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Short Research Article

Synthesis of (α-T)polyacrylic acid†

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Introduction

A polyacrylic acid (PAA) hydrogel with biotechnological, medical and pharmaceutical application was obtained by radio-polymerization of acrylic acid (AA) aqueous solutions at NIPNE Magurele Romania.[1] Due to its high capacity of water absorption the PAA hydrogel may be a good alternative for storage of low or medium-activity tritium liquid wastes.[2] The stability towards radiolysis of PAA:H_2O and self-radiolysis of PAA:HTO hydrogel was analysed by RES spectrometry and gel/sol ratio analysis using [T-G]PAA and [1-^{14}C]PAA.[3] For radiometric studies development and for confirmation of RES spectra solving from previous studies it was necessary to label the polyacrilic hydrogel in position 2. The labeled PAA was obtained in two main steps. In the first step, the sodium [2-T]acrylate monomer was obtained by catalytic hydrogenation of 2-bromoacrilyc acid. In the second step, the hydrogel was produced by radiopolymerisation of labeled monomer.

Results and discussion

Synthesis of 2-bromoacrylic acid

The 2,3-dibromopropionic acid was obtained by bromine addition in CCl_4 medium to 0.5 mol of freshly distillated acrylic acid. The crude product (114 g) was obtained in 98% yield and purified by two recrystallisations from ethanol/cholorform. After purification we obtained 93.5 g of white crystalline product (purification yield 80%). The product was characterized by determination of melting point, TLC analysis and FTIR ATR spectrometry. Dehydrohalogenation of the bromo-derivative was realized using $Ba(OH)_2$ in aqueous medium. After finishing the reaction the Ba^{2+} was removed from the reaction by acidification with H_2SO_4 (60%). The 2-bromoacrylic acid was extracted from reaction medium with diethyl ether. The product (37.49 g) was obtained with an extraction yield of 72%. The material was purified further by recrystallization from petroleum ether (25.12 g, 67%). The product was characterized by determination of melting point, TLC analysis and FTIR ATR spectrometry.

Synthesis of (2-D)acrylic acid and (2-T)acrylic acid

[2-D]Acrylic acid and [2-T]acrylic acid were obtained by catalytic hydrogenation of 2-bromoacrylic acid. The reaction took place at strongly alkaline pH (pH 11) in dioxane. To protect the vinyl group were used the Lindlar ($Pd/BaSO_4$ partially poisoned with quinoline) catalyst. The crude products were purified by TLC using GF254 Silicagel and as eluent a mixture of methyl isobutyl ketone:methanol:propanol:ammonia in the ratio 64:10:40:25 (v/v/v/v). The deuterated product was purified as sodium salt and was characterized by FTIR spectrometry, ^{1}H-RMN si HPLC.

After purification, the tritium labelled compound was dissolved in methanol and characterized by determination of radioactive concentration and radiochemical purity using radio TLC (Table 1). To 50 ml of methanolic solution of 30 MBq/ml radioactive concentration was added 0.5 g of sodium acrylate as carrier and the stock solution was stored at 5°C.

Preparation of the (2-T)polyacrilyc acid

Labeled sodium acrylate (20 ml of the methanol solution) was evaporated to dryness under vacuum and the

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Table 1 Experimental data for [2-T]NaAA and [2-T]PAA

Radioactivity of crude labeled monomer (MBq)	4884
Radioactivity of purified labeled monomer (MBq)	3626
Radiochemical purity detected by TLC (%)	90
Purification yields (%)	74
Volume of labeled NaAA solution (ml)	50
Radioactive concentration of a monomer methanol solution (MBq/ml)	37
Total activity of monomer solution (MBq)	1850
Volume of AA solution used in isotopical dilution of labeled 2-T-NaAA (ml)	20
Radioactivity of labeled PAA washing solution (MBq)	199.8
Monomer's and olygomer's concentration in labeled PAA (%)	10.8
Radioactivity of purified [2-T]PAA (MBq)	1650
Specific activity (MBq/g)	275

residue redissolved in unlabelled acrylic acid solution (20 ml of 30% v/v). The labelled polyacrylic acid was obtained by radiopolymerization of this solution using a ^{60}Co γ source. The irradiation dose was 4.5 kGy and irradiation dose rate 3 kGy/h.[1] The oligomers, unpolymerized monomer and labeled propionic acid were removed by swelling in 500 ml deionized water followed by dehydration with methanol. The radioactivity of resulting solution was determined using a β-counter and was used for correcting the total activity of labeled polyacrylic acid. The results obtained are illustrated in Table 1.

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