

Epoxide containing spherical beads from PVC

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Summary

Dehydrochlorination of poly (vinylchloride) (PVC) bead particles (410-840 μm) has been performed by heating in liquid paraffin or pre-treatment with KOH-isopropanol and subsequent heating at 200 $^{\circ}\text{C}$. These procedures give crosslinked dark-colored products with retention of the bead shapes. Catalytic epoxidation of the dehydrochlorinated products with t-butyl hydroperoxide yields gray-white to dark products with reasonable epoxide contents (1.7-4.7 mmol per gram). The method presented offers a simple pathway to prepare epoxidized spherical beads, starting from PVC. The resulting products are very useful as functional group carriers, due to high reactivity of the epoxy groups.

Introduction

Polymers with epoxy groups are important class of key materials for functional polymers, due to easy functionalization through the epoxy groups. There are few polymers with oxirane functions. Epoxidized polybutadiene [1] and phenol-formaldehyde resins with glycidyl groups [2] are common examples of such polymers. Glycidyl methacrylate is the only commercially available monomer having epoxy group.

This study deals with epoxidation of dehydrochlorinated PVC, in beads form. PVC is one of the most abundant and cheap polymers. PVC differs from simple alkyl halides in that; it does not give many substitution reactions. Instead a sequential elimination of hydrogen chloride occurs to yield polyene structures. At high temperatures, conjugated double bonds in the polyene segments undergo Diels-Alder reaction to give crosslinked dark products. Some nucleophiles such as, thiophenolate [3], thiocyanate [4], thiosulfate [5], azide [6] and nitrite [7] have been reported to be effective in substitution by simultaneous dehydrochlorination. Millan and Co-workers have published a series of papers for modification of PVC [8-10]. Recently, dehydrochlorinated PVC has been epoxidized by m-chloro perbenzoic acid, in high yields [11]. Structurally PVC has a very small quantity (0.3-1 % mol/mol) of active or labile chlorides [12], which greatly affect thermal and chemical stability of PVC.

In this work, we have targeted to prepare epoxide containing crosslinked polymer, in spherical beads form, starting from PVC. Direct heating of commercial PVC beads, obtained by suspension polymerization, yields melted amorphous products. In the study, two procedures have been described for dehydrochlorination of PVC yielding dark colored

spherical beads. In the last part of the study, epoxidation of the dark colored beads with t-butyl hydroperoxide has been investigated.

Experimental

Materials

Polyvinyl chloride (in spherical beads, 410-840 μ , K value 56-59) was supplied from Petkim (Turkish Chemical Co. Kocaeli- TURKEY). All the other chemicals used were analytical grade chemical products. t-butyl hydroperoxide (TBH) (70%) (Aldrich), Mo(AcAc)₂ (molibdenium acetyl acetonate) (Fluka), tetrahydrofurane (THF) (Fluka), dimethylformamide (DMF) (Fluka). They were used without further purification.

Dehydrochlorination of PVC beads

Commercial PVC beads (obtained by suspension polymerization) were sieved and 410-840 μ m size of product was elaborated in further reactions. Two different methods were employed for dehydrochlorination of PVC to retain spherical shape of the samples.

Method A

The PVC sample (10 g) was placed in a 250 mL of two-necked flask equipped with a reflux condenser and a dropping funnel. To the flask the solution of 9 g (0.16 mol) KOH in 50 mL isopropanol was added and the mixture was refluxed for 1 h. The mixture was cooled, filtered and washed with excess of water. Dark-brown beads were transferred into 25 mL ethanol and left to stand for 2 h. The product was filtered, washed with 10 mL ether and dried under vacuum at room temperature for 24 h (yield 10.2 g).

The brown product was divided into eight parts. Each part was cured in an oven at 200 °C for different periods. Final masses of the cured products were weighed and each product was placed in a Soxhlet extractor with 50 mL of tetrahydrofurane (THF). Soluble fractions were extracted for 24 h. The resulting samples were dried at 40 °C for 3 h under vacuum and weighed.

Method B

Five grams of PVC samples were added to 25 mL of liquid paraffin. Each mixture was heated at 220 °C constant temperature, for a predetermined period while stirring with a mechanical stirrer. The samples were dried under vacuum for 24 h, at room temperature. Then they were transferred to Soxhlet extractor to remove paraffin residues and soluble fractions by THF. After 24 h of extractions, the samples were dried under vacuum again for 24 h, and weighed. Relevant data were collected in Table 2.

Determination of the accessible double bond densities

This was determined by bromine addition method [13] as follows: 3 g of bromine was added to cooled CCl₄ and diluted to 100 mL. To 10 mL of this solution, there was added 0.11 g of the cured PVC sample (1 h) in a bottle. The bottle was tightly stoppered and mounted on a continuous shaker. After shaking for 24 h at room temperature, the mixture was filtered and 6 mL of the filtrate was mixed with 6 mL of 20 % KI solution. The mixture was stirred for 5 min. and titrated with 0.1 M Na₂S₂O₃ solution until disappearance of the color. 20.1 mL of titer (22.5 mL for 6 mL of blank) indicates 2.4 mmol of unreacted bromine.

This corresponds to 1.8 mmol of double bonds per gram of the polymer. Relevant data obtained from the samples cured for different time intervals were recorded in Table 1 and Table 2.

Porosity measurements

Pore volume data of dry samples were obtained from N_2 sorption isotherms and application of the BET (Brunauer-Emmet-Teller) theory. The instrument used was Quantachrome Autosorb with Windows version 1.19 software system.

The Epoxidation

Catalytic epoxidation of the dark colored spherical beads was performed by reacting with *t*-butyl hydroperoxide in CH_2Cl_2 using $Mo (AcAc)_2$ catalyst, as follows: 1 g of the dark coloured beads was placed in a 100 mL flask, equipped with reflux condenser. To the flask 25 mL CH_2Cl_2 , 10 mL of dry *t*-butyl hydroperoxide (dried by anhydrous Na_2SO_4) and 0.1 g $Mo (AcAc)_2$ was added. The mixture was refluxed for 72 h. After cooling the beads were collected by filtering and washed with alcohol, water and again with alcohol (10 mL). The product was dried under vacuum at room temperature for 6 h.

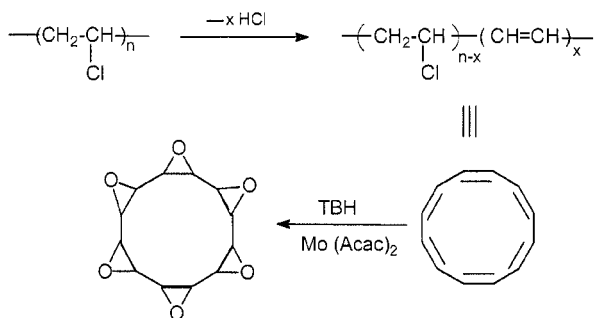
Determination of the epoxy contents

The epoxide contents were determined by pyridine-HCl method [14] as follows: 1.6 mL of concentrated HCl solution (37 %) was added to pyridine and diluted to 100 mL. Ten mL of this solution was boiled with 0.1 g. of epoxidized polymer sample (from epoxidation of the sample cured for 4 h). The mixture was cooled to room temperature and filtered. One milliliter of the filtrate was diluted to 5 mL and titrated with 0.05 M NaOH solution. Thus 16.7 mL of NaOH consumption indicates a 2.8 mmol epoxy group per gram of the polymer.

Results and Discussion

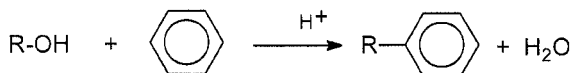
Dehydrochlorination of linear PVC beads and subsequent epoxidation give white-gray to dark colored crosslinked beads as depicted in Scheme 1. Thermal dehydrochlorination of commercial PVC by direct heating above 220 °C yields insoluble dark colored products. Our goal, in this study is to obtain crosslinked bead polymer with epoxy groups, starting from commercial PVC beads (with 410-840 μm size). In order to retain the spherical bead shapes, we have searched a proper method for the dehydrochlorination. However, most of simple dehydrochlorination procedures reported do not give satisfactory results. For instance, direct heating at 250 °C in an oven resulted in melting and sticking of the beads and overall result was loss of the bead shapes during the dehydrochlorination.

Long-term heating in concentrated NaOH solution, described by Shin and Co-workers [15] did not work in our hands. This method gave light-brown product, soluble in common solvents of PVC such as THF and DMF. Apparently in the procedure reported [15] hydrophobicity of the polymer does not allow diffusion of the NaOH solution into the beads. Bromine addition method indicates only few percent (3.4%) of unsaturation in this product.



Scheme 1. Dehydrochlorination and subsequent epoxidation of PVC beads

We have tried heating the PVC beads in a high-boiling liquid. Heating in diethylene glycol in the presence of small amounts of KOH gave insoluble dark product without losing the bead shapes. But the product did not show any mass-loss. Instead more than 10% of mass increase was observed. It is possible that, some portions of diethylene glycol might be entrapped in the densely crosslinked matrix. But only 1.3 % of soluble part was detected by Soxhlet extraction with THF. This result implies possible incorporation of diethylene glycol into the dehydrochlorinated product, presumably due to addition of OH groups to the double bonds by catalytic effect of evolved HCl. The reaction must be analogue to acid catalysed condensation of alcohols with aromatic rings yielding aryl alkyls.



Scheme 2. Acid catalysed condensation of alcohol with aromatic ring.

The samples dehydrochlorinated in diethylene glycol, even after long-term Soxhlet extraction (72 h) with THF still exhibit strong etheric C-O stretching vibrations at 1100 cm^{-1} , (Fig.1). This observation implies that the mass increase after heating in diethylene glycol must be mostly due to addition this compound rather than its entrapping in the crosslinked matrix. Among the dehydrochlorination procedures studied, two methods were found to be suitable i) partially dehydrochlorination in isopropanol solution of 18.7 % KOH and subsequent heating at $200\text{ }^\circ\text{C}$ in oven, ii) heating in liquid paraffin at $220\text{ }^\circ\text{C}$. The partial dehydrochlorination by refluxing for 1 h in 18.7 % KOH –isopropanol solution gives light brown samples, which are entirely soluble in THF. The light-brown colour can be ascribed 8-10 conjugated double bonds at outer parts of the bead particle surfaces [16]. No mass loss is observed in this stage. Heating those partially dehydrochlorinated samples at $200\text{ }^\circ\text{C}$ results in progressive dark colorization of the samples. Reasonably fast mass loss is observed at earlier stages of the heating. The dehydrochlorination at this temperature obeys roughly first order kinetics with $9.7 \cdot 10^{-5}\text{ s}^{-1}$ of rate constant. The reaction becomes slower after 5 h. Extent of the reaction, x/n can be correlated with mass loss \square , simply as follows: $\square\% = (36.5 / 62.5) \cdot 100 \cdot x/n$

Where 36.5 is molecular weight of HCl, 62.5 is molecular weight of the repeating unit in PVC, n is repeating units of PVC and x number of the double bands formed (see Scheme 1). Trends in mass loss and corresponding conversion curves seem to approximate saturation limits, after 5 h of cure times, probably due to an equilibrium of the dehydrochlorination. Whereas no appreciable colouration occurs with non-treated PVC

samples at this temperature, even after heating for 24 h. Apparently in our case, dehydrochlorination of the pre-treated samples at 200 °C is being triggered by allylic effect of the preformed unsaturations. In another words, the allylic effect makes it possible to proceed the reaction by zipper-like mechanism at 200 °C. Overall result is dehydrochlorination of the pre-treated PVC beads, without sticking to each other.

Table 1. Epoxide contents and dehydrochlorination characteristics of the beads evaluated by method A.

cure time (h)	mass loss %	Conv. (x/n) %	Unsaturation ^a (mmol.g ⁻¹)	Soluble ^b Portion %	accessible ^c double bond, mmol. g ⁻¹	porosity cm ³ .g ⁻¹	Epoxide Content Mmol. g ⁻¹
1.0	39.72	68.0	18.04	56.6	1.8	1.46.10 ⁻²	1.7
2.5	45.30	77.6	22.68	45.2	2.3	-	2.0
4.0	45.90	78.6	23.16	11.8	3.7	-	2.8
15	48.90	83.7	26.20	6.7	4.1	-	3.1
24	51.00	87.3	28.50	6.3	4.3	3.40.10 ⁻³	3.2

a) Calculated by mass loss , b) in Soxhlet extraction c) Determined by bromine addition method (after Soxhlet extraction)

We have also tried to follow extent of the dehydrochlorination by bromine addition method. However, this method gives only 1.8-4.3 mmol unsaturations per gram of the cured polymers. These amounts accounts for about 16.1 – 22.7 % of the unsaturations calculated by mass loss (Table 1).Some percents of the remaining part might have been consumed in Diels-Alder reaction for the crosslinking. Also appreciable amounts of the double bonds remain in non-diffusible points in the crosslinked matrix. Due to this fact, the double bonds determined by the bromine addition method represent only unsaturations at the accessible sites. Moreover the cured samples show very low porosities. The porosities of the samples greatly reduce by cure time due to increasing crosslinking densities.

Molar ratio of the accessible double bonds (determined by bromine addition method) to the evolved HCl is inversely proportional to extent of the dehydrochlorination. This ratio gradually decreases from 22.7% to 16.1% as the cure time increases. Indeed low porosities measured establish non-diffusibility of much of the double bonds inside the bead particles. Apparently some portion of the double bonds remains inaccessible in the crosslinked matrix and percentage accessibility of the double bonds decreases by cure time.

In method B, PVC samples were heated directly in liquid paraffin (with continuous stirring at 220 °C). Weights of dried products (after extraction of residual paraffin by Soxhlet extraction with THF) exhibit somewhat lower percents of mass losses.

We have chosen 220 °C as the cure temperature to avoid fusing and coalescence of the bead particles. Molar ratios of the accessible double bond densities gradually reduce from 50.2 % to 34.7 %. Those values are about twice of ones observed in the first method. The difference can be attributed to slightly higher porosity of the samples obtained by heating in paraffin. Indeed porosities of the samples are substantially higher than those of the first method (Table 2).

Table 2. Epoxide contents and dehydrochlorination characteristics of the beads cured in liquid paraffin

cure time (h)	Mass loss %	Conv. (x/n) %	Unsaturation ^a (mmol.g ⁻¹)	Soluble ^b Portion %	Accessible ^c double bond mmol. g ⁻¹	porosity cm ³ .g ⁻¹	epoxide content mmol. g ⁻¹
1.5	17.9	30.6	5.97	34.0	2.04	-	1.8
2.5	29.6	50.7	11.5	30.2	3.00	0.16	2.4
4	31.8	54.4	12.8	2.1	4.51	-	3.1
7	32.3	54.9	13.0	1.4	4.60	7.8.10 ⁻³	4.3
16	34.2	58.5	15.0	0.0	5.20	-	4.7

a) Calculated by mass loss , b) in Soxhlet extraction c) Determined by bromine addition (after Soxhlet extraction)

The conversion yields of the epoxidation with the molybdenum complex are nearly proportional to the unsaturations. When mass increase in epoxidation is taken into account, the epoxidations attained are nearly equal to the double bond contents determined by bromine addition method. Epoxidation yields of the samples dehydrochlorinated by the method B reach to 4.7 mmol.g⁻¹. Whereas lower epoxidation yields are attained for the samples prepared by method A. This difference can be attributed to low porosities in the later case. Epoxidation products are still dark in colour due to high percentage of double bonds unreacted. White-grey epoxidation products were obtained for the short cured sample (1h, 30 min) in paraffin.

In conclusion, both curing procedures presented give dark coloured crosslinked products with retaining the spherical bead shapes. Especially curing in liquid paraffin is very suitable for the catalytic epoxidation. Reasonable high epoxide contents (as high as 4.7 mmol.g⁻¹) can be attained by Mo (AcAc)₂ catalyst. Those epoxide contents are high enough to prepare functional polymers possessing any desired functionality. The preparative method presented here provides a versatile route to epoxidized beads, which are useful as trunk polymers. Having processing facility of the spherical bead particles modified forms of these materials are suitable to use in packed columns for various applications. The only disadvantages of those epoxidized bead products are their appearance, dark colour.

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