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

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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

<table>
<thead>
<tr>
<th>Inert polymer</th>
<th>Matrix</th>
<th>Resin name</th>
<th>Functional group</th>
<th>Type of resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purolite PC 150</td>
<td>Styrene - DVB Macroporous</td>
<td>Purolite C 150</td>
<td>−SO₃H</td>
<td>Strong Acid Cation</td>
</tr>
<tr>
<td>Purolite MN 200</td>
<td>Styrene - DVB Hyper-crosslinked</td>
<td>Purolite MN 500</td>
<td>−SO₃H</td>
<td>Strong Acid Cation</td>
</tr>
<tr>
<td>Purolite PA 500</td>
<td>Styrene - DVB Macroporous</td>
<td>Purolite S 930</td>
<td>−N(CH₂COOH)₂</td>
<td>Chelating Iminodiacetic acid</td>
</tr>
<tr>
<td>Purolite PA 100</td>
<td>Styrene - DVB Macroporous</td>
<td>Purolite S 950</td>
<td>−CH₂NHCH₂PO(OH)₂</td>
<td>Chelating Aminophosphonic acid</td>
</tr>
</tbody>
</table>
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 (q_{bulk}) and apparent density (q_{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_{BET, \text{N}_2})

- The structure was analyzed by scanning electron microscopy.
## Results

### Total Cumulative Pore Volume / (cm$^3$ g$^{-1}$)

<table>
<thead>
<tr>
<th>Polymer/Size fraction (μm)</th>
<th>PC 150 inert</th>
<th>C 150 -SO$_3$H</th>
<th>MN 200 inert</th>
<th>MN 500 -SO$_3$H</th>
<th>S930 inert</th>
<th>S930 Iminodiacetic</th>
<th>S950 inert</th>
<th>S 950 Aminophosphonic</th>
</tr>
</thead>
<tbody>
<tr>
<td>[-425+300]</td>
<td>0.49</td>
<td>0.23</td>
<td>1.1</td>
<td>0.65</td>
<td>0.69</td>
<td>0.66</td>
<td>0.49</td>
<td>0.28</td>
</tr>
<tr>
<td>[-600+425]</td>
<td>0.49</td>
<td>0.26</td>
<td>1.2</td>
<td>0.64</td>
<td>0.65</td>
<td>0.54</td>
<td>0.59</td>
<td>0.29</td>
</tr>
<tr>
<td>[-710+600]</td>
<td>0.52</td>
<td>0.22</td>
<td>1.1</td>
<td>0.68</td>
<td>0.67</td>
<td>0.58</td>
<td>0.46</td>
<td>0.32</td>
</tr>
<tr>
<td>[-900+710]</td>
<td>0.47</td>
<td>0.22</td>
<td>1.3</td>
<td>0.60</td>
<td>0.64</td>
<td>0.54</td>
<td>0.43</td>
<td>0.34</td>
</tr>
</tbody>
</table>
## Average pore diameter / Most frequent pore diameter (nm)

<table>
<thead>
<tr>
<th>Polymer/Size fraction (μm)</th>
<th>PC 150 inert</th>
<th>C 150 -SO$_3$H</th>
<th>MN 200 inert</th>
<th>MN 500 -SO$_3$H</th>
<th>S930 inert</th>
<th>S930 Iminodiacetic</th>
<th>S950 inert</th>
<th>S 950 Aminophosphonic</th>
</tr>
</thead>
<tbody>
<tr>
<td>[-600+425]</td>
<td>26/27</td>
<td>34/34</td>
<td>116/127</td>
<td>150/155</td>
<td>138/142</td>
<td>119/160</td>
<td>155/78</td>
<td>131/118</td>
</tr>
<tr>
<td>[-710+600]</td>
<td>25/29</td>
<td>34/34</td>
<td>121/124</td>
<td>143/148</td>
<td>136/141</td>
<td>147/159</td>
<td>131/97</td>
<td>194/193</td>
</tr>
</tbody>
</table>
### Specific surface area $S_{Hg}$ (m² g⁻¹) / Specific surface area $S_{BET, N_2}$ (m² g⁻¹)

<table>
<thead>
<tr>
<th>Polymer/Size fraction (µm)</th>
<th>PC 150 inert</th>
<th>C 150 -SO₃H</th>
<th>MN 200 inert</th>
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<th>S930 inert</th>
<th>S930 Iminodiacetic</th>
<th>S950 inert</th>
<th>S 950 Aminophosphonic</th>
</tr>
</thead>
<tbody>
<tr>
<td>[-425+300]</td>
<td>87</td>
<td>29</td>
<td>64/1043</td>
<td>26/297</td>
<td>30</td>
<td>22</td>
<td>27</td>
<td>10</td>
</tr>
<tr>
<td>[-600+425]</td>
<td>92</td>
<td>37</td>
<td>77/1047</td>
<td>26/313</td>
<td>29</td>
<td>26</td>
<td>25</td>
<td>14</td>
</tr>
<tr>
<td>[-710+600]</td>
<td>106</td>
<td>28</td>
<td>61/1023</td>
<td>27/356</td>
<td>29</td>
<td>25</td>
<td>23</td>
<td>11</td>
</tr>
<tr>
<td>[-900+710]</td>
<td>85</td>
<td>29</td>
<td>85/1006</td>
<td>20/360</td>
<td>29</td>
<td>23</td>
<td>23</td>
<td>14</td>
</tr>
</tbody>
</table>
## Porosity (%)

<table>
<thead>
<tr>
<th>Polymer/Size fraction (μm)</th>
<th>PC 150 inert</th>
<th>C 150 -SO₃H</th>
<th>MN 200 inert</th>
<th>MN 500 -SO₃H</th>
<th>S930 inert</th>
<th>S930 Iminodiacetic</th>
<th>S950 inert</th>
<th>S 950 Aminophosphonic</th>
</tr>
</thead>
<tbody>
<tr>
<td>[-425+300]</td>
<td>36</td>
<td>26</td>
<td>56</td>
<td>51</td>
<td>43</td>
<td>45</td>
<td>37</td>
<td>35</td>
</tr>
<tr>
<td>[-600+425]</td>
<td>36</td>
<td>36</td>
<td>52</td>
<td>48</td>
<td>41</td>
<td>42</td>
<td>44</td>
<td>-</td>
</tr>
<tr>
<td>[-710+600]</td>
<td>37</td>
<td>28</td>
<td>55</td>
<td>49</td>
<td>42</td>
<td>42</td>
<td>35</td>
<td>25</td>
</tr>
<tr>
<td>[-900+710]</td>
<td>32</td>
<td>30</td>
<td>59</td>
<td>49</td>
<td>41</td>
<td>44</td>
<td>27</td>
<td>36</td>
</tr>
</tbody>
</table>
## Bulk Density / Apparent Density (g cm\(^{-3}\) )

<table>
<thead>
<tr>
<th>Polymer/ Size fraction (μm)</th>
<th>PC 150 inert</th>
<th>C 150 -SO(_3)H</th>
<th>MN 200 inert</th>
<th>MN 500 -SO(_3)H</th>
<th>S930 inert</th>
<th>S930 Iminodiacetic</th>
<th>S950 inert</th>
<th>S 950 Aminophosphonic</th>
</tr>
</thead>
<tbody>
<tr>
<td>[-425+300]</td>
<td>0.744/1.17</td>
<td>1.12/1.52</td>
<td>0.504/1.15</td>
<td>0.786/1.60</td>
<td>0.628/1.11</td>
<td>0.680/1.23</td>
<td>0.758/1.20</td>
<td>1.22/1.87</td>
</tr>
<tr>
<td>[-600+425]</td>
<td>0.738/1.16</td>
<td>1.36/2.12</td>
<td>0.442/0.918</td>
<td>0.754/1.46</td>
<td>0.635/1.08</td>
<td>0.773/1.33</td>
<td>0.745/1.32</td>
<td>-</td>
</tr>
<tr>
<td>[-710+600]</td>
<td>0.713/1.13</td>
<td>1.26/1.74</td>
<td>0.522/1.17</td>
<td>0.730/1.44</td>
<td>0.621/1.07</td>
<td>0.726/1.26</td>
<td>0.746/1.14</td>
<td>0.773/1.03</td>
</tr>
<tr>
<td>[-900+710]</td>
<td>0.684/1.01</td>
<td>1.36/1.94</td>
<td>0.463/1.13</td>
<td>0.811/1.59</td>
<td>0.635/1.07</td>
<td>0.819/1.47</td>
<td>0.631/0.869</td>
<td>1.07/1.68</td>
</tr>
</tbody>
</table>
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
Scanning Electron Micrographs of the Macroporous St-DVB Polymer before and after Sulfonation

C 150 macroporous inert

C 150 macroporous sulfonated
Scanning Electron Micrographs of the Macronet St-DVB Polymer before and after Sulfonation

MN 200 inert macronet

MN 500 sulfonated macronet
Scanning Electron Micrographs of the Macroporous St-DVB Polymer before and after Chloromethylation followed by Amination and Grafting of Iminodiacetic Acid Groups
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
The comparison of the structure of the macroporous and macronet inert St-DVB
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!