Synthesis of 1-Polyisobutenamine-(2-^{14}C)

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Summary

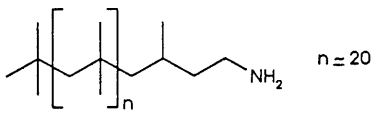
Starting from acetonitrile-(2-^{14}C) 1-polyisobutenamine-(2-^{14}C), a novel fuel additive, was synthesized. The radiochemical purity of the product, as checked by radio-TLC and radio-HPLC, was found to be > 98 %.

Keywords

1-Polyisobutenamine, ^{14}C-radiolabel

Introduction

1-Polyisobutenamine (PIBA, **1**) is a newly developed fuel additive. It is a mixture of oligomers with a mean molecular weight of 1 100.



1

For toxicological studies, necessary for registration purposes, a ^{14}C-labelled version was required. This synthesis is reported in the present paper.

Results and discussion

It was of great importance for the labelled compound to have the same molecular weight distribution as the marketed product. This requirement made it impossible to synthesize ^{14}C-**1** by polymerisation of labelled isobutene, as the polymerisation conditions used in the production process, when applied to a laboratory scale, resulted in a distinctly different molecular weight distribution.

An alternative strategy was to start from unlabelled polyisobutene **4** having the correct molecular weight distribution and to introduce a labelled alkylenamino function. For reasons of stability we decided to label carbon atom 2. The planned synthetic approach is depicted in scheme I.

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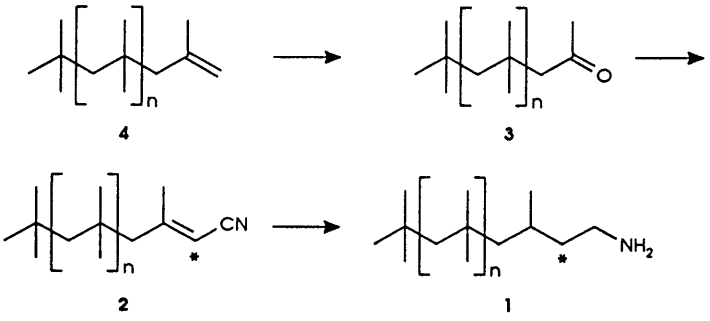
Scheme I



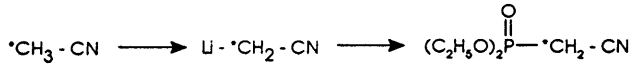
In order to retain the molecular weight distribution of **4** it was essential for all steps of the reaction sequence to proceed nearly quantitatively, otherwise preferential reaction of some fractions of the oligomer mixture might result in a deviation from the desired molecular weight spectrum.

Ketone **3** was to be synthesized by ozonolysis of **4** but unfortunately the reaction yielded a variety of side products that had to be separated by column chromatography. The molecular weight distribution of purified **3** no longer corresponded with that of **4**.

We then tried to synthesize **3** by Lemieux-oxidation of **4** with OsO_4 / Et_4NJO_4[1,2]. While the intermediate diole was formed readily (as determined by IR-spectroscopy) the subsequent cleavage of the diol to yield **3** proceeded very sluggishly.

We finally succeeded in obtaining **3** by oxidizing the crude product of the Lemieux-reaction with lead tetraacetate.

The cyanoethylene compound **2** was obtained by condensation of **3** with ^{14}C-labelled cyanomethylenphosphonate **5** in a Wittig-Horner-reaction. **5** was synthesized from diethylchlorophosphate and the lithium salt of acetonitrile-(2-^{14}C)[3]:



In order to achieve complete conversion of **3** into **2** we had to react **3** twice with an excess of phosphonate **5**.

Catalytic hydrogenation of **2** with Raney-nickel afforded crude PIBA (**1**) that after purification by column chromatography was obtained in > 98 % radiochemical purity. Gel permeation chromatography of **1** showed no difference in molecular weight distribution of labelled **1** and reference compound.

Experimental

1 1-Oxapolyisobutene (3)

27 g (62,4 mmol) tetraethylammonium periodate were added over the course of 15 min. at room temperature to a solution of 30 g (30 mmol) polyisobutene and 40 mg osmium tetroxide in 225 ml THF. After stirring for 14 h and the addition of 300 ml water the reaction mixture was extracted twice with 100 ml hexane. The organic phase was dried over Na_2SO_4 and concentrated to yield 26 g of a dark oil. 20 g of the latter were redissolved in 600 ml THF and a solution of 88 g sodium bisulfite in 400 ml water was added. After heating at 80° C for 1.5 h the reaction mixture was diluted with 500 ml water and extracted twice with 200 ml hexane. The organic phase was separated, dried over Na_2SO_4 and concentrated. The residue was redissolved in 350 ml benzene and treated with 7 g (39 mmol) lead tetraacetate for 2 h at room temperature. After addition of 750 ml water and 50 ml acetic acid, the mixture was extracted with 500 ml hexane. The crude **3**, obtained by concentration of the organic phase, was purified by chromatography (silicagel; mobile phase: hexane / toluene (1 / 3)).

Yield: 10.5 g (44 %); IR (C = O): 1 730 nm.

2 Cyanomethylene diethyl phosphonate-(2-^{14}C) (5)

445 µl (8.5 mmol, 7.46 GBq) acetonitrile-(2- ^{14}C) in 2.5 ml THF were added dropwise at - 75° C to a solution of 17.5 mmol LDA in 8 ml THF / 11 ml hexane, freshly prepared from n-BuLi and diisopropylamine. After 30 min. at - 75° C 1.57 g (8.4 mmol) diethylphosphoric acid chloride in 5 ml THF were added. The reaction mixture was stirred at - 75° C for 1 h, allowed to warm up to room temperature and quenched by the addition of 12 ml 20 % NH_4Cl solution. The organic phase was separated, dried over Na_2SO_4 and concentrated. The crude product **5** (1,0 g (59 %)) was used without further purification.

3 1-Cyano polyisobutene-(2-^{14}C) (2)

473 mg (2.7 mmol) of **5** were added at room temperature to a suspension of 67 mg (2.8 mmol) NaH in 3 ml THF. After 10 min. a solution of 1.0 g (1.0 mmol) **3** in 2 ml THF was added dropwise. The reaction mixture was stirred at 60 - 65° C for 12.5 hours, diluted with 25 ml heptane and washed twice with 25 ml water. The organic phase was separated, dried over Na_2SO_4 and concentrated. The oily residue was treated once again with **5** as described above.

Yield: 0.74 g (74 %); IR (C ≡ N): 2 220 nm.

4 1-Polyisobutenamine-(2-^{14}C) (1)

820 mg (0,82 mmol) of **2** were dissolved in a mixture of 20 ml ethanol, 35 ml THF, 0,2 ml conc. ammonia and 0,4 g Raney nickel were added. The mixture was hydrogenated for 16 h at 10 bar. The catalyst was removed by filtration and the filtrate concentrated to afford 818 mg crude **1** as a yellow oil that was purified by chromatography (LiChroprep-NH_2, mobile phase: toluene).

Yield: 370 mg (45 %); radiochemical purity > 98 % (HPLC, TLC). Gelpermeation chromatography (Ultrastyragel, mobile phase: toluene, RI-detection) showed no differences between the molecular weight distributions of the above synthesized **1** and a reference sample.

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References

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