabilized highly concentrated emulsions, *Langmuir*, **18**, 2549-2556, 2002.

15. Caldero G., Garcia-Celma M., Solans C., Ponts R., Effect of PH on mandelic acid diffusion in water in oil highly concentrated emulsions (Gel-Emulsions), *Langmuir*, **16**, 1668-1674, 2000.

16. Itsuno S., Uchikoshi K., Ito K., Novel method for halomethylation of cross-linked polystyrenes, *J. Am. Chem. Soc*, **112**, 8187-8188, 1990.

17. Hancock W., *CRC Handbook of HPLC for the separation of aminop acids, Peptides and Proteins*, Vol. II; CRC Pree, Inc, 23-43, 287-300, 357-362, 1984.

18. Espelt L., Clapes P., Esquena J., Manich A., Solants C., Enzymatic carbon-carbon bond formation in water-in-oil highly concentrated emulsions (Gel Emulsions), *Langmuir*, **19**, 1337-1346, 2003.

19. Alami S., Maguer D., Caze C., Influence of the preparation methods on the functional group distribution of chloromethylated styrene-divinyl benzene copolymers, *React. Polym.* **6**, 213-219, 1987.

20. Hodge P., *Synthesis and separations using functional polymers*, Wiley, New Yourk, Ch. 2, 43-50, 1988.

21. Crosby K., Guy A., Masao N., Halomethylation of polystyrene, *US Patent 3,995,094,* 1976.

22. Messing F, Sheldon H., Marylu B., Alan C., Process for preparing anion exchange resins by amination of haloalkylated polymers in the presence of metal halide and metal hydroxide, *US Patent 4,585,800,* 1986.

23. Pafford M., Reichl J., Rosenbaum B., Method for preparation of anion exchange resins, *US Patent 6,756,462,* 2004.

24. Alexandratos S., Brown G., Bonnesen P., Moyer B., Bifunctional anion-exchange resins with improved selectivity and exchange kinetics, *US*

Patent 6,059,975, 2000.

25. Foucher D., Stoffel N., Janezic R., Smith T., Luca D., Zhang B., Process for halomethylation of high performance polymers., *US Patent 6,187,512,* 2001.

26. Stone G., Graft polymeric membranes and ion-exchange membranes formed thereform, *US Patent 6,726,758,* 2004.

27. Darfiner K., *Ion Exchangers.* Wiley, New York, 230-232, 1991.