

Merrifield-like resin beads by acid catalyzed incorporation of benzyl chloride into dehydrochlorinated PVC

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Abstract

A method is presented for preparing Merrifield-like resin beads starting from poly (vinyl chloride) (PVC) in spherical bead form. In this method, first, PVC is partially dehydrochlorinated in boiling methanolic KOH (20%) solution to create minute amounts of allylic carbon centers. Those centers trigger the un-zipping process and make further dehydrochlorination possible at relatively low temperatures (180–200 °C), while retaining the bead shapes. Acid catalyzed reaction of the dehydrochlorinated PVC particles with benzyl chloride at 180 °C yields crosslinked spherical bead polymers possessing chloromethyl benzene functions as high as 3.4 mmol g⁻¹. Experiments showed that, high yields of benzyl chloride insertions can be attained by using PVC samples with 40–50% of unsaturations. In the study transformation yields in each step were followed by conventional analytical methods and IR spectrometry. It was also demonstrated that modification of the chloromethyl groups either with KCN or sodium acetate proceeds with nearly quantitative yields, as in the case for chloromethylated styrene-divinyl benzene resins.

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1. Introduction

Chloromethylated PS-DVB resin is one of the most important key materials for preparing functional polymers. The chloromethyl group offers numerous transformation possibilities via nucleophilic substitutions. Unlike to simple alkyl halides, the chloromethyl group linked to phenyl ring of PS is lack of β -hydrogen and does not undergo dehydrochlorination yielding alkene residues as side

reaction. Due to this advantage chloromethylated-PS resin, so called “Merrifield Resin”, has found extensive use as catalyst carrier [1], chelating group carrier [2], and intermediate [3] in various polymer-supported organic reactions.

Crosslinking copolymerization of vinyl benzyl chloride and chloromethylation of crosslinked PS-DVB resin are common routes for its preparation. Although the former method gives polymers with any desired functionality, a considerable amount of the chloromethyl groups remains embedded into the crosslinked polymer matrix [1].

The chloromethylation of crosslinked PS-DVB resin, on the other hand, involves the use of

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formaldehyde-hydrochloric acid mixture as a reagent (Blanc Chloromethylation). The resulting chloromethyl groups are completely accessible in further reactions [4]. However this reaction is not advisable for laboratory-scale preparations owing to formation of extremely carcinogenic by products, mono and dichloromethyl ethers.

Alternative procedures such as the use of chloromethyl ethyl [5] or octyl ethers [6] with Lewis acids and dimetoxymethane in combination with thionyl chloride and Lewis acid [7] are less common methods of the chloromethylation. An interesting approach is chlorination of 4-methylstyrene-styrene-DVB terpolymers in 40% conversion yields with bleaching liquor, under phase transfer conditions [8].

Herein we describe an alternative and relatively simple procedure for preparing chloromethylated-PS analogues starting from commercial PVC. The present process is based on acid catalyzed addition of benzyl chloride to dehydrochlorinated PVC.

Acid catalyzed reaction of alkenes with benzene nucleus is well known in organic chemistry. The reaction has been classified in the Friedel-Crafts alkylation reaction [9]. This typical aromatic electrophilic substitution reaction is believed to proceed with formation of carbocation from alkene and its attack to the aromatic ring. One common example is sulfuric acid catalyzed reaction of *iso*-butene with benzene, yielding *iso*-butylbenzene [10]. Effect of sulfuric acid as catalyst is somewhat different from those of typical Lewis acid catalysts, such as AlCl_3 . In contrast to aluminum chloride sulfuric acid does not cause to branching of the linear alkyl chains and it is selective to alkenes. For instance, in the presence of sulfuric acid reaction of metallyl chloride with benzene gives 1-chloro, 2-methyl, 2-phenyl propane [11].

Selectivity of sulfuric acid in the Friedel-Crafts alkylation envisaged us to investigate the reaction of the dehydrochlorinated PVC with benzyl chloride. By using this chemistry, in the present study, benzyl chloride was introduced to PVC beads (125–210 μm) via the double bonds created by its dehydrochlorination. Having chloromethyl groups the resulting bead product is reminiscent of chloromethylated PS-DVB resin (Merrifield resin). In this work the optimal reaction conditions were investigated and transformations in each step were followed by standard analytical techniques. Moreover reactivity of the chloromethyl groups was tested simply by derivatization with KCN and NaOOC-CH_3 .

2. Experimental

2.1. Material

Beaded polyvinyl chloride (PVC) was supplied from Petkim (Turkish Company, Izmit, Turkey). It was sieved and 125–210 μm size of fraction was used in the following reactions. All the other chemicals used were analytical grade chemicals; benzyl chloride (E. Merck), KCN (E. Merck). They were used as supplied.

2.2. Acid catalyzed addition of benzyl chloride to dehydrochlorinated PVC

PVC bead sample (20 g) was refluxed in 30 mL of methanolic KOH (20%) solution for 3 h. The resulting brown product was filtered, washed with 150 mL of water, 20 mL of ethanol and 20 mL of diethyl ether. Vacuum dried light brown product weighed 19.93 g.

A sample of this product (10.3 g) was heated to 200 °C in an oven for a predetermined time interval. Resulting pitch-dark spherical beads weighed 7.56 g. Five grams of this product was placed in a small flask. 0.2 mL concentrated H_2SO_4 and 10 mL benzyl chloride was added to the flask and the mixture was refluxed for 36 h without stirring to avoid mechanical disintegration of the bead particles. The mixture was let to come to room temperature and filtered. The solid was washed with ethyl acetate several times (4×10 mL), dried under vacuum at 50 °C for 6 h and weighed (8.4 g). Soluble fractions of the products were determined by extraction with tetrahydrofuran in Soxhlet apparatus.

2.3. Determination of the accessible double bond contents

Accessible double bond contents of the samples dehydrochlorinated at 200 °C were determined by bromine addition method as follows. 1.6 g (0.01 mol) Br_2 was dissolved in CCl_4 and made up 25 mL in a volumetric flask. 10 mL of this solution was added was mixed with 0.1 g of the dehydrochlorinated sample in a closed bottle. The mixture was shaken for 24 h on a continuous shaker at room temperature. 5 mL of the solution was added to 20 mL KI solution (5%) while stirring and the iodine liberated was titrated with 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ solution.

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