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Extractive-scintillating resin produced by radiation polymerization

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Abstract

The characterization of a resin material is presented, which contains selective complexing and scintillating molecules in chemically bound form. The resin material is produced via radiation polymerization of the solution of 2-(4-allyloxy-phenyl)-5-phenyl oxazole, 5-(allyloxy-phenyl)-2-[4-(5-phenyl-oxazole-2-yl)-phenyl] oxazole, diethylene glycol dimethacrylate (DEGMA), styrene and the allyl derivative of a 18C6 crown ether-dicarboxylic acid complexing agent. The product is a macroporous polymer matrix, which shows both excellent scintillation properties and ion binding capacity for radioanalytical purposes.

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Keywords: Radiation polymerization; Scintillation; Crown ether; Resin; Strontium

1. Introduction

The simultaneous use of scintillating and selective complexing agents for sensor purposes has already been attempted, where the sensor material is a so-called extractive-scintillating resin (Duffey et al., 2001). A typical resin is made of polystyrene or acrylic polymer impregnated with the selective agent (usually crown ethers) and the scintillating molecules (PPO, DM-POPOP, etc.). In this way, the combination of extraction chromatography and scintillation detection is achieved, thus providing an opportunity for the automatic on-line monitoring of certain radioactive isotopes in aqueous solutions.

The disadvantage of such combined resins is that—due to the physical adsorption of the complexing and scintillating molecules—their regeneration is difficult, hindering thus their multiple usage. Therefore in an automated analysis system, the so-called sequential injection renewable separation column technique (SI-RSC) has been proposed (Egorov et al., 1999). This successful approach could be more economical by using chemically stable resin material, which could be regenerated either in

on-line or off-line mode, thus reducing the cost of analysis and the amount of hazardous waste.

In one of our recent papers a possible synthesis of such a chemically stable resin material has been demonstrated (Vincze et al., 2007). It has been shown that a chemically stable macroporous scintillating polymer resin can be synthesized by gamma-ray-induced precipitation polymerization technique from the solution of 2-(4-allyloxy-phenyl)-5-phenyl oxazole, 5-(allyloxy-phenyl)-2-[4-(5-phenyl-oxazole-2-yl)-phenyl] oxazole, diethylene glycol dimethacrylate (DEGMA), styrene and the allyl derivative of a 18C6 crown ether-dicarboxylic acid complexing agent. The fluorescent property and ion binding capacity of that strontium binding resin seemed promising for radioanalytical purposes.

In this paper, the scintillation properties of such a new type of resins are presented as a function of composition, which enables the optimization of the final resin material as far as sensitivity and scintillation intensity is concerned.

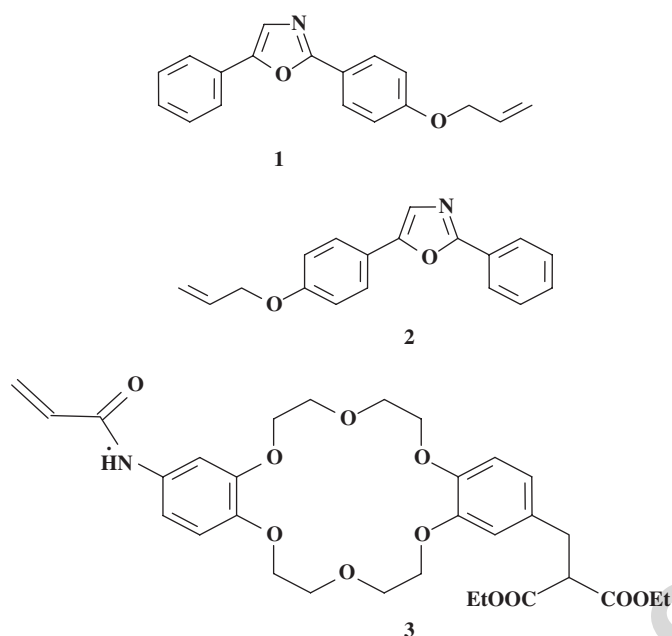
2. Experimental

The detailed synthesis of these molecules, the fluorescent and adsorption properties of the resin are published elsewhere (Vincze et al., 2007). The key molecules of a

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strontium selective scintillating resin are shown in Scheme 1. Ethyl-acetate and chloroform solutions with co-monomer compositions that was given in Table 1 were prepared, degassed with nitrogen and irradiated with a ^{60}Co gamma source at room temperature without stirring, with a dose rate of 15 kGy/h and a dose of 30–100 kGy. The obtained resin was washed several times with ethyl-acetate and dried at room temperature.



Scheme 1. Key molecules for the synthesis of strontium selective scintillating resin: **1**: 2-(4-allyloxyphenyl)-5-phenyl oxazole (PPOA); **2**: 5-(4-allyloxyphenyl)-5-phenyl oxazole (APPO); **3**: 4'-acrylamido-5''-(2,2-bisethoxycarbonyl-ethyl) dibenzo-18-crown-6 (CROWN).

Table 1
Composition of the solutions irradiated and the theoretical composition of the synthesized resins at 100% polymerization yield

Sample code	DEGDMA (%)	STYRENE (%)	PPOA (%)	CROWN (%)
<i>Solution composition</i>				
S1	27.5	0.0	1.1	2.3
S2	26.1	1.0	1.1	2.2
S3	24.5	2.4	1.1	2.2
S4	22.4	4.6	1.1	2.2
S5	18.3	7.8	1.1	2.3
S6	22.7	5.1	0.5	2.2
S7	23.0	4.1	1.6	2.2
S8	22.4	5.6	2.3	2.2
<i>Resin composition</i>				
S1	89.1	0.0	3.6	7.3
S2	85.9	3.5	3.5	7.2
S3	80.9	8.0	3.7	7.4
S4	73.8	15.3	3.6	7.2
S5	62.0	26.5	3.8	7.6
S6	74.3	16.7	1.8	7.2
S7	74.4	13.2	5.2	7.1
S8	69.1	17.3	7.0	6.7

The same amount of resin matrices with different compositions were equilibrated with the aqueous solution of $^{86}\text{RbCl}$ (500 Bq, Amersham Biosciences) in an LSC vial and kept in 10 °C for 2 days. The scintillation intensity of the samples was measured in an LSC spectrometer (PACKARD TRI-CARB 1500) and compared to that of a standard LSC cocktail (ULTIMA GOLD AB). The scintillation sensitivity of the optimized resin was also studied by the variation of the radioactivity of the $^{86}\text{RbCl}$ salt in the system and compared with that of a standard LSC cocktail.

3. Results and discussion

It has been reported that if the DEGDMA monomer in a good solvent is irradiated, below about 20 w/w% monomer concentration monodisperse microspheres are formed (Yoshida and Kaetsu, 1987), between 20 and 40 w/w% monomer concentration monolith formation can be observed (Grasselli et al., 2001; Vincze et al., 2007), and further increase in monomer concentration leads to the formation of a glassy polymer gel. When styrene, a monomer needed for the improvement of the energy transfer from the nuclear radiation to the fluorescent molecules in the matrix (a well-known phenomenon in the field of plastic scintillation detectors; L'Annunziata, 2003) was added to DEGDMA, even at monomer concentrations below 20 w/w%, with increasing styrene concentration microsphere formation turned to resin formation, as illustrated in Fig. 1A–D. For this phenomenon both the aromatic character and the monofunctionality of styrene play a role. When only a DEGDMA solution is irradiated, the microsphere formation is divided into two processes (Naka and Yamamoto, 1992): expansion of the microsphere by propagation reaction (mostly a reaction of the first vinyl group of the DEGDMA molecule) and shrinking by the crosslinking reaction (mostly a reaction of the second vinyl group). The growth of the particle is controlled by the competition of these reactions. When a monofunctional monomer is added, the probability of crosslinking that depends on the ratio of di-vinyl to monovinyl monomer, will be reduced. Since styrene is a monofunctional monomer, the increasing ratio of styrene to DEGDMA (while keeping the overall monomer concentration constant) in the solution will favor the propagation reaction over the crosslinking, and a resin will form. When the overall monomer concentration was higher than 20 w/w%, a resin was obtained even at lowest DEGDMA/styrene ratio. The resin was porous at lower styrene concentrations, and therefore suitable for further use (Fig. 1E and F). The various compositions, both of the starting solutions and the obtained resins, are summarized in Table 1. Addition of PPOA and the CROWN to the solution did neither affect the resin formation nor its porosity.

The usefulness of the resin for scintillation measurements was investigated by measuring the scintillation intensity

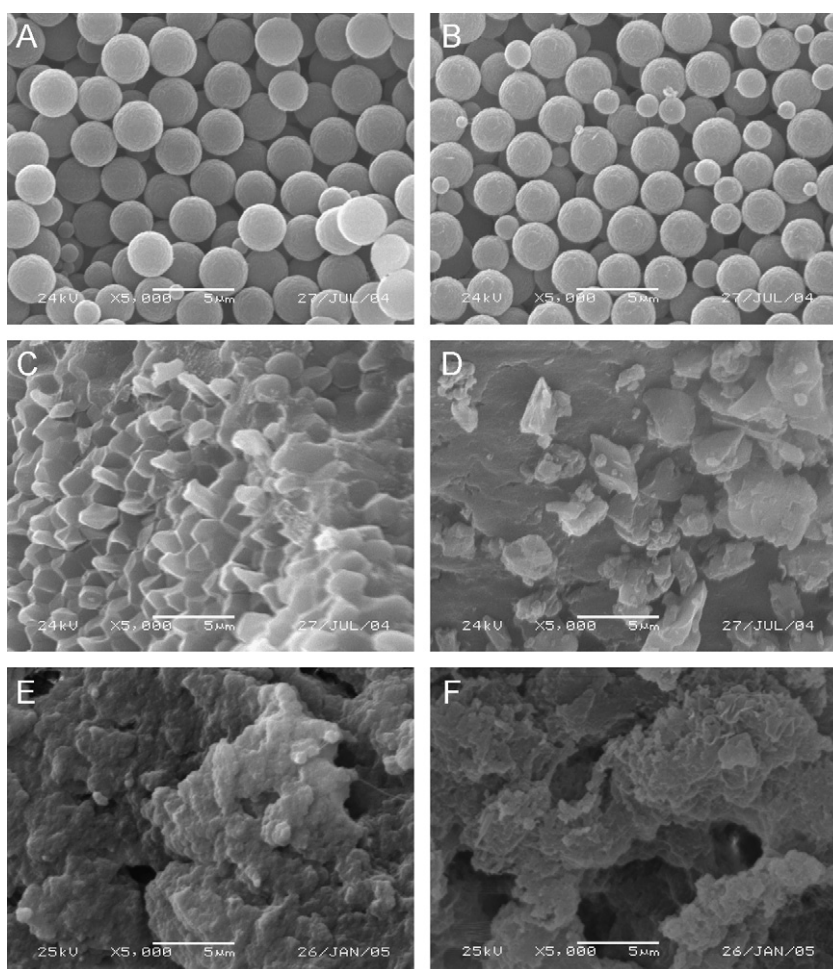


Fig. 1. SEM photographs of the DEGMA/STYRENE co-polymers of various compositions synthesized under identical conditions (irradiation with 50 kGy dose at room temperature): 10 w/w% monomer concentration, DEGMA:STYRENE = 1:0 (A); 10 w/w% monomer concentration, DEGMA:STYRENE = 0.87:0.13 (B); 10 w/w% monomer concentration, DEGMA:STYRENE = 0.73:0.27 (C); 10 w/w% monomer concentration, DEGMA:STYRENE = 0.51:0.49 (D); 25 w/w% monomer concentration, DEGMA:STYRENE:PPOA = 0.80:0.16:0.04 (E); 25 w/w% monomer concentration, DEGMA:STYRENE:PPOA:CROWN = 0.68:0.18:0.04:0.1 (F).

both as a function of the styrene and the PPOA content in the resin. These results are shown in Figs. 2 and 3, respectively. It is seen that the scintillation intensity has a maximum with the styrene content of the resin at the value of 8 m/m%. From Fig. 3, we can observe that the scintillation intensity as a function of the scintillator content is reaching a plateau already at 2 m/m% and remains almost the same up to 8 m/m%.

From the point of view of practical application, the sensitivity of the resin matrix to nuclear radiation is a critical characteristic. In Fig. 4 the scintillation intensity as a function of the exciting radioactivity is plotted for sample 3 and compared with the standard liquid scintillation cocktail (ULTIMA GOLD AB). It is clearly seen that the sensitivity of our resin matrix to detect radioactivity is just as good as that of the standard liquid scintillation cocktail generally used in liquid scintillation spectroscopy for the detection of alpha/beta emitting nuclides. It should be noted however, that although the efficiencies corresponding to the resin matrix and that of the liquid scintillation

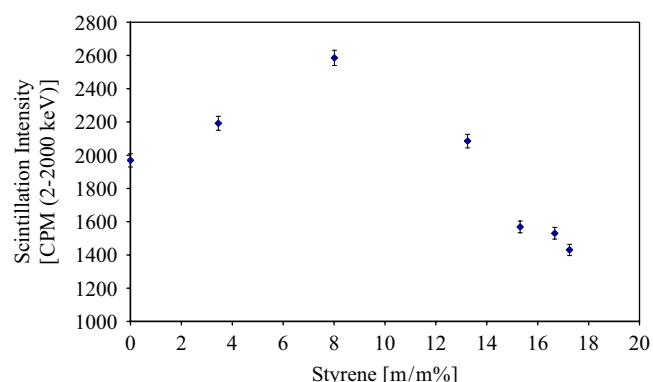


Fig. 2. Dependence of the scintillation intensity on the styrene content of the samples are presented in Table 1. The samples were mixed with 5 ml solution of $^{86}\text{RbCl}$, containing 500 Bq activity.

cocktail are almost identical, there is a significant difference in the SIS value of the different spectra, that of the liquid scintillation cocktail being one order of magnitude higher

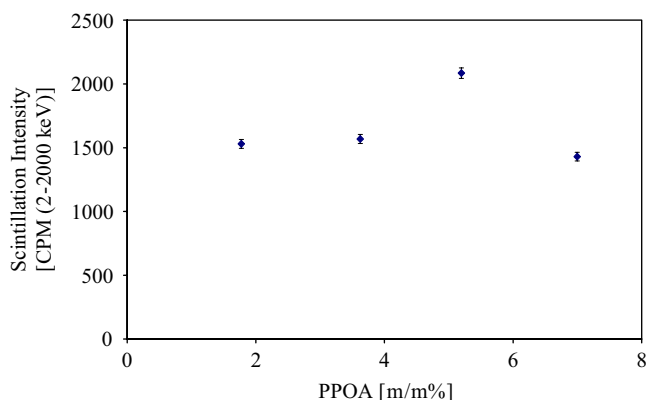


Fig. 3. Dependence of the scintillation intensity on the PPOA content of the samples with practically identical styrene composition (S4 and S6–S8) presented in Table 1 with 5 ml solution of $^{86}\text{RbCl}$, containing 500 Bq activity.

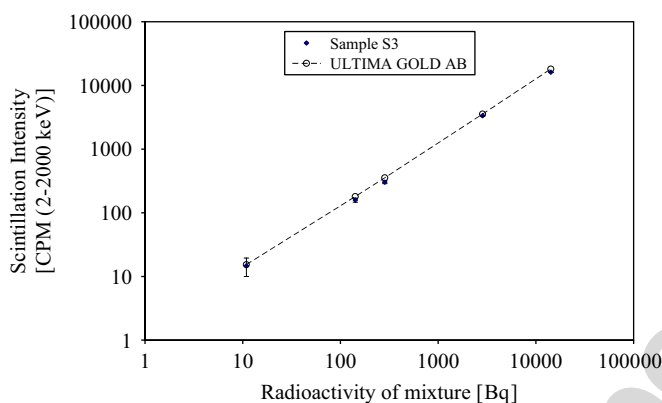


Fig. 4. Dependence of the scintillation intensity on the activity of the $^{86}\text{RbCl}$ solution. Values for a standard liquid scintillation cocktail are also shown for comparison.

(~200 and ~10, respectively). In standard liquid scintillation spectrometry, the value of the spectral index of the sample (SIS) parameter, which uses the sample isotope spectrum to monitor the quench of the solution, decreases as quench increases, reflecting the shift of the spectrum to lower energies. In the case of the resin material most of the intensities measured is in the low-energy part of the spectrum (below 100 keV), most likely due to the heterogeneity of the sample. Because of the selective complexing characteristic of our resin material, not the actual spectrum, but the scintillation intensity is important,

therefore this drawback does not affect the analytical goal negatively.

In addition, the linearity of the response is fairly good, enabling a good calibration in practice.

4. Conclusion

The results presented prove that a chemically stable macroporous scintillating polymer resin can be synthesized by radiation polymerization technique. We have shown that the scintillating properties of the resin material are just as good as that of a standard liquid scintillation cocktail. In our previous work (Vincze et al., 2007) we have shown, that the ion binding capacity of this resin is also excellent, and having its maximum in the pH range of 5–7, making it ideal for the continuous monitoring of natural water samples.

Therefore, we can conclude, that a stable extracting-scintillating resin could successfully be synthesized by the applied radiation polymerization technique.

Further optimization and selectivity studies are being carried out for the strontium selective resin, and resins for other type of ions are now being synthesized.

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