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Chemical Modification of Halogenated Polymers Under Phase Transfer Conditions

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ABSTRACT

The chemical modification of several polymers including poly (vinyl bromide), poly (chloromethyl styrene), poly (vinylidene bromide), and poly (epichlorohydrin) was studied using various nucleophiles in multiphase systems with the assistance of a phase transfer catalyst. Satisfactory results were obtained using *o*-dichlorobenzene as solvent and powerful nucleophiles. The use of dimethylformamide as solvent often resulted in large increases in both reaction rates and conversions but sometimes created other problems. With several polymers dehydrohalogenation or chain cleavage were observed and in general the more basic nucleophiles were more destructive. With poly (vinyl bromide) the reaction was used to produce efficiently polymers containing alkyl sulfide, methyl sulfone, vinyl sulfone, or thioethanol side chains with little apparent polymer degradation.

INTRODUCTION

The preparation of functional polymers by chemical modification¹⁻³ is an important technique which has been used extensively both industrially to modify the properties of polymers for various technological applications, and in an area such as polymer-

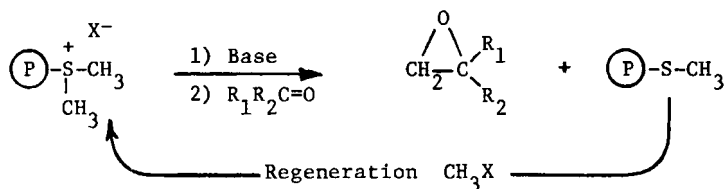
supported chemistry^{4,5} to prepare chemically reactive polymers to be used as reagents, supports, protecting groups, or catalysts. The polymer which has been used most extensively for this type of application is poly (chloromethyl styrene)⁶ which can be modified easily due to the high reactivity of its chloromethyl groups³. For example, it can be converted easily and essentially quantitatively to the corresponding quaternary ammonium polymer for use in ion exchange⁷, or into polymeric phosphine ligands which are useful in the field of catalysis⁸.

While the chemical modification approach is attractive for its apparent simplicity and the fact it can lead to polymers which have structures not readily obtainable through other routes (e.g. poly (vinyl alcohol)), it also suffers from one major drawback: the inability to purify the polymers after modification. If the reactions which are used in chemical modification are not quantitative, the new polymer will necessarily contain some impurities in the form of unreacted groups or other functionalities resulting from side reactions. The purity of the modified polymer will vary with the nature of the starting polymer and with the type of reaction which is used to modify it. In some cases, the presence of just a few impurities will impair the performance of the modified polymer, while in other cases, even appreciable amounts of such impurities will not have a significant influence on the end use or the reactivity of the modified polymer.

RESULTS AND DISCUSSION

Most of our recent work on the chemical modification of polymers has been centered on the introduction and the modification of various functionalities on crosslinked polystyrene³, poly (vinyl pyridine)⁹, or copoly (styrene acrylonitrile)¹⁰ resins. Over the past few years, phase transfer catalysis has received much attention for its numerous applications in general organic¹¹ or organometallic¹² chemistry. The first published application¹³

of phase transfer catalysis to the chemical modification of a polymer was the preparation of a crosslinked resin containing free thiol groups by reaction of 1,4-butanedithiol with crosslinked chloromethylated polystyrene in the presence of hydroxide and a phase transfer catalyst. The use of this system led to the formation of a product in which most of the dithiol molecules had become attached to the polymer through one extremity only. In contrast, similar reactions carried out in dimethylformamide without phase transfer catalyst led to extensive double binding of the dithiol. Another illustration of the usefulness of phase transfer catalysis for the chemical modification of polymers is afforded by our study of the use of crosslinked polystyrene-based sulfonium salts¹⁴ as alkylidene transfer reagents according to the following scheme.

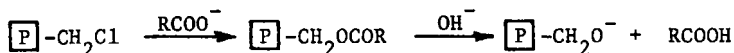


A thorough study of this reaction showed that when a base such as potassium *t*-butoxide was used to generate the sulfur ylide, the polymer was degraded extensively and could not be regenerated to its initial activity. In contrast, when the reaction was carried out in a three phase system consisting of a suspension of the polymeric sulfonium salt in dichloromethane with aqueous sodium hydroxide containing a small amount of tetrabutyl ammonium hydroxide, the reaction proceeded in higher overall yield and the polymeric sulfide by product could be regenerated and reused repeatedly without apparent loss of activity. These initial results which showed clearly the usefulness of phase transfer catalysis in reactions on polymeric substrates have been extended to numerous other systems¹⁵⁻¹⁷ involving nucleophilic displacements on chloromethylated polystyrene, additions to formylated polystyrene, or reactions in which the polymers themselves acted as the nucleo-

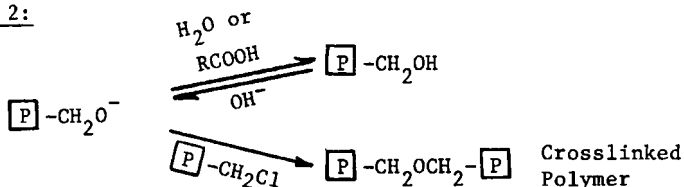
philes. A similar approach involving the use of phase transfer catalysts to promote the modification of chloromethylated polymers has been described by Boileau and coworkers^{18,19}. It is worthwhile noting that in the case of chloromethylated polystyrene most of our reactions were performed in dichloroethane or o-dichlorobenzene which are not miscible with water, while Boileau et al. have used dimethylformamide in most of their phase transfer reactions. The main advantage of using DMF as solvent is that the reaction proceeds at a much higher rate than in hydrocarbons; this is likely due to the higher solubility of the reactive ionic species in the more polar DMF. As DMF has a high affinity for water, it is debatable whether the term "phase transfer catalysis" can be used for reactions such as the ones described by Boileau et al.; the term "ionic assistance" might be more appropriate. Although separate phases can be obtained when mixing DMF and 50% aqueous sodium hydroxide, a significant amount of water is present in the "DMF phase". This in turn affects the reactivity and may even in some cases affect the outcome of the reaction. Another factor which deserves some consideration is the fact that DMF is not stable under strongly alkaline conditions. For example, overnight stirring of a mixture of equal volumes of 50% aqueous sodium hydroxide and DMF containing a little tetrabutyl ammonium hydroxide (a recipe which approximates that used in many phase transfer reactions) produces a two phase system. Analysis of the "DMF phase" shows that it actually contains very little DMF but is rich in dimethylamine and water. Thus the use of DMF as a solvent in phase transfer reactions involving concentrated aqueous hydroxide should be restricted to cases where the dimethylamine which is produced cannot interfere with the transformations being carried out. A second problem with the use of DMF - aqueous hydroxide systems in phase transfer modifications is that unless very large amounts of DMF are used, addition of aqueous hydroxide to the solution of polymer in DMF causes precipitation of such hydrophobic polymers as poly (epichlorohydrin) or chloromethylated polystyrene.

An example of the subtle differences which may result from the choice of one solvent or another in a phase transfer reaction is afforded by the reaction of a solution of chloromethylated polystyrene with an aqueous solution containing both carboxylate and hydroxide ions in the presence of tetrabutylammonium hydroxide. When the reaction is carried out in DMF^{19, 20} at 70°, it is complete within a few hours and it produces a soluble hydroxymethyl polymer. In contrast, the same reaction carried out in o-dichlorobenzene is much slower and eventually produces a lightly crosslinked hydroxymethyl polymer.²² In both cases the reaction fails in the absence of carboxylate ion in the aqueous phase. An explanation for this difference is that in the case of the reaction in o-dichlorobenzene, displacement of chloride by carboxylate produces first a polymer with ester sites. Saponification of these by action of hydroxide produces alkoxide sites (reaction 1 below) which, in turn, can become protonated to yield the hydroxymethyl sites, or can attack directly any neighboring chloromethylated sites to produce a crosslinked material (reaction 2).

Reaction 1:



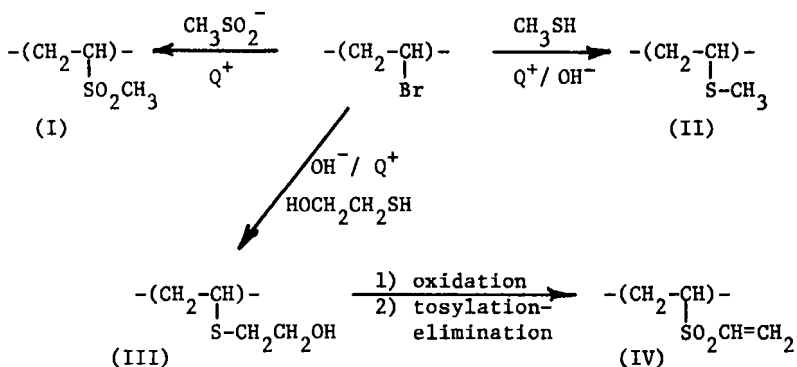
Reaction 2:



The concentration of alkoxide in the organic phase is a function of the concentrations of water and alkoxide in the o-dichlorobenzene. Since little water is ever present in this solvent, a relatively high concentration of alkoxide is responsible for the crosslinking which occurs. In the DMF case, the concentration of water in the DMF phase is much higher and thus the importance of

alkoxide ions in the overall process becomes insignificant, a small increase in molecular weight may be observed²⁰ but the polymer remains soluble. A close examination of the analytical data provided by N'Guyen^{20, 21} also reveals that in DMF a second reaction may have occurred and remained undetected. While the elemental analysis of the starting chloromethylated polymer is satisfactory, it is less so for the product of the reaction (sum of % C, H, O = 96.4). Since no chlorine remains in the polymer after reaction and the functional yield of the reaction calculated from the Cl analysis of the starting polymer (10.2% for a degree of functionalization of 0.35) and the oxygen analysis of the final polymer (4.1% for a degree of functionalization of 0.29) is only 83%, it can be concluded that a by-product has been formed. The DMF or one of its degradation products may be responsible for this side reaction which does not occur when *o*-dichlorobenzene is used as solvent in the phase transfer reaction.

In the case of poly (vinyl bromide) the replacement of Br by various nucleophiles under phase transfer conditions occurred very slowly in halogenated hydrocarbons but much more rapidly in DMF. The reactions which were successful are summarized below:



While polymer (I) can be obtained by anionic polymerization of methyl vinyl sulfone²³, polymers such as (III) and (IV) are not readily obtainable through the simple polymerization of vinyl monomers. The pendant vinyl groups of (IV) are very reactive and can

be used in further chemical modification reactions, crosslinking, etc.

The reaction of poly (vinyl bromide) with sodium methyl sulfinate under phase transfer conditions gave a product which was darker than the light beige starting material and which contained a large number of sulfone groups as shown by elemental analysis and infrared spectroscopy. Figure 1 shows the IR spectra of poly (vinyl bromide) and of polymer (I).

In addition to the strong sulfone stretching bands centered at 1130 and 1300 cm^{-1} , the IR spectrum of (I) exhibits weaker bands at 1620 and 3025 cm^{-1} which correspond to the C=C stretch and the C=C-H stretch of unsaturated portions of the polymer backbone. In addition to this spectroscopic data, analysis of the products of several similar reactions carried out under a variety of conditions, indicated that in most cases substitution did not exceed 70% while elimination to form double bonds accounted for 20-30% of the

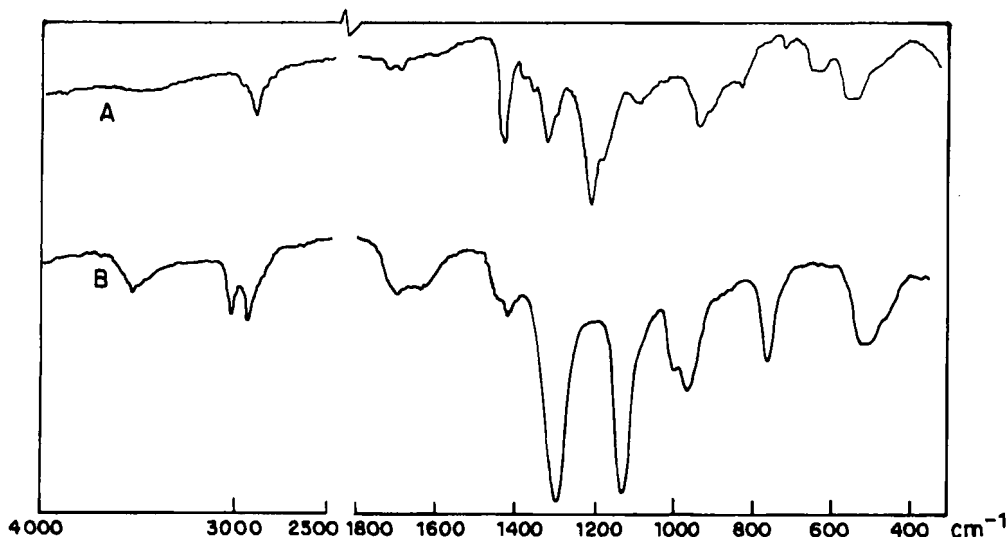
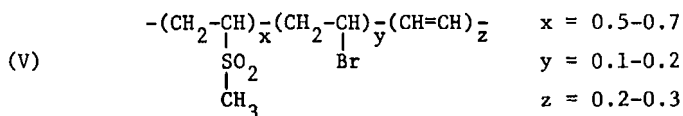


FIG. 1. IR spectrum of poly (vinyl bromide) before (spectrum A) and after (spectrum B) reaction with sodium methyl sulfinate under phase transfer conditions.

sites with usually 10-20% unchanged brominated units. Thus, a more accurate representation of polymer (I) would be that given below for structure (V).



A similar reaction attempted with the less nucleophilic trifluoromethyl sulfinate anion gave only a maximum of 20% substitution while most of the bromine remained on the polymer. In addition, this reaction only occurred when DMF was the solvent. Best results in the substitution reaction were obtained using powerful nucleophiles of low basicity such as the mercaptides of methyl mercaptan or 2-mercaptoethanol with no free hydroxyl present in the reaction mixture. For example, the reaction of poly (vinyl bromide) with an aqueous solution of the anion of 2-mercaptoethanol in the presence of a tetrabutyl ammonium salt acting as phase transfer catalyst, proceeded smoothly to yield a water soluble product which contained essentially no bromine, with up to 90% substitution. The IR spectrum of (III) included a large hydroxyl band centered at 3500 cm^{-1} , and elemental analysis indicated a sulfur to oxygen ratio of 1:1. Several derivatives of polymer (III) have been prepared by further chemical modification under classical conditions. For example (III) was acetylated to give a product with no hydroxyl absorption in the IR but with a large carbonyl band at 1730 cm^{-1} . In another reaction, (III) was oxidized to the corresponding sulfone, then transformed into its vinyl sulfone derivative (V) by a conventional tosylation-elimination reaction sequence. These reactions and the applications of (IV) will be described elsewhere.

The chemical modification of poly (epichlorohydrin) under phase transfer conditions was much less successful than that of either chloromethylated polystyrene or poly (vinyl bromide). In all cases side reactions including main chain cleavage were ob-

served. In a typical reaction a solution of poly (epichlorohydrin) was treated with a concentrated aqueous solution of acetate and hydroxide ions in the presence of tetrabutyl ammonium hydroxide. In halogenated hydrocarbons the reaction was very slow and only low degrees of substitution (< 10%) could be obtained. In hot DMF high degrees of substitution could be obtained and the final polymer was soluble in water. However, this type of reaction has little value as the polymer chains are cleaved extensively during the reaction. This behavior of poly (epichlorohydrin) has also been observed recently by Boileau et al.¹⁸ for a similar reaction involving the replacement of chloride with carbazole. We are currently studying the reaction of poly (epichlorohydrin) with several softer nucleophiles under various conditions, in all cases our preliminary results indicate incomplete substitution and some chain degradation.

With polyvinylidene bromide the reaction was slightly complicated by the fact that the commercially available starting material already contained some unsaturation as evidenced by its elemental analysis and IR spectrum. Reaction of the polymer with aqueous solutions of sodium methylsulfinate or the anions of methyl mercaptan or 2-mercaptoethanol under phase transfer conditions was always accompanied by substantial elimination and, in the most favorable case, the degree of substitution did not exceed 55%. The final polymers were usually very dark in color and had a relatively low solubility. Substitution with sodium methylsulfinate produced a polymer containing 46% of the theoretical amount of sulfur and had an IR spectrum with the expected large sulfone stretching bands at 1135 and 1305 cm^{-1} .

EXPERIMENTAL

Poly (epichlorohydrin) was purchased from Aldrich Chemical Co. (# 18, 186-2). Poly (vinylidene bromide) was purchased from Polysciences Inc. (# 7654), the polymer was light beige-brown in

color and contained only 77% bromine (theory 86%); its IR spectrum showed clearly some unsaturation. Poly (vinyl bromide) purchased from Polysciences Inc. (# 4387) was a dark brown-black material partially unsaturated which could not be used in this study, a preparation of poly (vinyl bromide) is given below. Polystyrene was purchased from Polysciences Inc. (# 3432); the white polymer had a nominal molecular weight of 20,000 and an actual molecular weight of $M_n = 11,500$ and $M_w = 56,000$ (GPC, Styragel columns in THF). The phase transfer catalysts, Adogen 464 and tetrabutyl ammonium hydroxide were purchased from Aldrich Chemical Co. All other chemicals and solvents were reagent grade, used without further purification except as indicated.

Infrared spectra were recorded on a Pye Unicam SP 1100 or a Perkin Elmer 281 infrared spectrophotometer using potassium bromide pellets. NMR spectra were recorded on a Varian HA 100 or CFT-80 spectrometer. Elemental analyses were performed by MHW laboratories or by Guelph Chemical Laboratories Ltd.

Preparation of the Polymers

Chloromethylated polystyrene was prepared using a modification of the procedure of Pepper et al.²⁴ A solution of 50 g polystyrene (Polysciences Cat. # 3432) in 500 mL chloroform and 100 mL chloromethyl ether was treated dropwise and with vigorous stirring with a total of 10 mL anhydrous stannic chloride. After 2 hours at room temperature, 20 mL methanol and 4 mL water were added and most of the solvent was removed under vacuo. The polymer was then precipitated into 1000 mL of methanol. After reprecipitation and drying, a chlorine analysis indicated that the capacity of the polymer was 3.0 mequiv./g (degree of functionalization D.F. = 0.36).

Poly (vinyl bromide) was prepared in a 600 mL stirred pressurized vessel by emulsion polymerization of 50 g vinyl bromide in 70 mL deoxygenated water with 3 drops Anti-foam A, 2 g sodium dodecyl benzenesulfonate, a trace of copper sulfate, and 0.4 g ammonium persulfate. Once the stirring was started, the mixture

was heated to 50° and a solution of 0.5 g sodium sulfite in 10 mL water was added over a period of two hours. After four hours the mixture was cooled and the latex was coagulated to yield 29.5 g of dry poly (vinyl bromide). The polymer was slightly colored. Analysis: calculated 74.5% Br; found 74.6% Br.

Chemical Modification of Chloromethylated Polystyrene

This reaction was carried out as described previously²² using a solution of 1 g of the polymer in 10 mL 0-dichlorobenzene with 0.1 g tetrabutyl ammonium hydroxide and an aqueous phase containing 2 g potassium acetate and 2 g sodium hydroxide in 6 mL distilled water. The mixture was stirred rapidly at 80-85° for two days and formation of a gel was observed. The gel was collected on filter, washed repeatedly with various organic solvents and dioxane-water mixtures, then dried under vacuo to yield 0.63 g of the crosslinked hydroxymethyl polymer. Analysis: Cl, 0.23%; O, 4.74%. The D.F. of the final polymer calculated from the oxygen analysis is 0.34 for a 95% functional yield.

Chemical Modification of Poly (vinyl bromide)

The general procedure used for these reactions was as follows: The polymer (1 g) was dissolved in 10-25 mL of 1,2-dichloroethane or dimethylformamide and approximately 0.1 g of the phase transfer catalyst was added. The phase transfer catalyst was tetrabutyl ammonium hydroxide for reactions involving aqueous hydroxide and Adogen 464 in all other cases. The aqueous phase (3-10 mL) containing an excess of the nucleophile was added to the polymer solution and the mixture was stirred for 1-4 days at 70-80°. In some cases the nucleophile was added in several portions over the course of the reaction. The polymers were purified by precipitation and reprecipitation, or in the case of water soluble products, by dialysis against distilled water followed by freeze-drying. In all cases the modified polymers were much darker than their off-white precursor.

For example, the reaction with sodium methylsulfinate was carried out in dimethylformamide with 3 mL of a 30% solution of sodium methylsulfinate and with Adogen 464. Three subsequent additions of 0.5 g sodium methylsulfinate were made at 4 hour intervals. After purification and drying the polymer contained 9.8% bromine and 18.9% sulfur.

Reaction of Poly (vinylidene bromide) with Sodium Methylsulfinate

1 g of poly (vinylidene bromide) (Polysciences Inc., 77% bromine) was dissolved with stirring in 40 mL DMF at 75°. After addition of 0.2 g Adogen 464, 3 g sodium methanesulfinate and 5 mL water the mixture was stirred at 80° overnight. The polymer was precipitated by pouring the reaction mixture in a large amount of distilled water. After filtration and washing, the polymer was reprecipitated, then dried in vacuo. The infrared spectrum of the polymer had large sulfone peaks at 1135 and 1305 cm^{-1} and showed some insaturation. Analysis: Br 28.4%, S 13.95%.

ACKNOWLEDGEMENTS

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