

IEX 2008, 9 - 11 July, Cambridge, UK



Polymeric Ion Exchangers Based on Styrene-Divinylbenzene Matrix. Textural and Structural Modifications after Grafting Different Functional Groups

Corina M Bohdana¹, Daniela S Cantea¹, James A Dale²,
Eugen Pincovschi³ and Ana Maria S Oancea³

¹*Purolite S.R.L., Aleea Uzinei no.11, Victoria, Brasov County, 505700, Romania*

²*Purolite International Ltd., Llantrisant Business Park, CF72 8LF, U.K.*

³*Department of Inorganic Chemistry, University Politehnica of Bucharest, Gh. Polizu no.1, Bucharest 011061, Romania*

Introduction

- The main objective of the present work was to investigate both structural and textural modifications of macroporous and macronet polystyrene – divinylbenzene copolymer networks after incorporation of ionogenic groups in industrial conditions
- The polystyrenic skeletons obtained by suspension polymerization have a notable physical and chemical stability and are used by all manufacturers to obtain a large variety of ion exchangers by grafting different functional groups. This type of matrix is still the most important, because styrene monomer is relatively cheap and abundantly available
- The final properties of the ion exchanger depend on the nature of the functional groups, the properties of the matrix of the initial inert polymer and its transformation during grafting the functional groups
- The macroporous polystyrenic polymers have permanent porosity due to a phase separation arising during polymerization, induced by the presence of a porogen in the reaction mixture. The corresponding ion exchangers compared with the gel ones have the advantage to exchange also larger ions and are more resistant to fouling by organic matter present in natural surface water
- The macronet resins are relatively new commercial products obtained by Purolite, a third generation of polystyrenic resins proposed by prof. Davankov and dr. Tsyurupa. These resins are hyper-crosslinked styrene-divinylbenzene polymers obtained by post-crosslinking the polymers swelled in a solvent in excess with conformational rigid bridges. These materials contain micro-, meso- and macropores and have a large surface area.

Investigated Materials

Inert polymer	Matrix	Resin name	Functional group	Type of resin
Purolite PC 150	Styrene - DVB Macroporous	Purolite C 150	-SO ₃ H	Strong Acid Cation
Purolite MN 200	Styrene - DVB Hyper-crosslinked	Purolite MN 500	-SO ₃ H	Strong Acid Cation
Purolite PA 500	Styrene - DVB Macroporous	Purolite S 930	-N(CH ₂ COOH) ₂	Chelating Iminodiacetic acid
Purolite PA 100	Styrene - DVB Macroporous	Purolite S 950	-CH ₂ NHCH ₂ PO(OH) ₂	Chelating Amino-phosphonic acid

Experimental

- The investigated resins and their corresponding inert polymers were dried and separated in the following size fractions: [-900+710], [-710+600], [-600+425] and [-425+300] μm
- The pore size distribution, total cumulative pore volume (TCPV), specific surface area (S_{Hg}), average pore diameter (d), most frequent pore diameter (d_{fq}), total porosity, bulk density (ρ_{bulk}) and apparent density (ρ_{app}) were measured by mercury intrusion porosimetry
- The specific surface area of the macronet inert and sulfonated polymers was measured also with the BET method using dinitrogen, ($S_{\text{BET, N}_2}$)
- The structure was analyzed by scanning electron microscopy.

Results

Total Cumulative Pore Volume / (cm³ g⁻¹)

Polymer/ Size fraction (μm)	PC 150 inert	C 150 -SO ₃ H	MN 200 inert	MN 500 -SO ₃ H	S930 inert	S930 Imino- diacetic	S950 inert	S 950 Amino- phospho- nic
[-425+300]	0.49	0.23	1.1	0.65	0.69	0.66	0.49	0.28
[-600+425]	0.49	0.26	1.2	0.64	0.65	0.54	0.59	0.29
[-710+600]	0.52	0.22	1.1	0.68	0.67	0.58	0.46	0.32
[-900+710]	0.47	0.22	1.3	0.60	0.64	0.54	0.43	0.34

Average pore diameter / Most frequent pore diameter (nm)

Polymer/ Size fraction (μm)	PC 150 inert	C 150 -SO ₃ H	MN 200 inert	MN 500 -SO ₃ H	S930 inert	S930 Iminodi acetic	S950 inert	S 950 Amino- phos- phonic
[-425+300]	28/ 29	36/ 35	123/ 124	153/ 156	149/ 153	168/ 167	127/ 110	175/ 181
[-600+425]	26/ 27	34/ 34	116/ 127	150/ 155	138/ 142	119/ 160	155/ 78	131/ 118
[-710+600]	25/ 29	34/ 34	121/ 124	143/ 148	136/ 141	147/ 159	131/ 97	194/ 193
[-900+710]	27/ 29	34/ 34	123/ 126	145/ 148	133/ 148	143/ 155	161/ 170	167/ 179

Specific surface area S_{Hg} ($m^2 g^{-1}$) / Specific surface area S_{BET, N_2} ($m^2 g^{-1}$)

Polymer/ Size fraction (μm)	PC 150 inert	C 150 -SO ₃ H	MN 200 inert	MN 500 -SO ₃ H	S930 inert	S930 Imino diace tic	S950 inert	S 950 Amino- phos- phonic
[-425+300]	87	29	64/ 1043	26/ 297	30	22	27	10
[-600+425]	92	37	77/ 1047	26/ 313	29	26	25	14
[-710+600]	106	28	61/ 1023	27/ 356	29	25	23	11
[-900+710]	85	29	85/ 1006	20/ 360	29	23	23	14

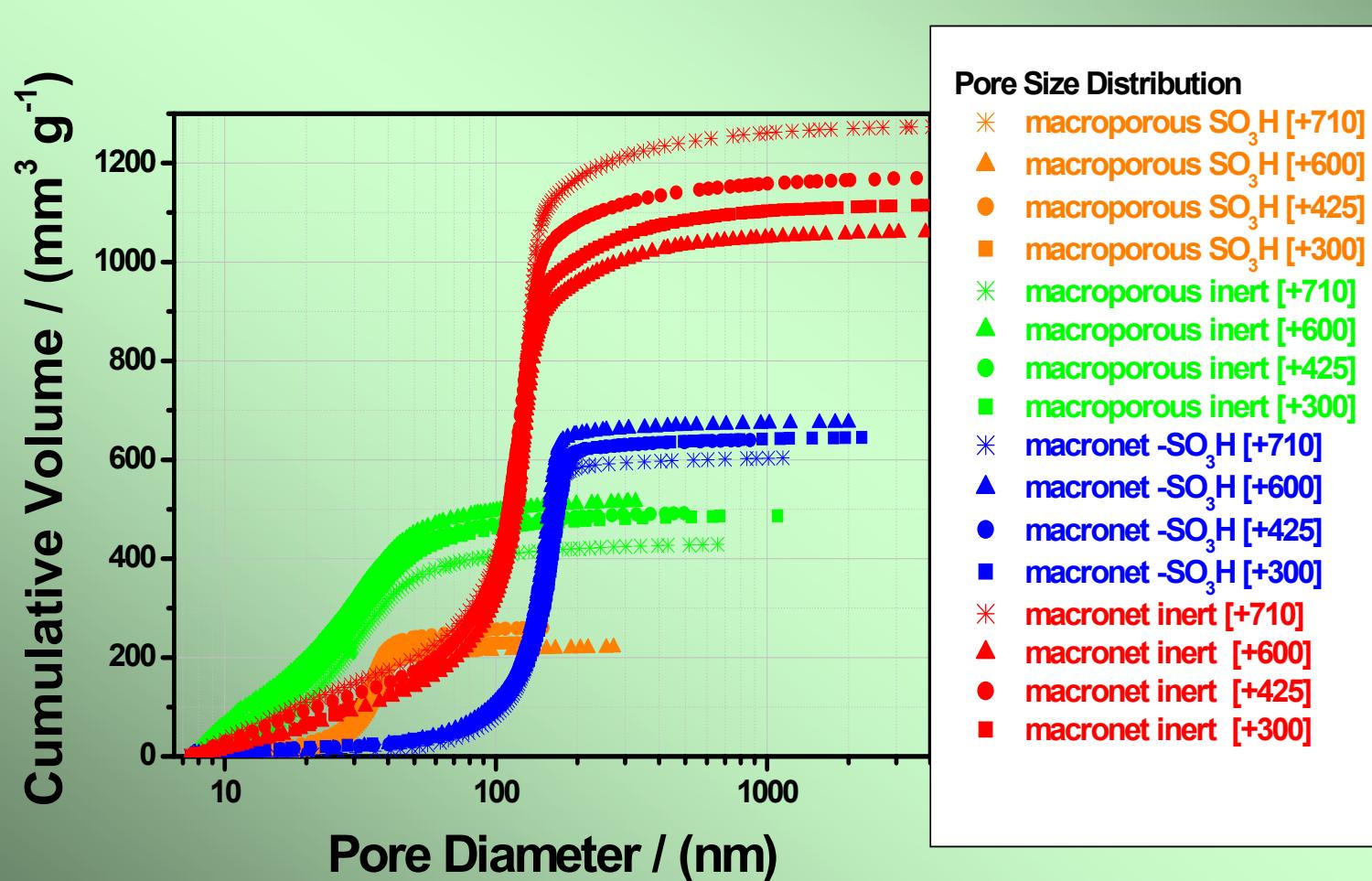
Porosity (%)

Polymer/ Size fraction (μm)	PC 150 inert	C 150 - SO_3H	MN 200 inert	MN 500 - SO_3H	S930 inert	S930 Imino- diacetic	S950 inert	S 950 Amino- phospho- nic
[-425+300]	36	26	56	51	43	45	37	35
[-600+425]	36	36	52	48	41	42	44	-
[-710+600]	37	28	55	49	42	42	35	25
[-900+710]	32	30	59	49	41	44	27	36

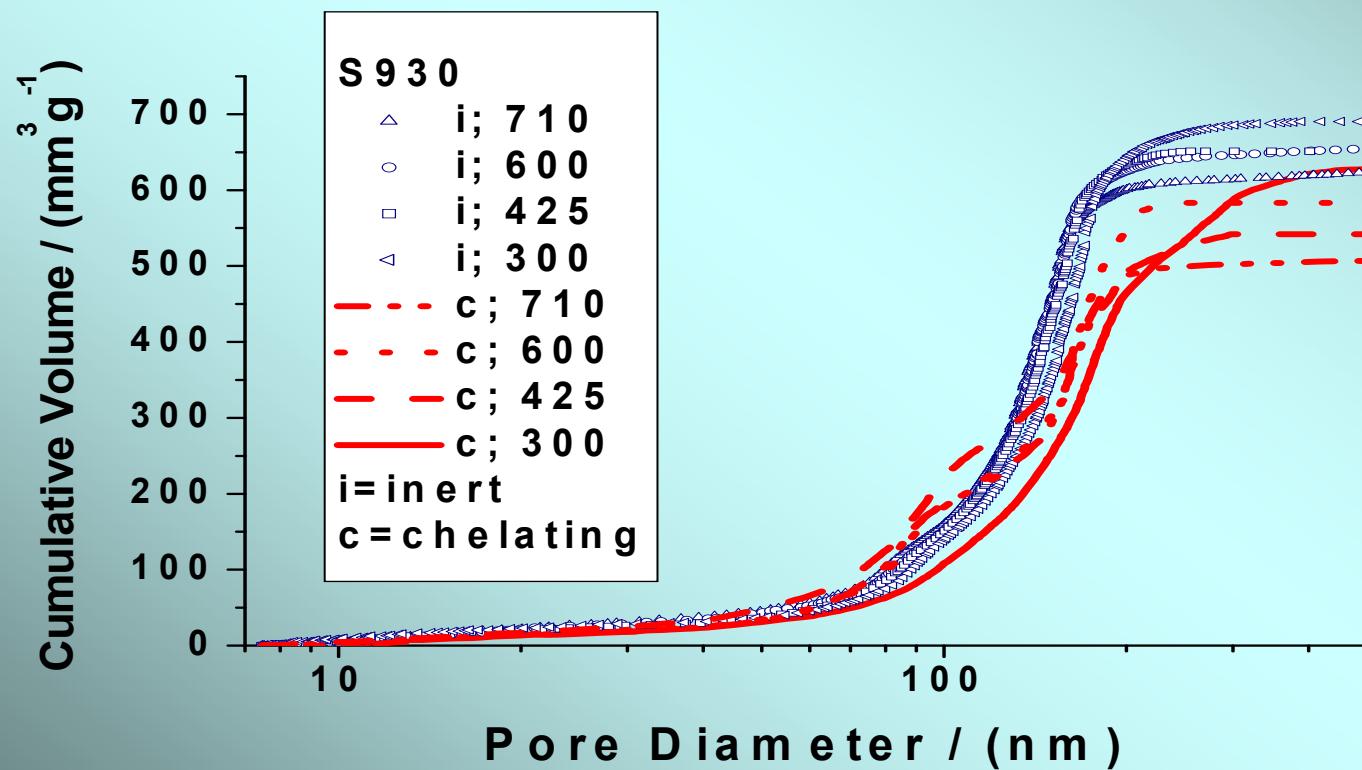
Bulk Density / Apparent Density (g cm⁻³)

Polymer/ Size fraction (μm)	PC 150 inert	C 150 -SO ₃ H	MN 200 inert	MN 500 -SO ₃ H	S930 inert	S930 Imino diace tic	S950 inert	S 950 Amino phos phonic
[-425+300]	0.744/ 1.17	1.12/ 1.52	0.504/ 1.15	0.786/ 1.60	0.628/ 1.11	0.680/ 1.23	0.758/ 1.20	1.22/ 1.87
[-600+425]	0.738/ 1.16	1.36/ 2.12	0.442/ 0.918	0.754/ 1.46	0.635/ 1.08	0.773/ 1.33	0.745/ 1.32	-
[-710+600]	0.713/ 1.13	1.26/ 1.74	0.522/ 1.17	0.730/ 1.44	0.621/ 1.07	0.726/ 1.26	0.746/ 1.14	0.773/ 1.03
[-900+710]	0.684/ 1.01	1.36/ 1.94	0.463/ 1.13	0.811/ 1.59	0.635/ 1.07	0.819/ 1.47	0.631/ 0.869	1.07/ 1.68

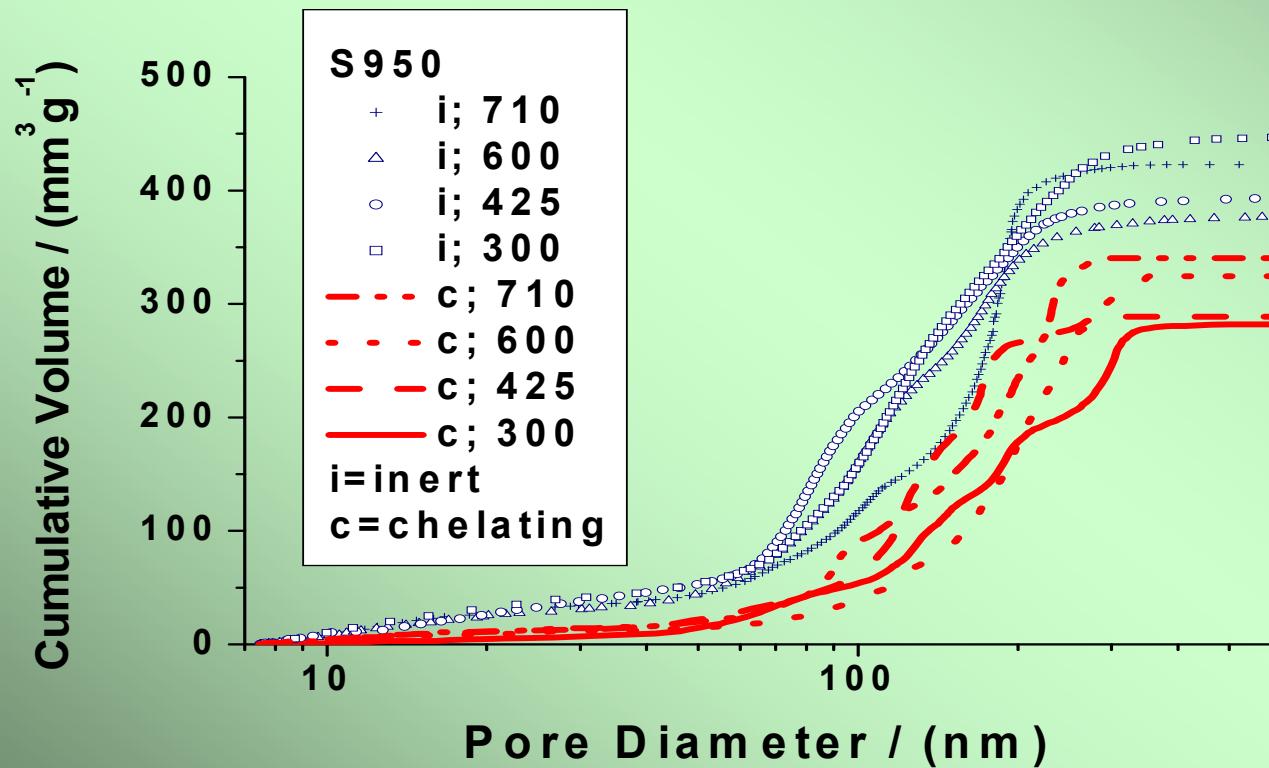
Integral pore size distribution of the macroporous and macronet St-DVB polymers before and after sulfonation



Integral pore size distribution of the macroporous St-DVB inert polymer and the corresponding iminodiacetic acid resin

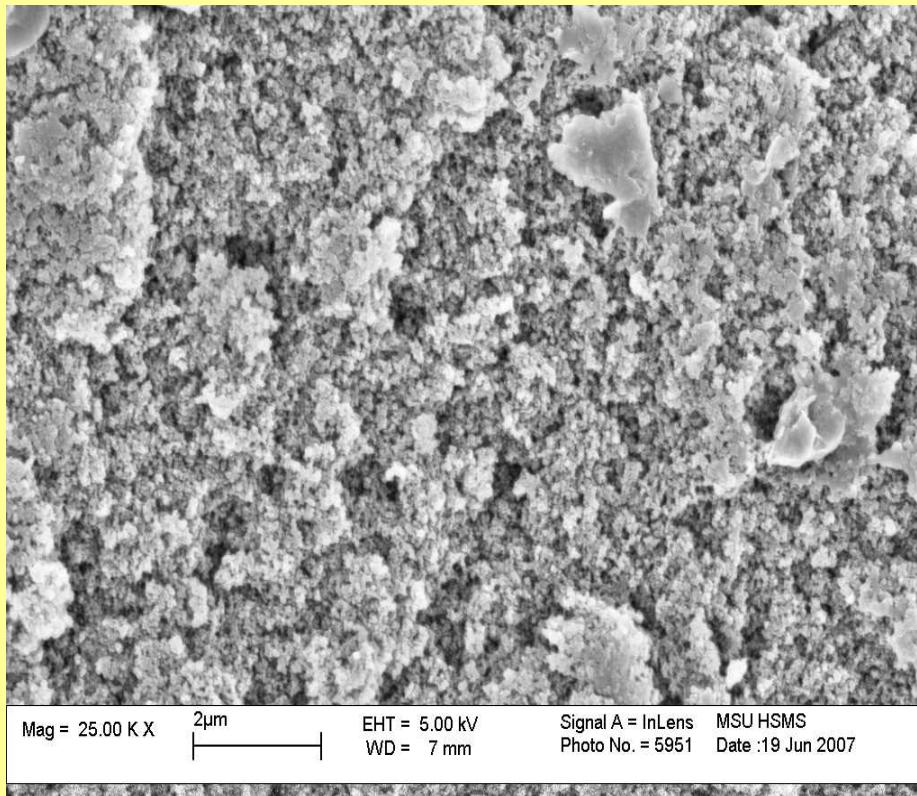


Integral pore size distribution of the macroporous St-DVB inert polymer and the corresponding aminophosphonic acid resin

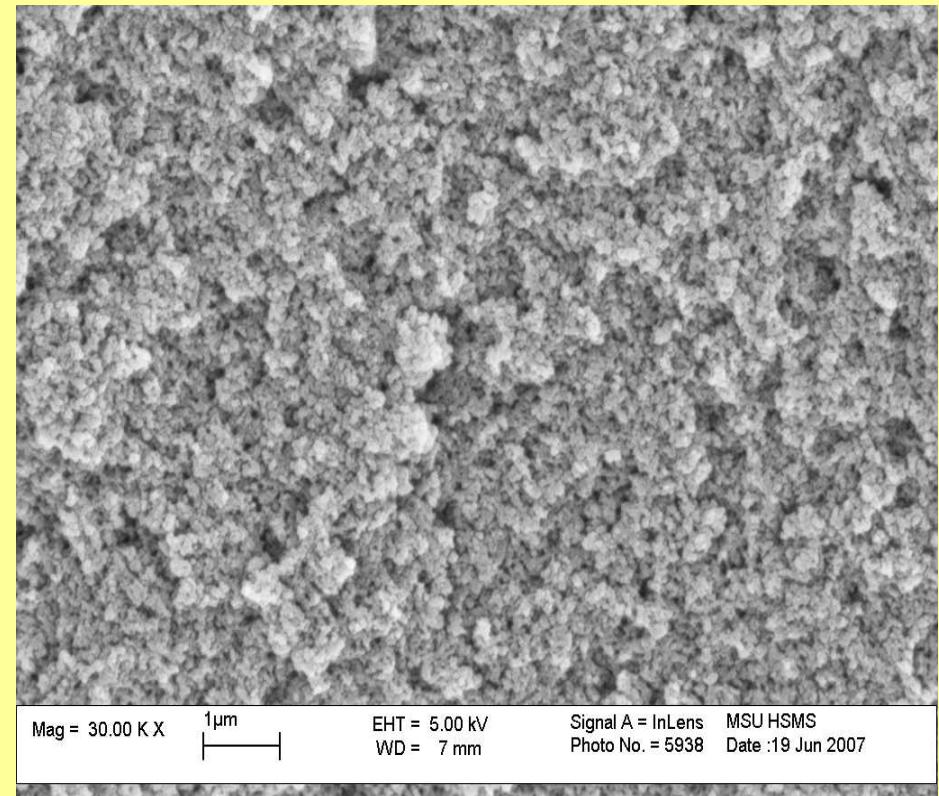


IEX 2008, 9 - 11 July, Cambridge, UK

Scanning Electron Micrographs of the Macroporous St-DVB Polymer before and after Sulfonation



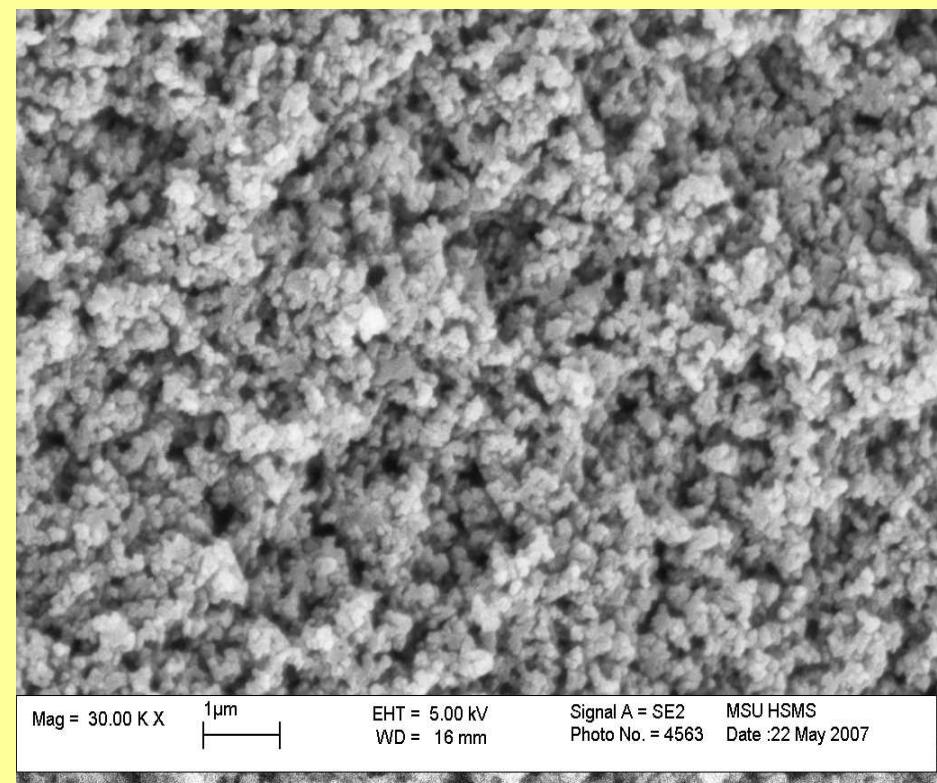
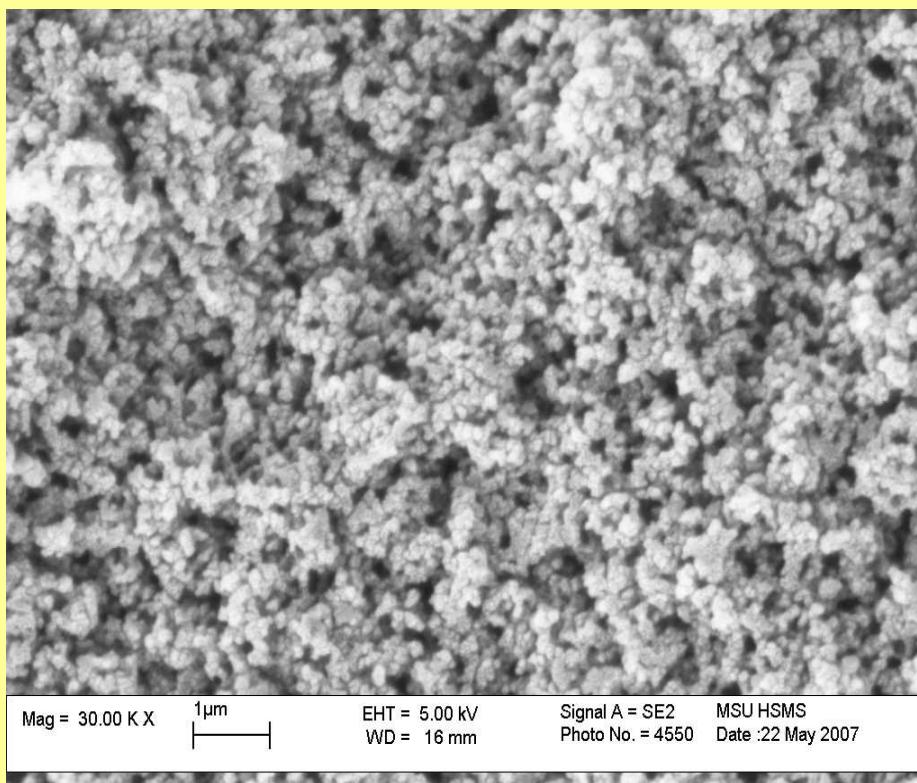
C 150 macroporous inert



C 150 macroporous sulfonated

IEX 2008, 9 - 11 July, Cambridge, UK

**Scanning Electron Micrographs of the Macronet St-DVB
Polymer before and after Sulfonation**

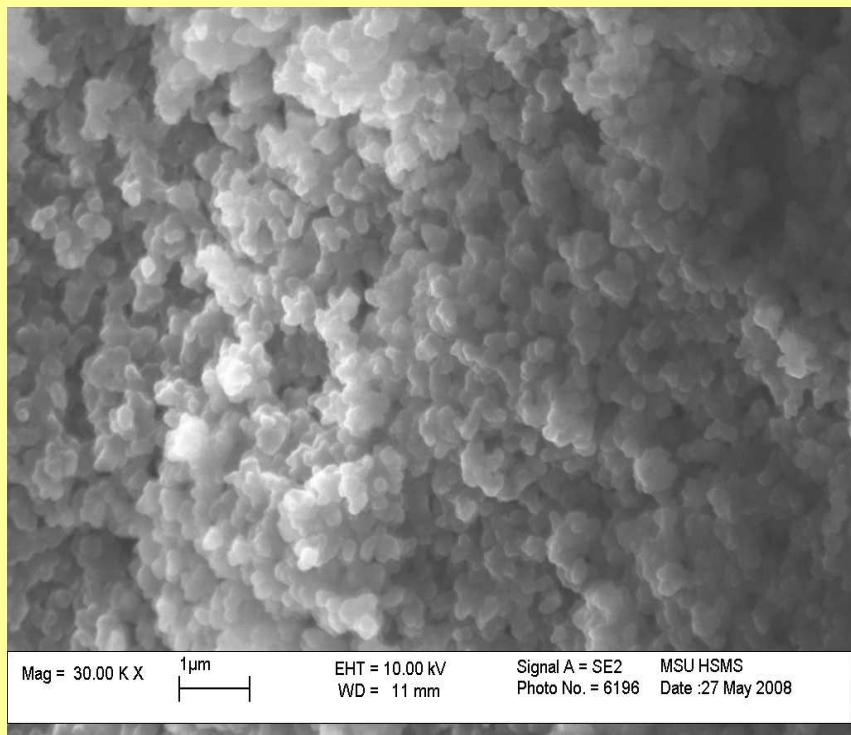


MN 200 inert macronet

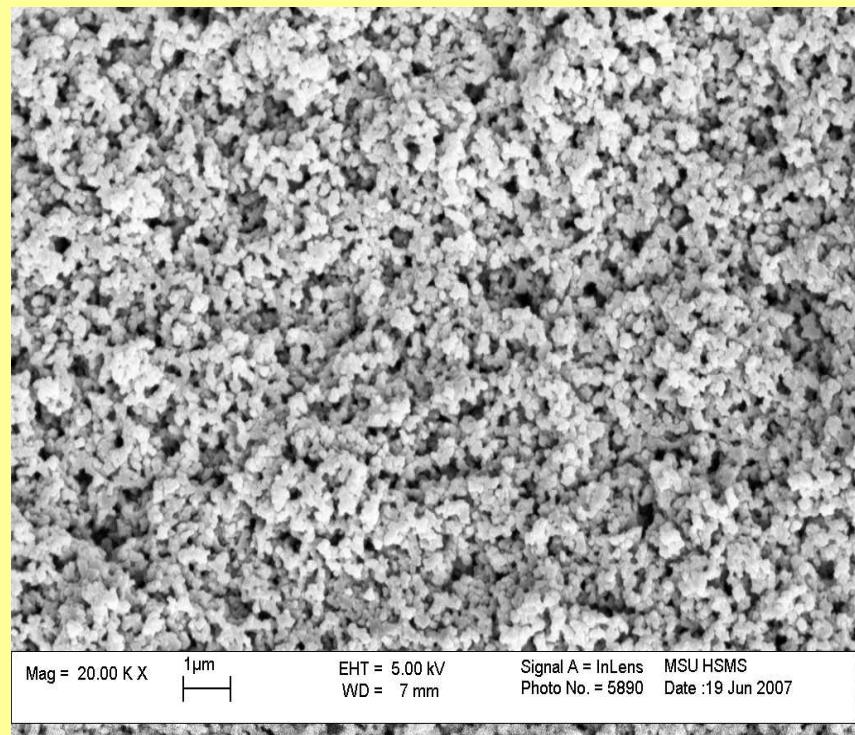
MN 500 sulfonated macronet

IEX 2008, 9 - 11 July, Cambridge, UK

Scanning Electron Micrographs of the Macroporous St-DVB Polymer before and after Chloromethylation followed by Amination and Grafting of Iminodiacetic Acid Groups

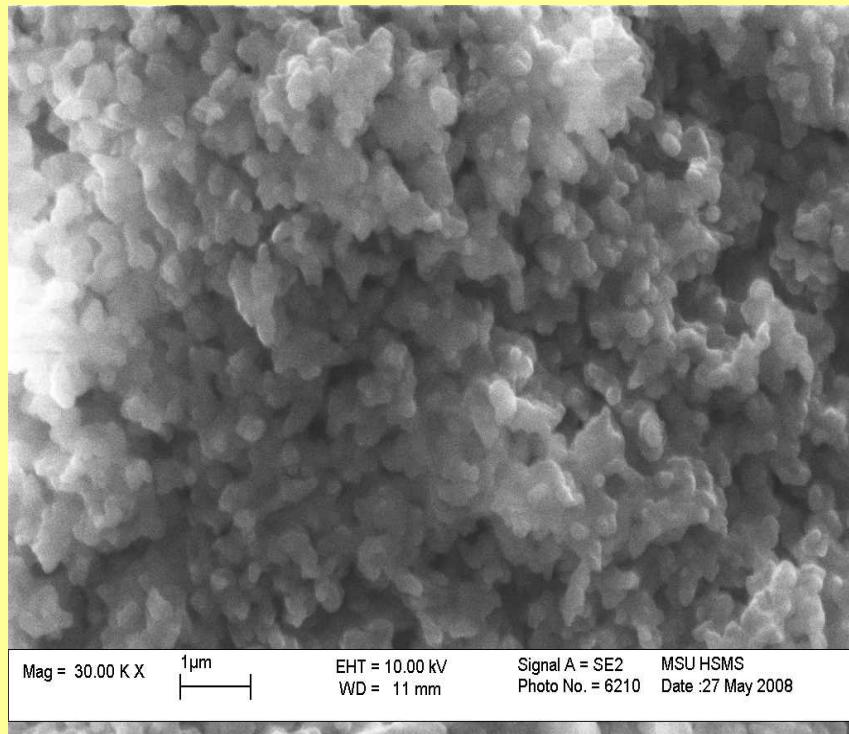


S 930 macroporous inert

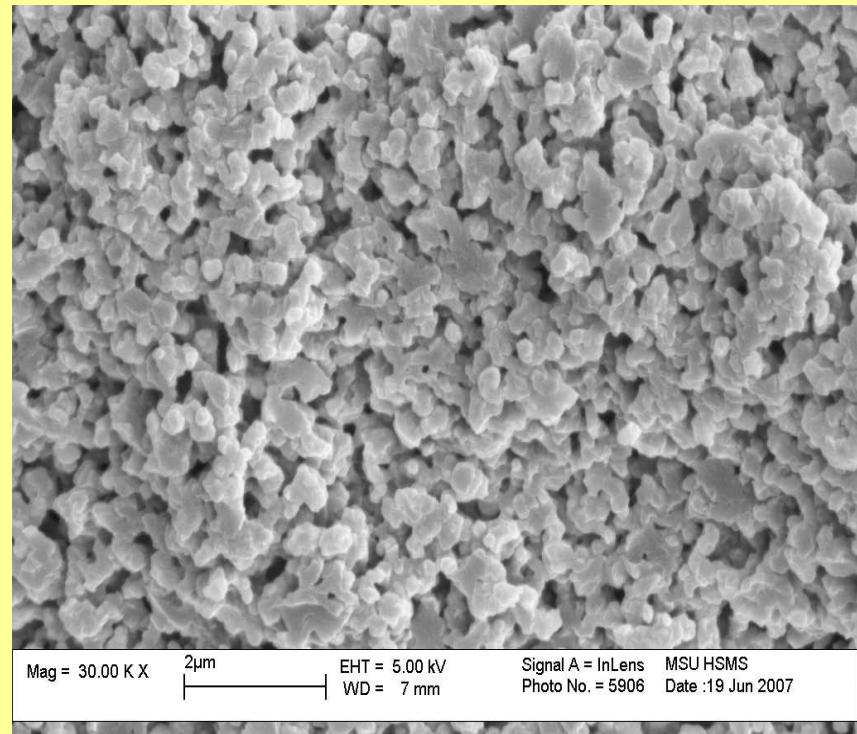


S 930 iminodiacetic chelating resin

Scanning Electron Micrographs of the Macroporous St-DVB Polymer after Chloromethylation followed by Amination and Grafting of Aminophosphonic Acid Groups



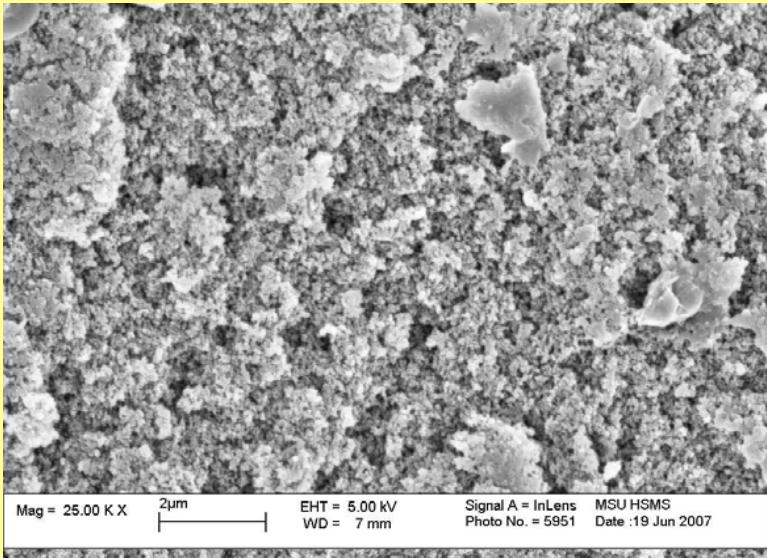
S 950 macroporous inert



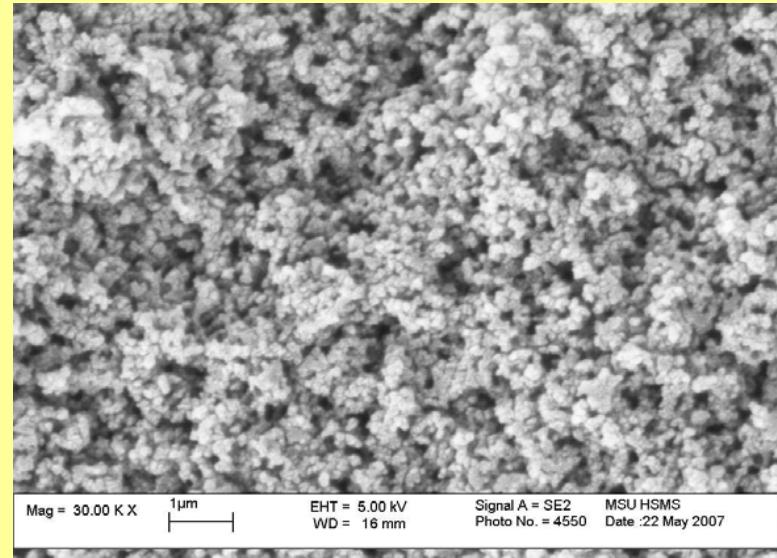
S 950 aminophosphonic chelating resin

IEX 2008, 9 - 11 July, Cambridge, UK

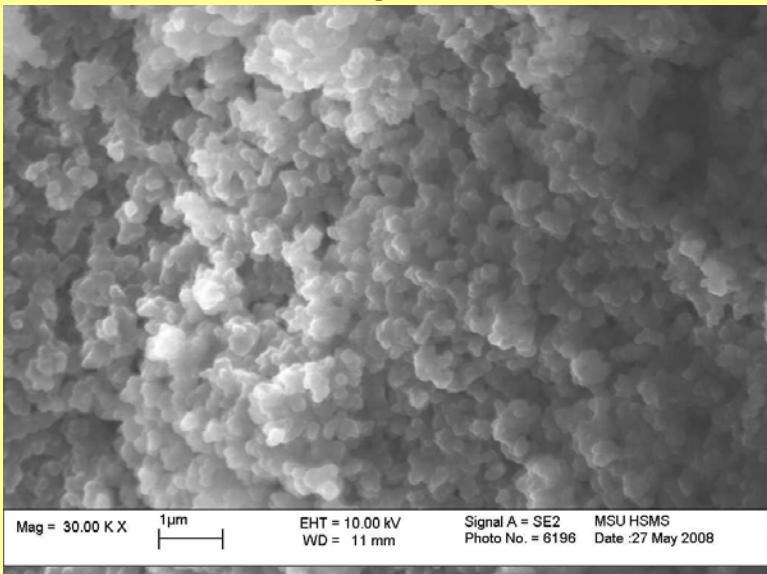
The comparison of the structure of the macroporous and macronet inert St-DVB



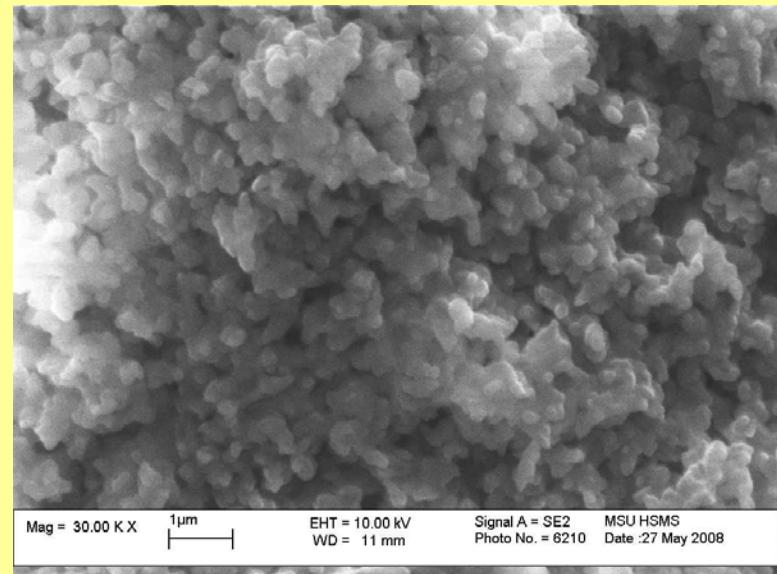
C 150 macroporous inert



MN 200 inert macronet



S 930 macroporous inert



S 950 macroporous inert

CONCLUDING REMARKS

- ❖ The sulfonation of macroporous and hypercrosslinked polystyrenic polymers induces similar effects on the textural properties of both resins: increase of the average pore diameter; decrease of the pore volume; narrowing of the pore size distribution; decrease of the specific surface area; decrease of the porosity and increase of the bulk and apparent densities
- ❖ During sulfonation in the strong acid media the bonds or van der Waals interactions are broken and new bonds and/or intermolecular interactions between microspheres are established and a different spatial arrangement of the microparticles is obtained
- ❖ Chloromethylation and amination with aminophosphonate of the corresponding macroporous inert polymer produces a larger modification of the skeleton than chloromethylation and amination with iminodiacetate of the corresponding macroporous polymer
- ❖ The sulfonation reaction produces drastic textural and structural modifications compared with the chloromethylation and grafting of chelating groups.

Acknowledgements

- The authors thank the Chemical Department of the Moscow State University for performing the Scanning Electron Micrographs
- This work has been supported by Purolite International Ltd. and by CNCSIS Romania under grant Code 75/2007.

Thank you for your attention!