

CHEMICAL MODIFICATIONS OF POLY (METHYL METHACRYLITE) RESINS FOR BINDING REACTIVE MOEITIES

A. AKELAH*
F. ABDEL-GALIL*
R.K. RENAWY*

SUMMARY: Chemical functionalizations of the hydroxymethyl groups of the reduced poly (methyl methacrylate), PMMA, resins have been achieved by esterification and etherification reactions to produce halogen containing polymers. However, in an attempt to achieve quantitative conversions of the hydroxymethyl into other reactive functional groups, activation of the reduced PMMA resins by tosylation has been carried out. The tosylated polymer is transformed into polymeric ether, thioether and amino derivatives by substitution reactions of the tosyloxy group with a number of nucleophilic reagents. The tosyloxy groups of this active polymer intermediate are good leaving groups for these displacement reactions as indicated by the degree of substitutions. The activity of the polymeric reagents based on PMMA resins has been examined in the direct bromination reactions of various organic compounds such as carbonyl compounds containing α -hydrogen, alkenes and arenes.

Key words: Poly Methyl methacrylate, resins.

INTRODUCTION

The utilizations of reactive functionalized polymers in solid phase synthesis have several advantages and offer a great promise for solving the problems accompanied the conventional chemical reaction procedures both in preparative purposes and in a commercial industrial scale (1,2). Accordingly, chemical modifications of polymers have been of increasing interest for the past years, which have been used extensively for a long time for modifications of polystyrene supports (3,4).

Recently, reactive macroporous polymers based on PMMA resins have been prepared by chemical modifications and investigated as potentially useful supports to be employed in a wide range of polymer supported reactions in order to overcome drawbacks of polystyrene support materials (5).

The object of the present work is directed towards functionalizations of PMMA resins by direct chemical

modifications of reduced PMMA beads and by activation via tosylation to afford versatile and general synthetic pathway towards PMMA functionalizations as well as the use of polymeric perbromide as brominating reagent in organic synthesis.

Experimental Part:

Preparation of p-Chlorobenzyl Derivative of Reduced PMMA Resins

To a stirred suspension of reduced PMMA resins⁶ (195 mmol), I, in dry dioxane (50 ml), 215 mmol of sodium hydride were added in small portions under cooling. After the complete addition of NaH, the reaction mixture was stirred overnight at room temperature and then refluxed for 2 days. The reaction was then cooled to 0°C and a solution of p-chlorobenzyl chloride (200 mmol) in 75 ml dioxane was added dropwise. The reaction mixture was stirred overnight at room temperature, then refluxed for 2 days, filtered and washed with water, ethanol and ether. Elemental analysis of the dried resins indicated that II contains 1,7 mmol Cl/g.

*From Chemistry Department, Faculty of Science, Tanta University, Tanta, A.R. Egypt.

Preparation of the Tosylated Derivative of Reduced PMMA Resins

To a cooled mixture (0°C) of I (50 mmol) and 40 ml pyridine, p-toluenesulfonyl chloride (90 mmol) was added in small portions under stirring. The reaction mixture was stirred overnight at room temperature and followed by heating at 80°C for 10 hours. The resins were filtered and washed with water, diluted HCl, water, dilute NaOH and water. Soxhlet extraction of the tosylated resins, III, with ethanol and drying give the microanalysis which indicate that it contains 3,7 mmol S/g.

Table 1: Loadings of PMMA Derivatives.

Polymer	Anal. Found			
	Cl/Br %	N %	S %	DS %
II	6.15	-	-	34
III	-	-	11.7	82.5
IVa	-	1.7	-	26
IVb	-	5.8	-	31
IVc	-	4.4	-	23.5
IVd	-	3.8	-	12
IVe	-	3.0	-	12
V	-	-	17.2	95
VI	-	1.0	-	16
VII	20.7	-	-	70
VIII	11.35	-	-	-17.5
IX	29.35	-	-	84.5

Aminations of the Tosylated Polymer

A mixture of tosylated polymer III (6.5 mmol), phthalimide (7.5 mmol) and anhydrous potassium carbonate (1 g) in 15 ml DMF was stirred at 60°C for 18 hours. The resins were filtered, washed with acetone, water, dilute NaOH, water, ethanol and methylene chloride, and dried under vacuum overnight. Elemental analyses of the resins IVa-e are listed in Table 1.

Thiolation of the Tosylated Polymer

The mixture of tosylated polymer III (4 mmol), p-thiocresol (6 mmol), anhydrous potassium carbonate (10 mmol) and tetrabutyl ammonium bromide (0.5 mmol) dissolved in 20 ml dry dioxane was stirred at 60°C for about 16 hours. After filtering and washing the resins as described for IV, the elemental analysis indicated that the obtained sulfide resins, V, contains 5.4 mmol S/g.

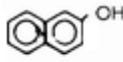
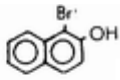


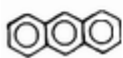
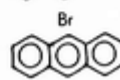
Esterification of the Tosylated Polymer

Esterification of the tosylated polymer III with p-nitrobenzoic acid was carried out as previously described for IV. The elemental analysis indicated that the polymeric ester derivative VI contains 0.71 mmol N/g.

Preparation of Polymeric Phosphonium-Perbromide Reagent

To a stirred suspension of 40 mmol of polymeric phosphonium salt, VIII; which was prepared by acetylation of I

Table: Brominations of Carbonyl Compounds, Alkenes and Arenes With Polymeric Perbromide Reagent IX

Substrate	Product	Time (hr)	Yield %
PhCOCH ₃	PhCOCH ₂ Br	2	69
p-O ₂ N-C ₆ H ₄ -COCH ₃	p-O ₂ N-C ₆ H ₄ -COCH ₂ Br	2	33.5
p-Me-C ₆ H ₄ -COCH ₃	p-Me-C ₆ H ₄ -COCH ₂ Br	12	80
p-HO-C ₆ H ₄ -COCH ₃	p-HO-C ₆ H ₄ -COCH ₂ Br	20	32.5
p-Cl-C ₆ H ₄ -COCH ₃	p-Cl-C ₆ H ₄ -COCH ₂ Br	12	79
Ph-CH=CH ₂	Ph-CHBr-CH ₂ Br	1/4	93
Ph-CH=CH ₂	Ph-CHBr-CH ₂ Br	1/4	66.5
Ph-CH=CH-COEt	Ph-CHBr-CHBr-COOEt	3	12
		1/2	79.5
		1/4	48.5
		12	73.5

+) regenerated polymeric reagent

with p-bromomethyl-benzoyl chloride followed by treatment with triphenyl phosphine (7); in 30 ml carbon tetrachloride, a solution of bromine (67 mmol) in 10 ml carbon tetrachloride was added dropwise at room temperature. After stirring the reaction mixture for 48 hrs, the orange resins were filtered and then Soxhlet extracted by carbon tetrachloride till no colour of bromine was observed. Analysis of the dried reagent IX indicated that it contains 1.2 mmol Br/g and 82% degree of substitution.

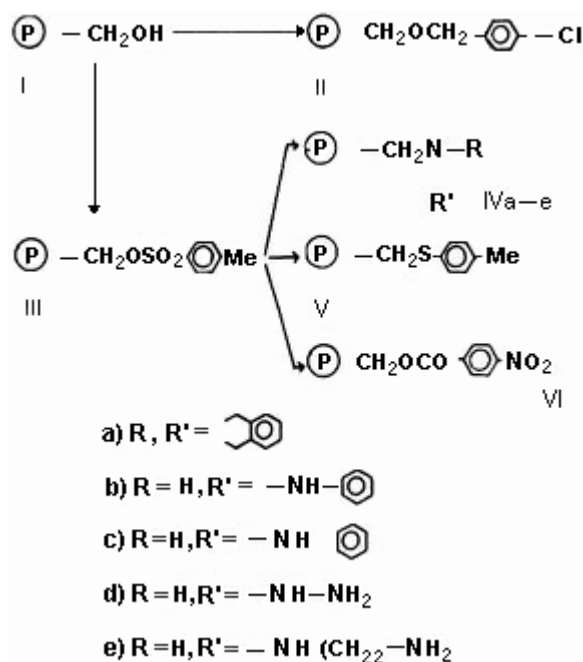
Brominations with Polymeric Perbromide Reagent

The substrate (5 mmol) was added to a stirred suspension of the polymeric perbromide reagent IX (10 mmol) in 20 ml methylene chloride and the reaction mixture was stirred at room temperature for the periods given in Table 2. The resins were filtered-off and the products were identified by microanalyses and by comparison with authentic samples.

RESULTS AND DISCUSSION

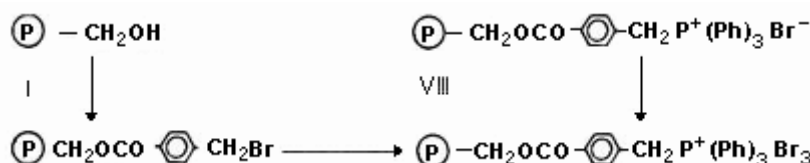
The structure of the polymer backbone is an interest effect on the reactivities of the functional groups supported on polymer, hence it is relevant to study the use of polymeric catalysts and reagents based on cross linked poly (methyl methacrylate), PMMA, resins in organic syntheses.

Starting with crosslinked macroporous PMMA resins, prepared by suspension polymerization of a mixture containing 98% wt of MMA and 2% wt divinylbenzene, DVB, as crosslinker, followed by reduction with LiAlH₄ give the reduced polymer I⁶. Conversion of the hydroxyl functions of I into ether moieties has been carried out through alkylation reaction to give the menzylated polymer II. However, the evaluation of the degree of substitution of the obtained polymer, as determined by the elemental analysis, indicates low conversion (Table 1).

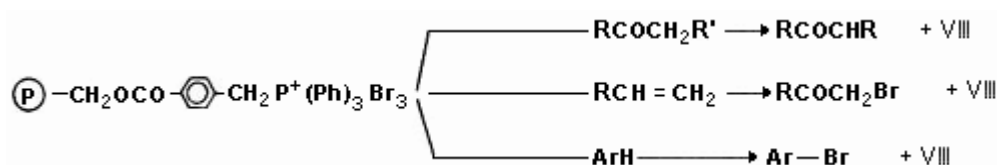


Scheme 1: Chemical Modifications of Reduced PMMA Resins.

In an attempt to accelerate the overall functionalization and hence to achieve quantitative degree of functionalization of PMMA resins by an appropriate sequence of simple chemical steps, the reduced PMMA resins, I, have been activated by tosylation with p-toluene-sulfonyl chloride. The tosyloxy group represents a good leaving group for the nucleophilic displacement reactions. This structural feature is required for enhancing rapidly and quantitatively transformation of reduced PMMA into functionalized polymers containing other reactive groups. Chemical conversion of the hydroxylated resins I to the tosylated derivative III has been achieved by treatment with p-toluenesulfonyl chloride in the presence of pyridine. The tosylated poly-



Scheme 2: Preparation of Polymeric Brominating Reagent.



Scheme 3: Bromination Reactions with Polymeric Brominating Reagent IX.

mer III has been modified into other reactive polymers through a number of substitution reactions under mild conditions as illustrated in Scheme 1. The aminations of III into polymeric amine derivatives IVa-e have been carried out by nucleophilic displacement with the corresponding amine anions. In addition, the polymer-bound sulfide moieties, V, has also been readily prepared by the displacement reaction of p-methylthiophenolate anion with the tosylated polymer III in quantitative yield. Alternatively, the polymeric ester VI has been obtained from III and the p-nitrobenzoate anion in a polar aprotic solvent as DMF. These polymeric derivatives are good intermediates toward other functionalities in order to be useful in other fields of applications.

Investigation of the activity of polymeric brominating reagent IX, prepared by the chemical modification technique of PMMA resins, has been examined in the brominations of organic compounds under mild conditions. The benzoylation of the reduced PMMA resins, I, with p-bromomethylbenzoyl chloride in the presence of anhydrous potassium carbonate as a base, and quaternization of the resulted polymeric bromomethyl-derivative VIII with triphenylphosphine to give the polymeric phosphonium salt VIII, were carried out as described previously (7). The polymeric perbromide reagent IX was easily prepared by treatment of the polymeric phosphonium salt VIII with bromine in carbon tetrachloride at room temperature. Analysis of IX indicated that it contains 1.2 mmol Br/g. It is obtained in the form of orange beads, remarkably stable and odourless, and can be stored for long periods without appreciable loss of bromine.

The bromination reactions of the carbonyl compounds containing α -hydrogen, alkenes and arenes with the polymeric perbromide reagent, IX, gave the corresponding brominated product according to the Scheme 3. In the case of acetophenone derivatives, the reactions with IX gave moderate yields of the corresponding monobromo-derivatives and no products resulting from an eventual

polybromination were obtained as shown in Table 2. The most interesting property of the polymeric reagent IX is the direct bromination of β -naphthol and other arene derivatives under mild reaction conditions. However, the reactivity of IX is comparable to the corresponding reagent based on poly (chloromethylstyrene) resins (8). The ease and simplicity of the method seem to provide an improvement over the other routes used for the bromination of arenes. In addition, the regenerated polymeric reagent by recyclization of the polymeric by-product was reused again in further brominations as active as the original polymeric reagent.

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Correspondence:

A. Akelah
Chemistry Department Faculty
of Science Tanta University
Tanta, EGYPT.