

## Polymer supported nitrite esters as diazotising reagent

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### Summary

Glycidyl methacrylate based terpolymer resin was prepared in spherical beads form by suspension polymerization of glycidyl methacrylate (0.4mol)-methyl methacrylate (0.5mol)-divinyl benzene (0.1mol) mixture. Acid catalysed reaction of the resin beads (110-220  $\mu\text{m}$ ) with excess of glycerol gives corresponding modified resin with hydroxyl functions (6.86  $\text{mmol g}^{-1}$ ). Upon standing in 2 M  $\text{HNO}_2$  solution, hydroxyl groups of the later esterified with nitrous acid (3.55  $\text{mmol g}^{-1}$ ). The nitrite ester functions of the resin have been demonstrated to be efficient nitrous acid precursor in diazotisation of aromatic amines. Diazotisation of aniline in 2 M  $\text{HCl}$  solutions at  $0^\circ\text{C}$  takes place in less than 15 minutes. Applicability and practical yields of the method presented have been investigated by diazo coupling reaction of  $\beta$ - naphthol.

### Introduction

Organic nitrite esters, such as isoamyl nitrite and ethyl nitrite have been used as nitrous acid source in organic solvents. Since free nitrous acid is unstable, the most common nitrous acid sources used are sodium or potassium nitrite, both are soluble only in water. Because of this fact, nitrous acid reactions of water - insoluble compounds were carried out by using nitrite esters in the past. But difficulties arise from the use of nitrite esters of water- immiscible alcohols. In those cases the resulting nitrosoation products might not be separated easily from the mixtures because of non-volatility of the higher alcohol remained. We have thought that the use of polymer supported nitrite makes it easier to separate the products, especially when a crosslinked polymeric support is employed.

There exists many crosslinked polymers with various functionalities. With the exception of hydroxyethyl methacrylate polymers[1] there appear no reports dealing with crosslinked polymers carrying hydroxyl functions. Cellulose beads[2] can also be considered, as hydroxyl carrier although the structure of the material is not crosslinked. Polyvinyl alcohol is the most common polymer with hydroxyl functions. Its post crosslinking in cold water with boric acid has been reported to give polymer beads[3]. However the crosslinking takes place via borate ester formation and borate esters are very susceptible to hydrolysis in presence of dilute mineral acids. This type of crosslinking has been termed as "mobile crosslinking". Similarly well-known reaction of polyvinyl alcohol with some dialdehydes gives crosslinked polymers via cyclic

acetale formation [4]. But acetals are also unstable hydrolytically and crosslinking by acetale formation is not suitable to prepare polymeric supports. Suspension polymerization of vinyl acetate together with a divinyl monomer and its subsequent hydrolysis might be considered as straightforward method to prepare hydroxyl bearing crosslinked polymers. However commercial divinyl monomers such as divinyl benzene and ethyleneglycole dimethacrylate give only poor yields of copolymers with vinyl acetate because of the great difference in their reactivity ratios.

According to a recent report published by Frechet et al [5], crosslinked polyvinyl acetate beads have been prepared using some divinyl esters such as divinyl adipate and divinyl succinate. But these materials seem not to be suitable for preparing crosslinked polyvinyl alcohol due to the fact that the crosslinkers themselves constitute with hydrolysable ester linkages.

In the present study, we searched a suitable hydroxyl bearing polymer to prepare polymers with nitrite ester functions. It was found that crosslinked glycidyl methacrylate could be used as trunk polymer to incorporate hydroxyl functions by ring opening reaction of the oxirane functions involved. Although glycidyl methacrylate polymer is also an ester, the methacrylate esters in general, exhibit exceptional high hydrolytic stability against acid and base hydrolyses. Due to this fact glycidyl methacrylate polymers have been presented as relatively inert support to carry functional groups [6].

In the present study, methyl methacrylate- glycidyl methacrylate-divinyl benzene terpolymer in beads form was prepared by suspension polymerization. By acid catalysed reaction of the crosslinked bead polymer with excess of glycerol, corresponding modified polymer with multihydroxyl functions was obtained. On standing in aqueous nitrous acid solution the hydroxyl groups on the polymer were esterified with nitrous acid in reasonable conversion yields as high as 3.55 mmol per gram of the polymer. In the study application of the polymer with nitrite esters in diazotisation reactions has been investigated.

## Experimental

Methylmethacrylate (Merck) and aniline (Merck) were distilled before use. All the other chemicals used were analytical grade commercial products, glycidyl methacrylate(Fluka), divinyl benzene (Merck), glycerol (Merck) ,they were employed as supplied. Sodium maleate- styrene alternating copolymer was prepared by copolymerization of styrene and maleic anhydride as described in the literature[7]. Hydrolysis of the copolymer in 10% NaOH solution gives clear solution on heating for 3 h. 4.0g of the copolymer was hydrolysed with 40 ml NaOH solution and precipitated in methanol (100 ml). Dry yield was 4.2g  
FT-IR spectra were recorded by using Jasco 5300 spectrometer.

### *Preparation of The GMA(40%)- MMA(50%)- DVB(10%) Terpolymer Beads:*

This polymer was prepared by modification of the procedure given in the literature[8]: Glycidyl methacrylate (28.4g, 0.20 mol), methyl methacrylate (25g, 0.25 mol), divinyl benzene(13g, 0.10 mol) were mixed with 67 ml of toluene. 0.82 g (5mmol) azoisobutyronitrile (AIBN) was dissolved in the mixture. In a one liter of three-necked flask 0.8g poly(sodium maleate-co-styrene) as suspension stabilizer was dissolved in 330 ml of distilled water. The flask was equipped with a condenser and a nitrogen inlet.

A motor driven rot was introduced through the third necked. The flask was placed in a silicon oil bath. The organic mixture was added to the flask and nitrogen was flushed through the mixture, while stirring. The temperature was adjusted to 65°C constant temperature and the mixture was stirred (450 rpm) for 6 h. At the end of this period the reaction content was poured into a large excess of water (1500 mL). The bead polymer was collected by filtration. After washing with excess of water and 50 ml methanol, the product was dried at 40 °C under vacuum for 24 h. The yield (63.5 g, 95.6%). The beads were sieved and the fraction in 210-420 μm sizes (34g) was used for further reactions.

*Determination of The Accesible epoxide content:*

This was performed by pyridine-HCl method which was described in the literature[9]. The epoxide content was found to be 3.4 mmol per gram of the polymer.

*Modification of The Polymer With Glycerol:*

Fifteen grams of the above polymer beads (210-420 μm size) was dispersed in 50 ml of glycerol and 0.2 ml concentrated H<sub>2</sub>SO<sub>4</sub> was added. The mixture was heated to 120 °C for 8 h. The reaction content was poured into water, filtered, washed with excess water and dried. Yield 19 gr. 4 g of weight increase implies 86.3% conversion of the epoxy functions.

*Esterification with Nitrous Acid:*

Hydroxyl groups of the polymer beads were esterified with nitrous acid as follows: Nine grams of polymer sample was added to aqueous solution of sodium nitrite ( 17.5g, 0.25 mol in 25 ml water). The mixture was cooled to 0°C in an ice- bath. While stirring at 0°C, 25 ml of concentrated HCl was added dropwise. The mixture in a tightly stopped bottle was left to stand in refrigerator for 3 days. While cold, the polymer beads were collected by filtering, washed with excess water and alcohol (20 ml) and dried under vacuum at room temperature. Practical yield was 8.7 g.

*Determination of The Nitrite Ester Content:*

The nitrite ester content was determined by a modified Libermann method as follows: A solution of 2, 7- dihydroxy naphthalene (2.5 g) in methanol (50 ml) was mixed with concentrated HCl solution (5 ml). To 10 ml of this mixture was added 0.1 g of the polymer and stirred for 1.5 h. The nitrite content of the filtrate was assayed based on the absorbance maxima at 440 nm, as described in the literature [10]. The nitrite ester content of polymer was found to be 3.55 mmol g<sup>-1</sup>.

*Diazotization of aniline and coupling with β- naphthol:*

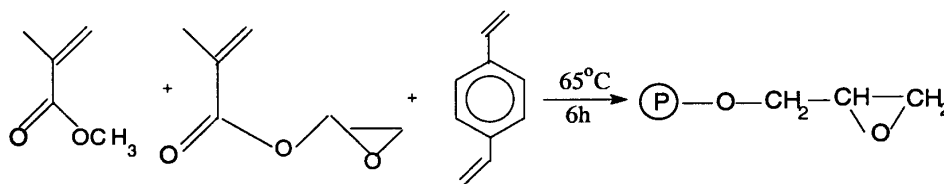
*Method A:* To an ice- cooled solution of aniline (0.7 g, 7.52x10<sup>-3</sup> mol) in 18 ml 1 M HCl there was added 2 g polymer sample with nitrous ester functions and stirred for 15 min. While cold the mixture was filtered and diazonium salt content of the filtrate was assayed by well- known diazo- coupling reaction of β- naphthol. For this purpose, the filtrate was cautiously added to the (1.1 g, 7.52x10<sup>-3</sup> mol) solution of β- naphthol and 0.3 g NaOH in 20 ml water. Orange-red crystals precipitated was collected by

filtering and dried at 40°C under vacuum for 24 h. Yield 1.2 g (64.5% based on aniline).

*Method B:* 2 gram the of polymer sample was added to the ice- cooled solution of 0.7 g ( $7.52 \times 10^{-3}$  mol)aniline in 15 ml ethanol. While stirring 1.6 ml conc. HCl (36.5%) was added to the mixture and stirred for 15 min. After filtration, the filtrate was reacted with  $\beta$ - naphthol solution and isolated as described above. The dye yield was 1.06 g (57%).

## Results and Discussion

Suspension polymerization of the monomer mixture GMA (0.4m)- MMA (0.5m)- DVB (0.1m) at 65°C, using sodium salt of the styrene- maleic acid copolymer as suspension stabilizer gives perfect spherical beads in relatively narrow size distribution (110-480  $\mu$ m) (Scheme 1). Epoxide content of the polymer determined by pyridine-HCl method gives a value 3.40 mmol  $g^{-1}$  which is slightly higher than the theoretical value (3.34 mmol  $g^{-1}$ ) calculated based on the feed composition. Apparently this might be because of the high reactivity ratio of GMA in the copolymerization with MMA ( $r_1:0.88$  and  $r_2:0.76$ )[11].

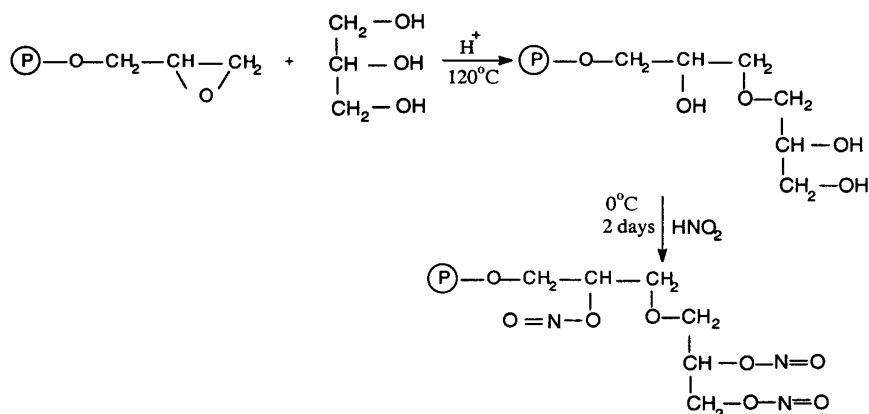


**Scheme 1:** Preparation of the ter-polymer beads with epoxy functions.

Also relatively low polymerization temperature, 65°C is effective to avoid ring opening of the epoxide group in GMA during the polymerization. Acid catalysed reaction of the beads with excess glycerol gives corresponding modified polymer with hydroxyl functions.( Scheme 2). A rough estimation based on 26.7% weight-increment indicates a 6.86 mmol  $g^{-1}$  hydroxyl group content. This corresponds to 86.3% conversion of the epoxy groups. Of course, to attain polymers with high hydroxyl contents poly(glycidyl methacrylate) without methyl methacrylate, can be considered as suitable starting polymer. Here methyl methacrylate was chosen deliberately to dilute the epoxide groups. Otherwise proximity of epoxide groups reduces the hydroxyl group density due to side reaction in which two or more epoxide groups may react with one glycerol molecule.

The resulting modified polymer beads when left in contact with 2 M HNO<sub>2</sub> solution for 2 days in refrigerator yields nitrous ester- resin with 3.55 mmol per gram capacity, which reveals a 58 % of conversion of hydroxyl functions. Relatively low conversion yield can be ascribed to the change in hydrophil-lphophil balance during the nitrosoation. Low molecular-weight nitrite esters are generally immiscible with water that increasing nitrosoation induces hydrophobicity to the polymer which brings a limitation to the extent of further nitrosoation. Of course this limitation can be overcome by using alcohol- water mixture as solvent. However in this study we have not studied optimisation of the nitrosoation reaction.

Formation of nitrite ester functions can be evidenced by comparison of IR spectra of the glycerol modified resin with those of its nitrosoated derivative. Two significant

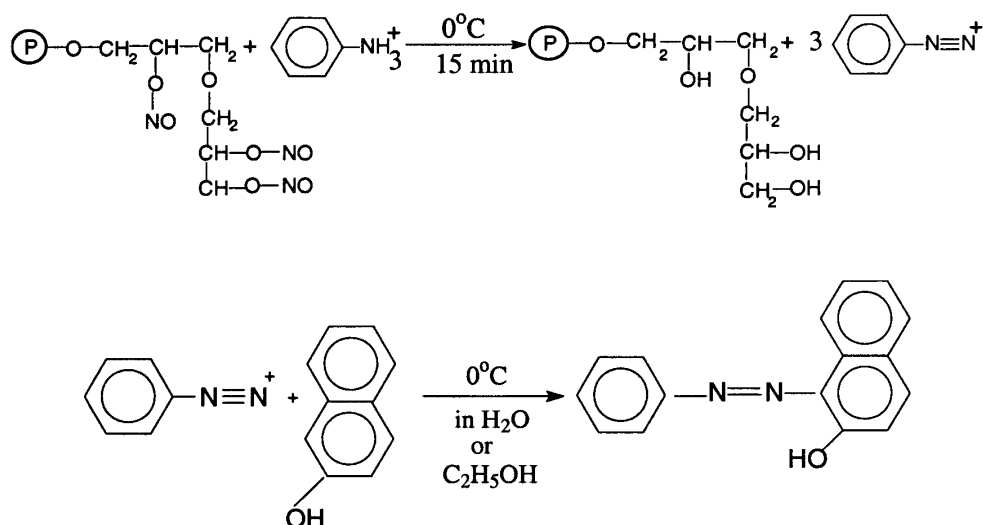


**Scheme 2: Formation and nitrosoation of the hydroxyl bearing polymer.**

differences are observed in their FT-IR spectra. Thus, the intensity ratios of the broad band at  $3500 \text{ cm}^{-1}$  arising from O-H stretching vibration to the one for C-H stretching vibration bands appeared at  $2900\text{-}3000 \text{ cm}^{-1}$  range is substantially lower in the case of the nitrosoated resin. A new band emerged around  $1600 \text{ cm}^{-1}$  can be ascribed to the asymmetrical stretching of the nitrite ester group, which is characteristic for nitrite esters and nitro groups.

*The Diazotisation:*

Diazotisation of aniline in HCl solution with nitrosoated polymer must proceed according to the following reaction scheme. As in the case for the diazotisations using low- molecular weight alkyl nitrites, the first step is hydrolysis of the nitrite ester liberating nitrous acid. The free nitrous acid acts upon anilinium cation to give the diazonium salt.



**Scheme 3: Diazotisation of aniline by polymer supported nitrite ester and coupling with  $\beta$ -naphthol.**

Here, the diazotization with aniline was followed by well-known diazo-coupling

reaction of  $\beta$ -naphthol. For this purpose aqueous HCl solution of aniline was simply interacted with the polymer sample at 0°C. After 30 min, the filtered solution was reacted with  $\beta$ - naphthol solution. When equivalent amounts of aniline (based on the nitrite ester content) is used practical dye yield 0.76 g per gram of the polymer which corresponds to 62.5 % of diazotisation yield per one mole of the nitrite ester function. To demonstrate the efficiency of the polymer in organic solutions the same experiment was repeated in alcohol- acetic acid (1:1) mixtures together with 2.5 moles of HCl per mole of aniline. In that case the diazotisation yield was 56.2% for 30 min diazotisation period

( Table1). Of course these are practical yields, but the results reveal that the polymer supported nitrite ester serves as nitrous acid precursor in aqueous or in organic solvents.

**Table 1.** Dye yields of the diazonium salts obtained from the nitrosoated resin.

Run	Solvent <sup>a</sup>	Reaction time (min)	Dye yield (%) <sup>b</sup>
1	Water	15	62.5
2	Water	30	64.5
3	Water	60	64.7
4	Ethanol	15	57
5	Methanol-acetic acid(1:1)	60	56.2
6	n-Butanol-acetic-acid(1:1)	60	47.3 <sup>c</sup>

<sup>a</sup>) Total volume: 30 ml, aniline: 0,7 ml, bead polymer 2 g

<sup>b</sup>) Practical yield of the 1- phenyl azo 2- naphthol

<sup>c</sup>) Precipitated in alcohol/ water (1:2) mixture

In order to follow the reaction kinetically, the aliquots were taken from the diazotisation after 15 minutes of stirring and coupled with  $\beta$ - naphthol to give 1-phenylazo 2- naphthol dye. Surprisingly it was observed that dye yields per milliliter of the samples taken at different time intervals were almost the same. This result clearly indicates that the diazotisation of aniline is rapid enough and completed within 15 minutes. This period is comparable even with  $\text{NaNO}_2 + \text{HCl}$  aqueous solutions. Presumably this might be due to the hydrophil- hydrophob balance changing in favour of the hydrophilicity of the polymer as extent of hydrolysis of the nitrite ester functions goes further.

In conclusion, the polymer supported nitrite esters can be used successfully in diazotisation reactions. Since the hydroxyl functions of the polymer are being regenerated in the hydrolysis step, polymeric nitrite esters can be used as recyclable nitrous acid source in diazotisation of aromatic amines in aqueous or in organic solvents. Some less probable side reactions of nitrous acid with the polymer backbone might be expected. Because nitrous acid is known to react with methylene groups of carbonyl compounds yielding  $\alpha$ - oximino ketones.

In order to inspect any interaction with the backbone in a separate experiment commercial poly(methylmethacrylate) (0.5 g) was left in contact with 20 mL of 0.1 M  $\text{HNO}_2$  solution for (prepared as described before) 2 days. Nitrite content of the solution was found to be almost the same. This inspection implies that practically nitrous acid does not affect on the polymer backbone. As a result the method presented seems to be promising for diazotisation of aromatic amines even in nonaqueous reaction conditions.

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