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Chemical Modification of Polystyrene Under Phase Transfer Catalysis

Introduction of *p*-Vinyl and *p*-Oxirane Pendant Groups*

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SUMMARY:

Styrene polymers containing pendant p-vinyl or p-oxirane functionalities on some of their aromatic rings have been prepared in excellent yields by chemical modification of chloromethylated polystyrene or carboxaldehyde-substituted polystyrene under phase transfer catalysis. The polymers containing pendant vinyl groups were obtained by Wittig reactions with aqueous formaldehyde while the polymers with p-oxirane pendant groups were obtained by reaction of the carboxaldehyde polymer with trimethyl sulfonium chloride or epoxidation of the p-vinyl substituted polymer.

INTRODUCTION

Functional polymers have been used extensively in numerous applications ranging from their use as protecting groups [FRECHET, 1981], reagents, supports, or catalysts [HODGE and SHERRINGTON, 1980] in organic synthesis, to supports for chromatography [DAVANKOV, 1979], etc.

A large number of functional polymers have been prepared by chemical modification of polystyrene [FRECHET et al., 1977] under classical conditions; more recently, phase transfer catalysis has been used in the modification of crosslinked polystyrene in three phase systems [FRECHET et al., 1979a, 1979b]. These reactions involved mainly nucleophilic displacements on chloromethylated polystyrene resins, additions to carboxaldehyde substituted polystyrene, or reactions of polystyrene derivatives having reactive nucleophilic pendant groups with various electrophiles. These reactions under phase transfer catalysis have now been extended to the modification of soluble chloromethylated polystyrene [NISHIKUBO et al., 1980, 1981; GOZDZ et al. 1981] and it has generally been found that the phase transfer catalyzed reactions afford better results than those carried out under classical conditions both in terms of polymer purity and in terms of functional yields.

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Polystyrene gels containing large amounts of pendant vinyl groups have been made previously by polymerization of divinylbenzene [FUNKE, 1977]. Soluble m- or p-vinyl styrene polymers with molecular weights of up to 100,000 have also been prepared by lithium diisopropylamide initiated polymerization of the corresponding divinylbenzenes in the presence of excess diisopropylamine [NITADORI and TSURUTA, 1978]. In contrast, the preparation of polystyrene resins with vinyl pendant groups by chemical modification of polystyrene has been much less successful [HODGE and WATERHOUSE, 1981]. Our interest in polystyrene containing vinyl or oxirane pendant group is due to the numerous potential applications of these polymers in the fields of polymer supported reactions and in resist technology.

RESULTS AND DISCUSSION

The use of the Wittig reaction for the preparation of crosslinked polystyrene resins with pendant substituted alkene groups was first studied by FRECHET and SCHUERCH [1971] in their search for supports for the solid phase synthesis of oligosaccharides. A classical Wittig reaction was used to prepare a resin with p-allyl chloride pendant groups by reaction of 2-chloroacetaldehyde with the ylid derived from the phosphonium salt of crosslinked chloromethylated polystyrene (II), a reaction which proceeded in approximately 50% yield. Similar reactions attempted a decade later by HODGE et al. [1981, 1982] under phase transfer catalysis gave excellent results with aromatic aldehydes such as thiophene-2-aldehyde or p-diphenyl phosphinyl benzaldehyde.

We have now completed a study of the preparation of poly-(p-vinylstyrene) according to Scheme 1 using both soluble or lightly crosslinked partly chloromethylated polystyrene (I) as starting materials. Phosphonium salt (II) can be obtained in quantitative yield [FRECHET and SCHUERCH 1971] by reaction of (I) with excess triphenyl phosphine in a suitable solvent such as dioxane or chloroform. The reaction is accompanied by the expected large weight increase and, as can be seen in Figure 1, by the disappearance of the C-Cl bending vibration band at 1265 cm^{-1} in the infrared spectrum, with a new sharp band appearing at 996 cm^{-1} and bands of increased intensity at 1109 and 1436 cm^{-1}. The Wittig reaction of crosslinked polymer (II) with aqueous formaldehyde in the presence of sodium hydroxide could be carried out with or without the addition of a phase transfer catalyst as the polymer itself acted as a phase transfer catalyst; similarly, although 1,2-dichloroethane and tetrabutyl ammonium hydroxide were sometimes added, the reaction did not require the use of any additional swelling agent as the polymer swelled in the aqueous formaldehyde solution. With soluble (II) best results were obtained when tetrabutyl ammonium hydroxide was added to the polymer solution. In all cases, good functional yields were obtained in the transformation of (II) into (III). The minimum capacity of polymer (III) after reaction could be estimated from bromine analyses on the product

SCHEME 1. Preparation of poly(p-vinylstyrene)

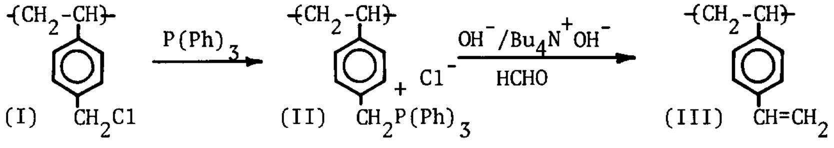
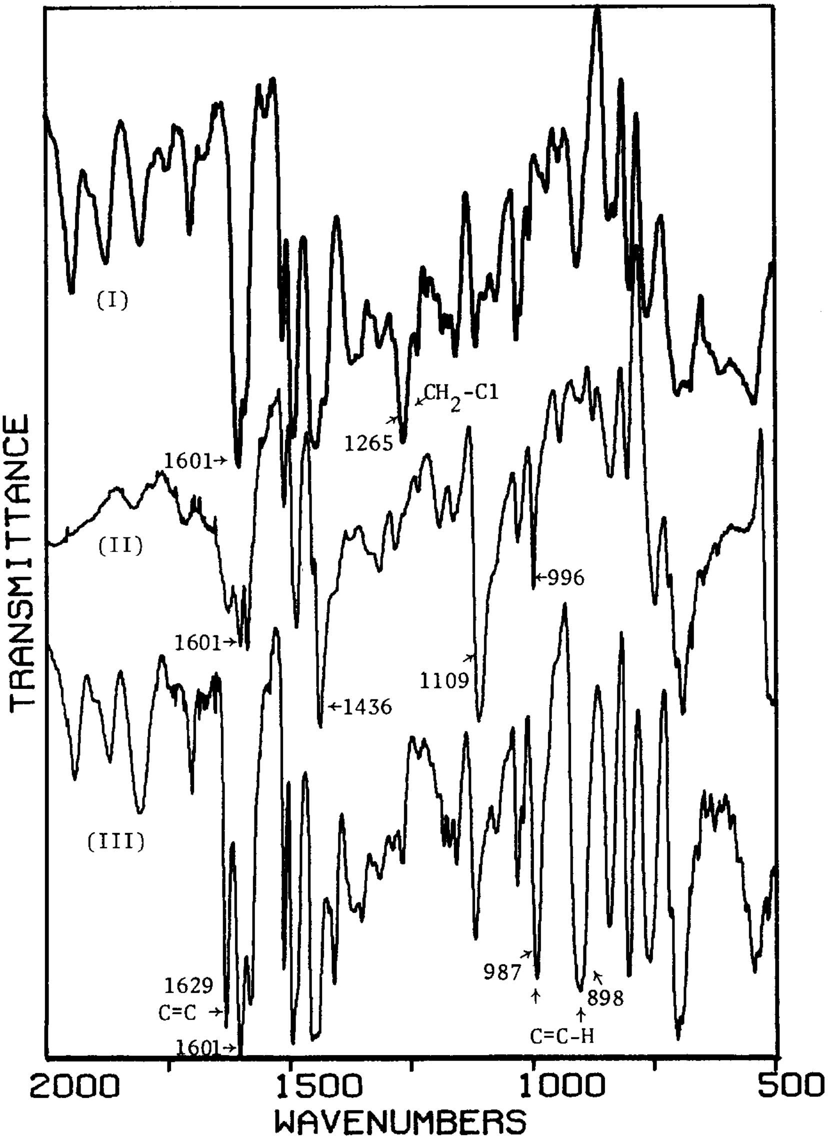


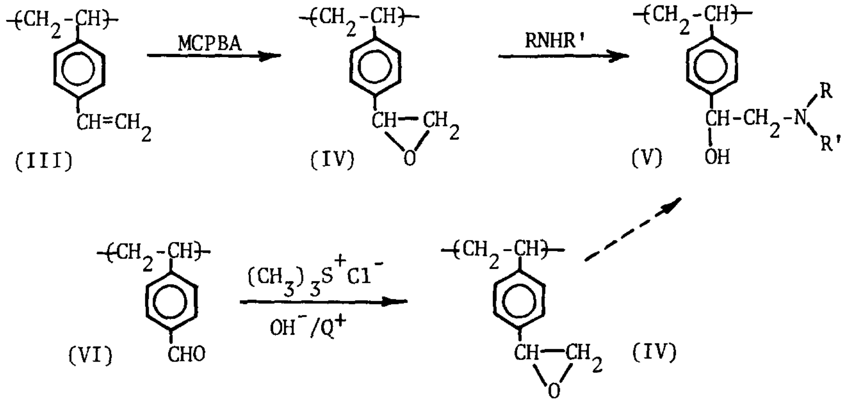
FIGURE 1. Infrared spectra of polymers (I), (II), and (III).



obtained after bromination of the pendant vinyl groups of the polymer [FRECHET and SCHUERCH 1971]. In a typical case, the Wittig reaction of polymer (II), obtained from (I) with a degree of functionalization (D.F.) of 0.54, with formaldehyde afforded (III) with D.F. = 0.43 (calculated for the dibromo derivative) for a functional yield of at least 79% in the two-step reaction from (I) to the dibromo derivative of (III). The infrared spectrum of (III) is shown in Figure 1 and includes characteristic vinyl bands at 3083 cm^{-1} (C-H stretching), 1629cm^{-1} (C=C stretching), 898 and 987 cm^{-1} (C=C-H out of plane bending).

The preparation of polystyrene with oxirane pendant groups (IV) was studied using two different procedures as outlined in Scheme 2. A first approach made use of the simple epoxidation of (III) with m-chloroperbenzoic acid (MCPBA) in dichloromethane, a reaction which gives satisfactory results but requires that (III) be available. The epoxidation reaction was found to be very sensitive to reaction conditions and somewhat prone to side reactions. For example the use of long reaction times caused the appearance of a carbonyl peak in the infrared spectrum of (IV) suggesting that opening of the epoxide ring had occured. The best method for the preparation of (IV) involved the reaction of polystyrene carboxaldehyde (VI) with trimethyl sulfonium chloride in the presence of a phase transfer catalyst. Carboxaldehyde pendant groups were introduced onto polystyrene by oxidation of chloromethylated polystyrene with dimethyl sulfoxide in the presence of an acid acceptor [AYRES and MANN 1965, FRECHET and SCHUERCH 1971]. The sulfonium ylid reaction gave poor results when attempted with trimethyl sulfonium iodide under phase transfer conditions; this result was not totally unexpected as iodides are often considered undesirable for phase transfer reactions due to their excessive solubility in organic medium. The same reaction carried out under classical conditions using potassium t-butoxide in DMSO or n-butyllithium in THF also gave poor results. In contrast, the reaction with trimethylsulfonium chloride and 50% aqueous sodium hydroxide in the presence of benzyl triethyl ammonium chloride gave excellent results and proved to be the reaction of choice for the preparation of (IV). The reaction was accompanied by the disappearance of both the C-H and C=O bands of the starting aldehyde polymer (VI) in the infrared spectrum, with appearance of epoxide stretching bands at 1254 and 905 cm^{-1} . As the functional yield of the epoxidation reaction could not be measured directly, the epoxide ring opening reaction of (IV) with amines such as dimethylamine or n-propylamine to afford (V) was studied and functional yields could be calculated from the nitrogen content of (V). Typically, the functional yields for the three-step reaction sequence (from I to VI to IV to V) were in the range 65-78% depending on reaction conditions suggesting that the epoxidation reaction itself had proceeded in excellent yield, likely 80% or over.As polymers (III) and (IV) contain reactive functionalities which can be transformed easily by reaction with various electrophiles or nucleophiles, both are useful precursors to a number of uniquely substituted styrene polymers for use in applications such as polymer-supported chemistry. Other applications of these polymers which contain easily polymerizable pendant groups are also under investigation.

SCHEME 2. Preparation of poly(p-oxirane-styrene)



EXPERIMENTAL

Infrared spectra were measured on a Nicolet MX-1 Fourier transform spectrometer. Elemental analyses were performed by MHW Laboratories (Phoenix AZ) and in this laboratory. Chloromethylated polystyrene (1% crosslinked, 4.2 meq/g) was obtained from Bio-Rad Laboratories or prepared by chloromethylation of Bio-beads SX-1 [PEPPER et al. 1953, FRECHET et al. 1979a]. Soluble chloromethylated polystyrene was prepared by copolymerization of styrene and p-chloromethyl styrene [KONDO et al. 1979]. D.F. refers to the degree of functionalization of the polymer.

Preparation of (II)

In a typical experiment 20 g of chloromethylated polystyrene (1% crosslinked, 4.2 meq Cl/g, D.F. 0.54) was added to 250 mL dioxane containing 27 g triphenylphosphine. The mixture was stirred at reflux for four days to ensure complete reaction, then filtered and the polymer was washed repeatedly with dioxane, 1,2-dichloroethane and ether. After drying, 41 g of (II) were obtained. The infrared spectrum of (II) is shown in Figure 1. A similar reaction sequence was used with a linear polymer (I) containing 3.1 meq Cl/g, with precipitation of the final product in ether.

Preparation of (III)

The polymer prepared above (41 g) was suspended into 350 mL of 37% aqueous formaldehyde and the mixture was stirred rapidly as

100 mL 50% aqueous NaOH was added slowly keeping the reaction temperature below 60°. After stirring overnight, the resin was filtered and washed repeatedly with water, methanol, THF-water 4:1, methanol, dichloroethane, chloroform and ether. After drying in vacuo 18.5 g of (III) were obtained (see IR spectrum in Fig. 1).

In an alternate procedure, linear polymer (II) was dissolved in a concentrated solution of formaldehyde in methanol, a small amount of tetrabutyl ammonium hydroxide was added, and the mixture was treated slowly with a 50% solution of NaOH while stirring. The polymer which precipitated during reaction was filtered, rinsed, dissolved in THF, and precipitated in hexane. The reaction with crosslinked (II) could also be carried out in the presence of 1,2-dichloroethane and tetrabutyl ammonium hydroxide under phase transfer conditions. The product obtained by this procedure was identical to that prepared above.

For analytical purposes a small amount of polymer (III) could be transformed into its dibromide derivative by reaction with bromine [FRECHET and SCHUERCH 1971]. For example, the dibrominated resin prepared from polymer (I) with 4.2 meq Cl/g contained 4.68 meq Br/g (2.34 mmole/g) for a D.F. of 0.42 and a functional yield of 79% for the 3 step reaction from (I).

Preparation of (IV)

Carboxaldehyde substituted polystyrene (VI) was prepared by DMSO oxidation of (I) in the presence of potassium bicarbonate. Polymer (VI) (5g from polymer I with 2.1 meq Cl/g) in 50 mL dichloromethane containing 0.2 g benzyl triethyl ammonium chloride and 5 g trimethyl sulfonium chloride was treated with 25 mL 50% aqueous NaOH in an ice bath. After complete addition of the NaOH solution the stirred solution was brought to room temperature and the mixture was stirred for 3 hours. The polymer was then collected and washed with water, methanol and ether. After drying an infrared spectrum showed that the aldehydic C-H and C=O bands of the starting polymer had essentially disappeared.

In an alternate procedure 1.5 g (III) in 20 mL dichloromethane was treated with 1.3 g MCPBA. After stirring 90 min. the polymer was recovered and washed free of acid. The infrared spectrum of the dry polymer had a small carbonyl band at 1729 cm^{-1} suggesting that partial opening of the epoxide rings had occured.

Preparation of polymer (V)

A 0.8 g sample of polymer (IV) was treated with 10 mL aqueous dimethyl amine at 60° for 24 hours. After filtration, the polymer was washed repeatedly with water, methanol, dichloroethane, methanol and ether ther dried. Elemental analysis of the final product showed that it contained 2.2% N for a D.F. of 0.19 and a functional yield of 78% for the three-step reaction from (I).

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