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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 nucleophylic 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

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 aparatus.

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 $Na_2S_2O_3$ solution.

Thus, 37.0 mL of titer (in the case for 30 min of the dehydrochlorination) corresponds to 1.85 mmol of excess bromine. This indicates a 3.0 mmol of accessible double bond content per gram of the dehydrochlorinated sample.

2.4. Determination of total chlorine content

A sample of the acid catalyzed reaction product (0.1 g) was mixed with 1 g of NaOH (pellets) and 3 g anhydrous Na_2CO_3 in a porcelain crucible and fused at 1100 °C for 1 h. After cooling the crucible content was washed with water, filtered and transferred into a 500 mL volume of flask. Chloride content of the solution was assayed by colorimetric method, using $Hg(SCN)_2$ as described in the literature [12].

2.5. Determination of the chloromethyl group contents

Chloromethyl group contents of the samples with chloromethyl benzene functions were estimated as follows; 0.2 g was added to 20 mL ethanol solution of NaOH (15%) and refluxed for 2 h. The mixture was cooled and filtered. Five milliliter of the filtrate was transferred into a volumetric flask and diluted to 500 mL. Chloride content of the solution was assayed as described above. Thus, 3.4×10^{-4} M of chloride concentration for acid catalyzed reaction product obtained from 30 min of the dehydrochlorination, indicates a 3.4 mmol g^{-1} of reactive chloromethyl group in the structure.

2.6. Reaction with NaOOCCH₃

A half gram of the above product was placed in a 100 mL volume of canonical flask equipped with a reflux condenser. To the flask there was added 5 mL ethanol and 5 mL of 30% sodium acetate solution and the mixture was refluxed for 16 h. The mixture was cooled, filtered, washed with distilled water and dried.

The filtrate and washings were combined and stored for analysis of the chloride content. This solution was diluted to 500 mL in a volumetric flask. Chloride content of the solution was determined by the colorimetric method as described above and found to be 3.36×10^{-3} M. This corresponds to 3.36 mmol g^{-1} of replaced chloride in the modified spherical bead polymer.

2.7. Reaction with KCN

The reaction with KCN was performed by a similar procedure as described for sodium acetate, using 5 mL of 30% aqueous potassium cyanide. Analysis of chlorine content of the resulting product by the procedure described in 2.5 did not give any detectible chlorine indicating quantitative substitution of accessible chlorines (Kolbe nitrile reaction).

3. Results and discussion

Acid catalyzed reaction of dehydrochlorinated PVC with benzyl chloride gives rise to polymers with chloromethyl groups (Scheme 1). In order to obtain polymers with bead shape we have started from commercial PVC in spherical bead form (125–220 μm). Whereas, thermal curing of PVC bead particles by direct heating at the dehydrochlorination temperature of the original PVC, 250 °C results in melting and concomitant destruction of the bead shapes.

In order to retain the spherical bead shapes a two-step dehydrochlorination was followed as described before [13]. In the first step PVC was partially dehydrochlorinated by refluxing in methanolic KOH solution for 3 h to give a dark-brown product. Only negligible mass loss (0.01%) was observed in this step.

Allylic protons created in this step were considered to trigger further dehydrochlorinations at lower temperatures. Further heating of this product in dry state at 210 °C gives pitch dark product while retaining the bead shapes. 26.6% mass loss in this step (Run 2) indicates a 0.4555 mol of double bond per repeating unit (Scheme 1). However bromine addition method yields 3.0 mmol g^{-1} of accessible double bond content for this sample. This corresponds to 0.1376 mol brominated double bond per repeating unit.

That means that, more than two thirds of the double bonds (0.3179 mol) remain embedded within the tightly crosslinked matrix. Some part of this portion must be consumed in Diels–Alder reaction yielding crosslinking. The polyene structure (formed by HCl elimination from PVC) undergoes a dien-dienophil coupling to form cyclohexene units in the polymer matrix (Scheme 2).

Although we are unable to estimate extent of the Diels–Alder reaction, persistent dark color of the brominated sample implies existence of reasonable
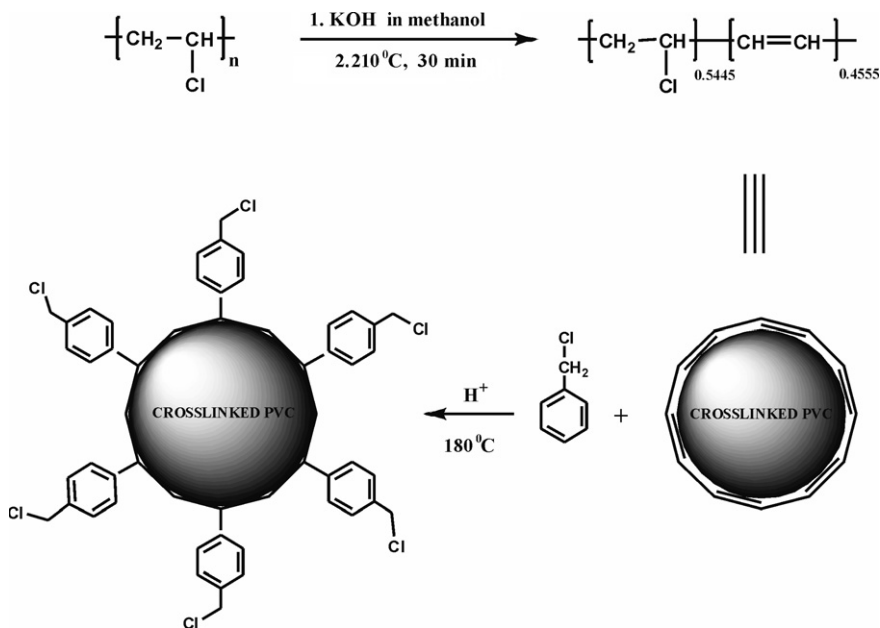
Scheme 1. Preparation of spherical bead polymer with chloromethyl groups, from PVC.
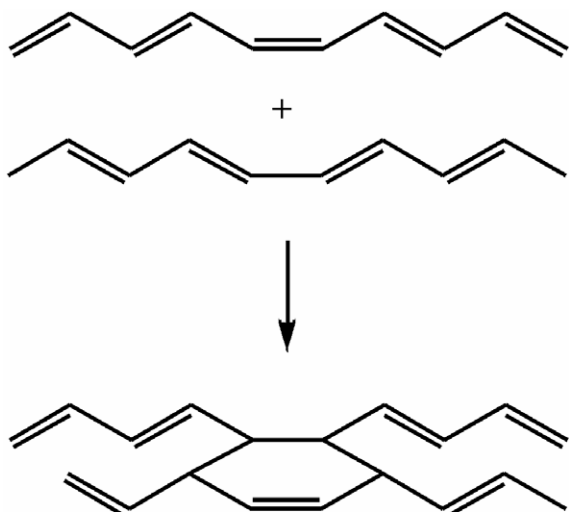
Scheme 2. Crosslinking by Diels–Alder reaction between the polyene chains.

quantity of conjugated double bonds located at inaccessible sites of the matrix.

Extension of the dehydrochlorination by heating for longer periods, however, slightly increases percentage of double bonds reacting with bromine (Table 1).

Acid catalyzed reaction of the dehydrochlorinated sample with benzyl chloride yields 68% of mass increase with retention of the spherical bead shapes. The mass increase corresponds to 3.2 mmol g^{-1} of chloromethylbenzene units incorporated. But considering with extension of the dehydrochlorination during the reaction with benzyl chloride, this assumption might not be correct. For precise estimation of the chloromethylbenzene content, the sample was boiled in methanolic solution of NaOH and the chloride ion released was assayed by colorimetric method. This analysis gave 3.4 mmol g^{-1} of chlorine. It was assumed that the chlorines remained in the base polymer do not interfere analysis of the chloromethyl group, as only negligible mass loss was detected in the partial dehydrochlorination of fresh PVC while treating with NaOH in methanol. The reaction with benzyl chloride can be depicted as shown in Scheme 3.

Composition of the resulting product can be estimated more precisely by correlating the mass increment with the chloromethyl group content (based on Scheme 2) as follows.

From the mass balance:

$$\frac{62.5(1 - x - y) + 26x + 152.5y}{62.5 \times 0.5445 + 26 \times 0.4555} = 1.68$$

From the chlorine content:

$$\frac{y}{62.5(1 - x - y) + 26x + 152.5y} = 3.4 \times 10^{-3}$$

Table 1
Physical characteristics of the reaction products of dehydrochlorinated PVC with benzyl chloride

Run	Dehydro-chlorination time at 210 °C	Accessible[a] double bond content	Mass increase in the reaction with benzyl chloride	Soluble[b] fraction	Chloromethyl group content	Shape
1	–	3.8 mmol g^{-1}	42.3%	56.6%	4.84 mmol g^{-1}	Amorphous
2	30 min	3.0 mmol g^{-1}	68.0%	0.01%	3.40 mmol g^{-1}	Spherical bead
3	120 min	3.4 mmol g^{-1}	20.2%	0.0	1.43 mmol g^{-1}	Spherical bead
4	240 min	3.3 mmol g^{-1}	12.1%	0.0	1.07 mmol g^{-1}	Spherical bead

[a] Determined by bromine addition method.
[b] Soluble fraction of the polymer with chloromethyl benzene functions in THF.
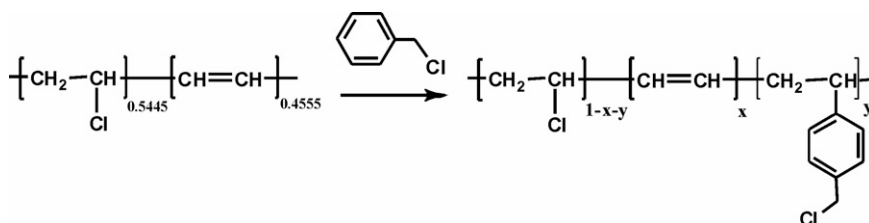
Scheme 3. Acid catalyzed reaction of the dehydrochlorinated PVC.

where 62.5, 26 and 152.5 are molecular weights of the PVC, vinylene and chloromethylstyrene segments, respectively. Solution of the two equations gives:

$$x = 0.247, \quad y = 0.262, \quad 1 - x - y = 0.491$$

Amount of the chloromethyl benzene units in the polymer is 0.262 moles per mole of the repeating unit, which is far more than the accessible double bond content of the starting polymer (0.1376 mol). Mole percent of the vinyl chloride segment reduces from 54.45% to 49.1% due to extension of the dehydrochlorination during the reaction with benzyl chloride at high temperature.

The difference $0.262 – 0.1376 = 0.1244$ mol is partially compensated by the extended dehydrochlorination $(0.5445 – 0.491 = 0.0535)$ during the reaction with benzyl chloride. There is still excess benzyl chloride involved. The remaining portion of benzyl chloride must be added through the double bonds which become accessible during the process. But logically changing mole percent of the inaccessible double bonds seemed to be impossible. We thought that this controversy might be because of the errors in the analytical measurements carried out.

However careful repeating of the experiments gave almost the same results. Most plausible explanation of this phenomenon is retro-Diels–Alder reaction lessening the crosslinking density which allows penetration exceeding amount of benzyl chloride during the reaction at 180 °C.

Moreover, total chlorine content of this sample was found to be 9.4 mmol g^{-1} by alkaline fusing method in which the sample is embedded in powdered mixture of NaOH–Na$_2$CO$_3$ and burned up. Then chloride ion formed is transferred in aqueous solution and determined as usual. The result found is fairly consistent with the expected value 9.77 mmol g^{-1}.

The total chlorine content (9.77 mmol g^{-1}) must be sum up of chlorines of the residual vinyl chloride segments and benzyl chloride introduced.

Direct heating of the partially dehydrochlorinated sample in benzyl chloride (Run 1), on the other hand, gave an amorphous product with 56.6% of soluble portion. This reveals that, acid catalyzed addition of benzyl chloride to the double bonds takes place simultaneously with evolution of HCl. But rate of the former must be greater than that of the later. Accordingly a loosely crosslinked product is obtained. Main disadvantages of this

approach are loss of the bead shapes and large amount of the soluble fraction.

The reaction with highly dehydrochlorinated samples (Runs 3 and 4), however, did not give satisfactory results. The mass increases and corresponding chloromethyl group contents were significantly low in those cases (Table 1). This must be due to higher crosslinking densities resulting from the longer heating periods for the dehydrochlorinations.

Comparison of these results reveals that extension of the dehydrochlorination is critical for successful incorporation of benzyl chloride. Although we have not performed a detailed optimization, one can conclude that, 40–50% of dehydrochlorination is satisfactory for insertion of benzyl chloride without scarificing the spherical bead shapes.

4. The derivatization

In order to test reaction efficiencies and accessibilities of the chloromethyl groups, the sample of Run 2 was reacted with KCN and sodium acetate in alcohol–water mixtures (Scheme 4).

The reaction with sodium acetate proceeds almost quantitatively as it was evidenced by chlorine analysis of the final solution.

FT-IR spectra of the products are shown in Fig. 1. The intense peaks in 1500–1750 cm^{-1} range represents highly conjugated double bonds in the dehydrochlorinated product (Fig. 1b). Characteristic stretching vibration of CN group is clearly observed at 2325 cm^{-1} for the sample derived by reaction with KCN (Fig. 1d).

Although characteristic carbonyl vibration of the acetoxy derivative is being obscured by unsaturation bands of the base material, the broad band observed at 1770 cm^{-1} can be assigned to its stretching vibration. Overall result shows that, the benzyl chloride moieties incorporated give typical substitu-
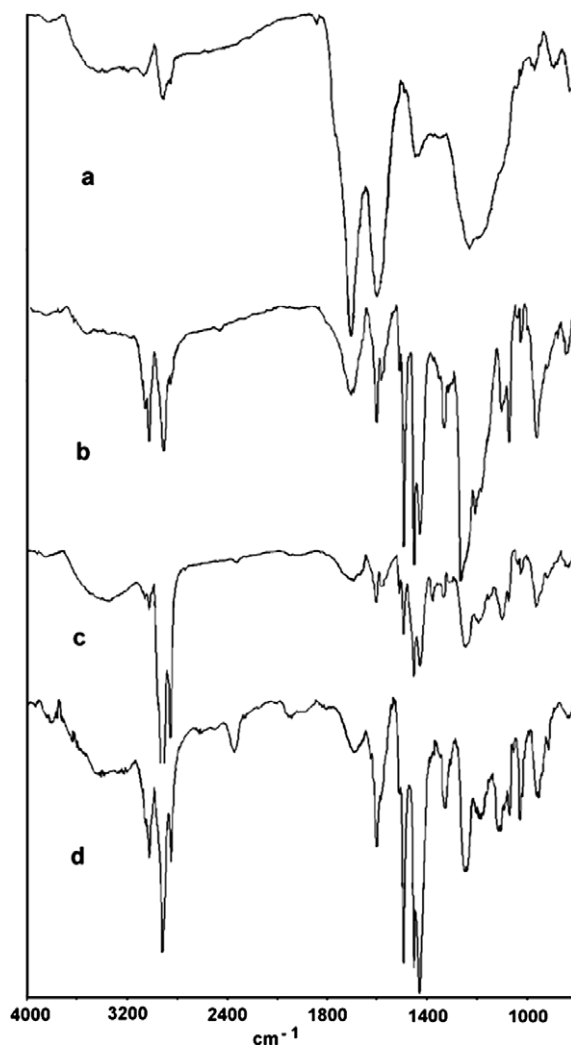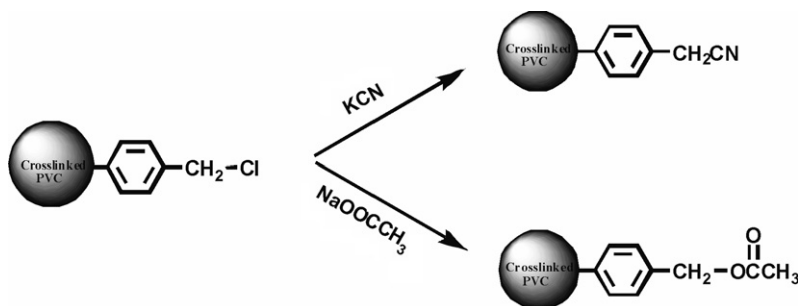

Fig. 1. FT-IR spectra of the dehydrochlorinated PVC (a), its acid catalyzed reaction product with benzyl chloride (b), acetoxy (c) and nitrile (d) derivatives of the product.

tion reactions of chloromethylated styrene-divinyl benzene resins.

Scheme 4. Nitrile and acetate derivatives of the chloromethyl groups of the polymer.

5. Conclusion

In conclusion, the method presented provides a simple route for preparing spherical bead polymers having reactive chloromethyl groups starting from PVC beads. The most important aspect of this method is to avoid dangerous Blanck chloromethylation reaction in preparation of Merrifield resins. Incorporation of chloromethyl benzene units might be in 1.07–3.4 mmol g^{-1} range depending on extent of the dehydrochlorination and those groups are reactive enough for further derivatizations. In application viewpoint, the dehydrochlorination at 210 °C for 2 h and followed heating with benzyl chloride at 180 °C seems to be the best way of obtaining functional resin (Run 3) with chloromethyl group density of 1.43 mmol g^{-1}. The Merrifield-like resin so obtained is attractive due to simplicity of the process and cheapness of the starting chemicals. Perhaps only drawback of this procedure is dark color of the resulting bead product.

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