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## High porosity scintillating polymer resins for ionizing radiation sensor applications

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### ABSTRACT

Due to their high sorption capacity, nanoporous polymer resins can be used as an active material for ionizing radiation sensor applications. This contribution reports on the molecular design and synthesis of scintillating styrene-based resins with controlled bead size, porosity and surface functionality. In a working sensor device, the adsorption of radioactive analyte species on the resin can be monitored via incorporation of specially designed fluor molecules to convert ionizing radiation (specifically,  $\alpha$ -particles and  $\beta$ -particles) into light. Porous polystyrene (PS) and poly(4-methylstyrene) resins of various compositions and structure were synthesized via suspension polymerization technique. 1,4-Bis(4-methyl-5-phenyl-oxazol-2-yl)benzene (DM-POPOP) was incorporated into the resin by adding it to the dispersed phase. Polymerization conditions were adjusted to achieve a desirable range of polymer beads size and porosity (pore size distribution, specific surface area). The porosity of the resin beads could be controlled by the type and concentration of the porogen, as well as by the degree of PS matrix crosslinking with divinylbenzene. Three different porogens (toluene, n-heptane or span-80 nonionic surfactant) were used to achieve a broad variation of the nanopore size distribution within the same matrix. The structure, porosity and optical fluorescence properties of the synthesized PS beads were analyzed with nitrogen adsorption porosimetry, optical/UV confocal, scanning electron and helium ion microscopy, and fluorescence spectroscopy. A broad variation of the pore size distribution, specific surface area and optical properties within the same system were demonstrated. Findings from this study can be used for the development of more efficient environmental sensors to monitor contamination of ground water with trace amounts of radioactive materials.

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### 1. Introduction

Porous polymer resins can be fabricated by a diverse range of techniques and have become important media in analytical chemistry and modern industry [1–5]. Applications of nanoporous polymers are numerous and include chemical and biological separation media and membranes, polymer electrolytes in energy storage systems, templates for nanomaterials synthesis and sensing technologies. In the latter case, a porous polymer membrane or porous resin beads of desirable size and high specific surface area present functional “recognition groups” on the surface that enable selective binding of target molecules or atoms. The adsorption of the analyte species on a resin can be monitored either directly by detection of the emitted light intensity (if the analyte molecules

have fluorescence centers) or indirectly via inclusion of specially designed fluor molecules into the resin to convert radiation (X-rays, gamma-rays, electrons, alpha-particles or neutrons) into light. Incorporation of the fluor in the polymer structure can be accomplished either during resin synthesis (mixing) or as a post treatment (diffusion). Recent reviews demonstrated several successful approaches for synthesis of porous polymer particles [6–10]. The traditional approaches use emulsion, suspension or dispersion polymerization protocols. Several recently developed, novel synthetic routes include template self-assembly or membrane polymerization protocols that allow better control of the bead size distribution and morphology.

Porous polymer resins can be classified according to their pore size as macroporous (average pore size above 50 nm), mesoporous (pore sizes in the range of 2–50 nm), and microporous (average pore size below 2 nm). Nowadays, increased research interest lies in nanoporous materials having pore sizes less than 50 nm. Despite a large number of published results, there is a lack of comparative

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studies considering performance and advantages and drawbacks of polymer resins fabricated via different approaches. In this contribution, we compare the morphological features, porosity and optical properties of polystyrene based polymer resins prepared by suspension polymerization as a function of porogen choice.

## 2. Experimental section

### 2.1. Materials

Styrene (St, 99+%, with 10–15 ppm of 4-TBC inhibitor), 4-methyl styrene (96%), and divinylbenzene (DVB, technical grade 80% mixture of isomers, with 1000 ppm of 4-TBC inhibitor), all from Sigma–Aldrich, were used as monomers for polymerization. Benzoyl peroxide (BPO) (reagent grade >98%, Sigma–Aldrich) was used as an initiator. N-heptane (HPLC grade, Alfa Aesar), toluene (HPLC grade, Fisher Scientific), or sorbitan monooleate nonionic surfactant (Span 80, Sigma–Aldrich) were used as porogen additions to the monomer (oil) phase. 1,4-Bis(4-methyl-5-phenyl-oxazol-2-yl) benzene (DM-POPOP, 98% scintillation grade, Sigma–Aldrich) was the fluor.

Poly(vinyl alcohol) (PVA, average MW 65–124 kDa, degree of hydrolysis 87–89%, Sigma–Aldrich) was used as a polymer surfactant and emulsion stabilizer. NaCl (reagent grade, Fisher Scientific) was used to adjust the ionic strength of the aqueous phase. Hydroxypropyl methylcellulose (HPMC, Methocel, Dow Chemical) was used as a seeding (nucleation) agent for dispersing of the monomer phase in water. Hydroquinone (HQ) (analytical grade, Sigma–Aldrich) was used in some cases as an inhibitor to prevent secondary nucleation in the aqueous phase.

Methanol and acetone (HPLC grade, Fisher Scientific) were used to precipitate and wash the resin particles. All these reagents were used as received. Water was distilled and then deionized using ion-exchange resins (DI water).

### 2.2. Suspension polymerization

Table 1 presents a standard recipe used for suspension polymerization of porous PS resin. The mixture of monomer, cross-linking agent (DVB), porogen, DM-POPOP, and BPO was used as the dispersed phase (monomer phase or oil phase). PVA, NaCl, and HPMC were dissolved in hot water (64 °C), which constituted the continuous phase (aqueous phase). The aqueous phase was then cooled below 40 °C. The components of the oil phase were mixed separately at room temperature and were aged for 15–60 min before adding to the aqueous phase. An emulsion was prepared by dispersing the oil phase into the aqueous phase in a four-neck glass flask equipped with a BDC250 Caframo Petite Digital stirrer

**Table 1**  
Typical recipe for porous microspheres preparation.

Ingredients	Function	Amount
<i>Continuous phase (water phase)</i>		
Poly(vinyl alcohol)	surfactant	300 mg
Hydroxypropyl methylcellulose	co-surfactant, seeding	300 mg
Sodium chloride	ionic strength adjustment	2.5 g
Water	reaction medium	300 mL
<i>Dispersed phase (oil phase)</i>		
Styrene	monomer	9 ml
Divinyl benzene	cross-linker	3 ml
Toluene <sup>a</sup>	porogen	12 ml
DM-POPOP	fluor	60 mg (0.5%)
Benzoyl peroxide	polymerization initiator	300 mg

<sup>a</sup> Toluene, n-heptane or span-80. 1:1 (v/v) of the porogen to monomer was used for toluene and n-heptane; 1:3 (v/v) of Span-80 to monomer was used.

operated with an anchor-type radial flow impeller (1/2" × 1/2" wide blade), a condenser, and a nitrogen inlet nozzle. The reactor was placed in a water bath, which resided on a programmable heater-stirrer apparatus for better temperature control. The setup allowed simultaneous heating of the reaction mixture to a desirable temperature and its agitation with a magnetic stirrer on the bottom, mechanical agitator on the top, or both. The reactor was purged with nitrogen for 30 min prior to mixing the oil phase with the aqueous phase and an additional 2 h during polymerization. The temperature of the aqueous phase was raised to between 58 and 70 °C before adding the oil phase to create the suspension. The suspension temperature is defined as the temperature at which the phases were mixed. After forming the suspension, the temperature was raised to the reaction temperature of 75 °C under continuous stirring at 200–600 rpm. Particularly, to achieve the targeting bead size of 100–400 μm higher stirring speed (400–600 rpm) in combination with lower suspension temperature (58 °C) was typically applied for toluene and n-heptane porogens. For span-80 porogen the same bead size was reached at higher temperatures (>64 °C) and lower stirring speeds (200–300 rpm).

The polymerization reaction lasted 10–12 h. The resulting polymer particles (beads) were filtered with 25 μm pore size Whatman filter paper and washed by water and methanol at least three times (with 5 times volume excess) to extract the porogen and unreacted monomers. For porosity measurements the particles were washed further by extraction with acetone for 24 h. This step was omitted for leaching experiments as it was expected to influence the result of the leaching test. The particles were finally dried first in air at 40–50 °C for 1–2 h and then in vacuum at room temperature for at least 24 h. The yield of particles was calculated by the weight of dried polymer microspheres.

### 2.3. Characterization

Nitrogen adsorption and desorption isotherms were performed at 77 K with a Micromeritics ASAP 2020 volumetric adsorption system. Before the experiments, the samples were outgassed at 80 °C (i.e., below the glass transition of polystyrene) to constant vacuum (10<sup>-4</sup> kPa). Brunauer-Emmett-Teller (BET) surface area, Barrett-Joyner-Halenda (BJH) pore size distributions, and the total pore volume,  $V_t$ , were computed using the Micromeritics software package associated with the instrument [11,12]. The BET surface area was deduced from the isotherm analysis in the relative pressure range of 0.04–0.20. The total pore volume was calculated from the amount adsorbed at a relative pressure of 0.99. In the case of the BJH pore distributions, the data were derived from the adsorption branch of each isotherm.

Scanning electron microscopy (SEM) imaging of polymer beads was performed with a Hitachi S4800 High Resolution Scanning Electron Microscope using 25 kV accelerating voltage. To avoid surface charging, a 50 nm platinum layer was sputtered on the samples before imaging.

An Orion TM helium ion microscope (HIM) was applied to visualize pores on the surface of the beads without any additional coatings [13]. During high resolution imaging the surface was exposed to a flux of electrons (using a low energy electron flood gun) to compensate charging the sample under the helium ion beam. Also, to avoid radiation damage of the surface during nanometer resolution imaging, the ion beam current was reduced to 0.2–0.5 pA.

Optical properties of the beads were studied with a Celestron LCD II digital optical microscope and a double monochromator Photon Technology International Inc. Quanta Master 60 fluorescence system applied in the range of 250–600 nm. For fluorescence measurements polymer bead samples were attached as a

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