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Polymeric acyl transfer reagents: synthesis of amides using polystyrene supported oximino esters

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Divinyl benzene-crosslinked polystyrene supported oximino esters were prepared and developed as a new class of recyclable solid phase acylating reagents. The preparation of these reagents involved a series of polymer analogous reactions starting from styrene–divinyl benzene crosslinked polymer. The introduction of acetyl, benzoyl and *p*-nitrobenzoyl groups into the polymer system and acylation reaction using these polymeric acyl transfer reagents are described. The spent polymeric reagent after the acylation reaction step can be easily removed by filtration and can be regenerated many times without loss in activity.

(Keywords: polystyrene oximino esters; polymeric acyl transfer reagents; polymer analogous reactions)

INTRODUCTION

Synthetic reagents bound to a polymeric backbone have been widely used in organic chemistry during the past two decades.[1–4] These insoluble reagents have the advantages over their soluble counterparts of easy separation from the reaction mixture and regenerability. In addition, the polymer matrix can provide selectivity in a reaction due to the steric constraints imposed by the macromolecular matrix or due to microenvironmental effects.[5–7]

Fridkin *et al.*[8] introduced the polymeric reagent method for peptide synthesis which made use of an insoluble polymer-supported amino acid active ester as the carboxyl component for coupling with the soluble amino component. Polymeric benzoic anhydrides have been used to benzoylate alcohols and amines[9] and *N*-trifluoroacetyl nylons have been employed for the trifluoroacetylation of alcohols and amines[10].

We report here the preparation of a polymeric acyl transfer reagent that contains oximino esters and their use in the selective acylation of amino groups. Polystyrene bound oximino esters were found to activate the carboxyl component for the formation of amide or peptide bonds. Preparation of acylating agents with different structural environments, the reaction conditions used for the acylation reactions and the effect of macromolecular support characteristics on the extent of acylation reactions are described in this paper.

RESULTS AND DISCUSSION

Preparation and characterization of polystyrene supported aldoximino and ketoximino esters

Polystyrene supported aldoximino and ketoximino esters were prepared by a series of polymer-analogous reactions starting from styrene–divinyl benzene crosslinked polymer. The reaction sequence is depicted in *Scheme 1*. The aldehyde group was introduced into copolystyrene–2% divinyl benzene resin (**1**) by chloromethylation[11] and subsequent oxidation using DMSO[12]. The aldehyde resin (**4a**) gave a yellow colour with 2,4-dinitrophenyl hydrazine reagent. The residual chlorine content was found to be 0.16 meq g^{-1}. The formation of the aldehyde resin was supported by the i.r. spectrum which showed peaks at 1725 cm^{-1} (C=O str) and 2920, 2860 cm^{-1} (C–H str) characteristic of the aldehyde group.

The keto group was introduced into polystyrene resin (**1**) by Friedel-Crafts reaction with acyl halide using Lewis acid catalyst[13]. In the present study the acyl halides used were CH_3COCl, C_6H_5COCl, and p-NO_2-C_6H_4COCl. The keto functional resin (**6a**, **8a**, **10a**) gave an orange colour with 2,4-dinitrophenyl hydrazine reagent which was characteristic of the keto group. The i.r. spectrum showed a strong carbonyl absorption band around 1700 cm^{-1}. In the case of acetyl resin, the extent of conversion was determined by iodoform method. The CH_3-CO-capacity of the acetyl resin was 2.88 meq g^{-1}. The functional group capacity of benzoyl and *p*-nitrobenzoyl resins were determined from the weight changes during their formation. The values were 2.96 and 3.2 meq g^{-1} respectively.

A nitro group was introduced on the 3-position of the phenyl group of chloromethyl polystyrene (**2**) and acetyl, benzoyl and *p*-nitrobenzoyl polystyrene (**6a**, **8a**, **10a**)

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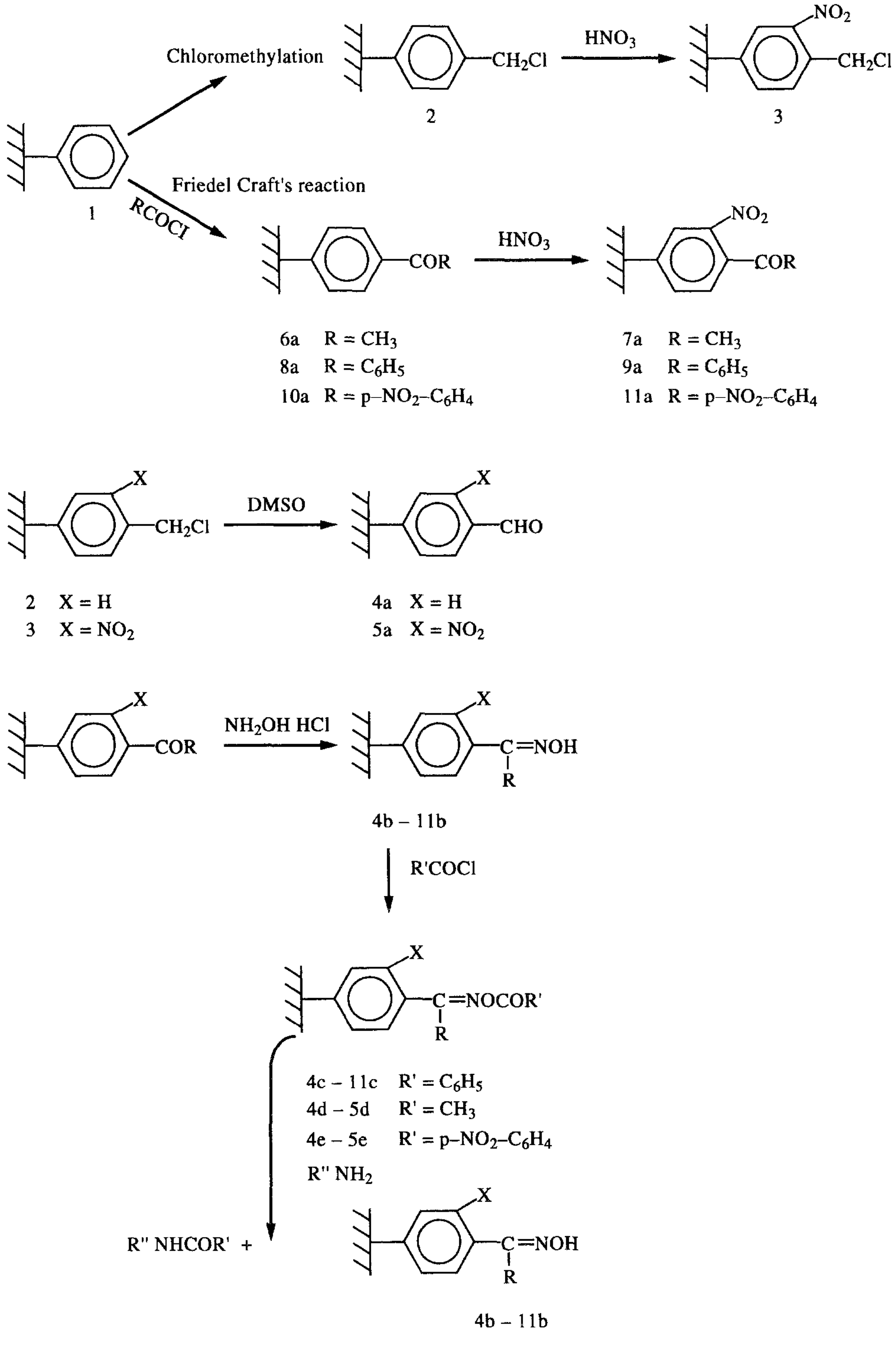

Scheme 1 Preparation of polystyrene based oximino esters and their acyl transfer reactions

backbone by nitration using fuming nitric acid[14]. The presence of a NO_2 group was supported by elemental analysis. The i.r. spectrum showed strong absorption bands at 1525 cm^{-1} and 1350 cm^{-1} characteristic of the -NO_2 group. The aldehyde/keto group in polystyrene was converted to the corresponding oximes by refluxing a mixture of the aldehyde/keto resin and hydroxylamine hydrochloride in the presence of trace amounts of pyridine[15]. The formation of oxime was supported by elemental analysis and an i.r. spectrum. The i.r. absorption band around 1700 cm^{-1} due to carbonyl stretching vibrations disappeared completely and new bands around 3400 cm^{-1} (OH str) and 1650 cm^{-1} (C=N str) appeared, indicating the complete conversion of the aldehyde and keto groups to the corresponding oximino group. The oxime capacity was determined by acetylation using an acetylating mixture[16].

The aldoxime/ketoxime resin was converted to the corresponding acyl derivative, otherwise named as polystyrene oximino esters by treating the former with acyl chlorides in the presence of trace amounts of pyridine as catalyst. The solvent used was a mixture of acetonitrile and chloroform in 1 : 1 v/v. The acyl chlorides used were C_6H_5COCl, CH_3COCl and p-NO_2-C_6H_4COCl. The formation of polystyrene oximino esters was supported by elemental analysis and estimation of

Table 1 Effect of structure of the reagent function on functional group capacity and extent of acyl group transfer[a]

Resin	R Group	X Group	R′ Group	Acyl group capacity (meq g^{-1})	Yield[b] (%)
4c	H	H	C_6H_5	1.60	62
5c	H	NO_2	C_6H_5	2.05	68
6c	CH_3	H	C_6H_5	1.70	65
7c	CH_3	NO_2	C_6H_5	2.10	70
8c	C_6H_5	H	C_6H_5	1.52	58
9c	C_6H_5	NO_2	C_6H_5	1.60	62
10c	*p*-NO_2-C_6H_4	H	C_6H_5	1.40	55
11c	*p*-NO_2-C_6H_4	NO_2	C_6H_5	1.52	58
4d	H	H	CH_3	1.25	50
5d	H	NO_2	CH_3	1.28	52
4e	H	H	*p*-NO_2-C_6H_4	1.75	65
5e	H	NO_2	*p*-NO_2-C_6H_4	2.10	70

[a] Using aniline as the substrate; solvent, chloroform; molar ratio, 2 : 1; temperature, 30°C

[b] Isolated yield of pure product noted after 3 h

Table 2 Acyl transfer reactions using polystyrene supported aldoximinobenzoate resins **4c** and **5c**

No.	Amine	Solvent	Duration[a] (h)	Percentage yield using **4c**	Percentage yield using **5c**
1	Aniline	$CHCl_3$	3	62	68
2	*o*-Toluidine	$CHCl_3$	3.5	65	70
3	*m*-Toluidine	$CHCl_3$	3.5	58	60
4	*p*-Toluidine	$CHCl_3$	3.5	60	65
5	*m*-Chloroaniline	$CHCl_3$	3.5	52	56
6	*p*-Chloroaniline	$CHCl_3$	3.5	50	52
7	*o*-Aminophenol	$CHCl_3$	3.5	58	60
8	Glycine	Dioxane: water (1 : 1)	5	55	60
9	Methyl amine	Dioxane	5	70	72
10	2,4-Dimethylaniline	$CHCl_3$	4	42	43
11	2,5-Dimethylaniline	$CHCl_3$	4	45	48
12	2,6-Dimethylaniline	$CHCl_3$	4	48	50

[a] Indicates time for maximum conversion

Table 3 Acyl transfer reactions using polystyrene supported aldoximinoacetate resins **4d** and **5d**

No.	Amine	Solvent	Duration[a] (h)	Percentage yield using **4d**	Percentage yield using **5d**
1	Aniline	$CHCl_3$	3	50	52
2	*o*-Toluidine	$CHCl_3$	3.5	55	57
3	*m*-Toluidine	$CHCl_3$	3.5	48	50
4	*p*-Toluidine	$CHCl_3$	3.5	52	52
5	*m*-Chloroaniline	$CHCl_3$	3.5	42	46
6	*p*-Chloroaniline	$CHCl_3$	3.5	40	45
7	*o*-Aminophenol	$CHCl_3$	3.5	48	55
8	Glycine	Dioxane: water (1 : 1)	5	50	52
9	Methylamine	Dioxane	5	58	60
10	2,4-Dimethylaniline	$CHCl_3$	4	32	38
11	2,5-Dimethylaniline	$CHCl_3$	4	35	40
12	2,6-Dimethylaniline	$CHCl_3$	4	35	42

[a] Indicates time for maximum conversion

Table 4 Acyl transfer reactions using polystyrene supported aldoximino-p-nitrobenzoate resins **4e** and **5e**

No.	Amine	Solvent	Duration[a] (h)	Percentage yield using **4e**	Percentage yield using **5e**
1	Aniline	$CHCl_3$	3	65	70
2	*o*-Toluidine	$CHCl_3$	3.5	68	72
3	*m*-Toluidine	$CHCl_3$	3.5	60	65
4	*p*-Toluidine	$CHCl_3$	3.5	63	68
5	*m*-Chloroaniline	$CHCl_3$	3.5	60	62
6	*p*-Chloroaniline	$CHCl_3$	3.5	55	58
7	*o*-Aminophenol	$CHCl_3$	3.5	64	70
8	Glycine	Dioxane: water (1 : 1)	5	60	62
9	Methyl amine	Dioxane	5	74	78
10	2,4-Dimethylaniline	$CHCl_3$	4	50	52
11	2,5-Dimethylaniline	$CHCl_3$	4	52	58
12	2,6-Dimethylaniline	$CHCl_3$	4	55	60

[a] Indicates time for maximum conversion

acyl group capacity. The disappearance of the i.r. band due to OH stretching frequency and the appearance of a new carbonyl absorption band around 1700 cm^{-1} is indicative of the completion of acylation reaction.

In order to determine the active acyl group capacity of polystyrene oximino esters (**4c–11c**, **4d** and **5d**, **4e** and **5e**), acylation of a standard solution of aniline was conducted using the polystyrene oximino esters. The unreacted aniline was determined by a titrimetric method. Values of the acyl group capacity obtained are given in *Table 1*.

When the extent of acyl group transfer is measured in terms of the efficiency of the leaving group, it is found that *p*-NO_2-benzoyl group has the highest capacity. Polystyrene aldoximino-*p*-nitrobenzoate has a capacity of 1.75 meq g^{-1} whereas the corresponding benzoate has a capacity of 1.6 meq g^{-1} and the acetate, 1.25 meq g^{-1}. *p*-Nitro-benzoyl group is supposed to be a better leaving group compared to benzoyl and acetyl groups.

Acyl transfer reactions using the polystyrene oximino esters

The polystyrene oximino esters, on reaction with amines, transfer their acyl groups to the amine forming an amide (*Scheme 1*).

The reaction involved stirring of the amine with the polystyrene oximino esters in 1 : 2 molar ratio in solvents like chloroform at room temperature. The reaction was monitored by t.l.c. After the reaction, the mixture was filtered, the resin was washed with the solvent, the filtrate and washings were collected together, which on evaporation afforded the product. In cases where complete conversion of the amine did not take place, before evaporation of the filtrate, the excess amine was extracted with dilute HCl. The products were recrystallised and characterized by comparison with authentic samples (i.r. and melting point).

In order to study the influence of the structure of the group -R on the extent of acyl group transfer, reaction of aniline with the different polystyrene oximinobenzoate resins was conducted and the results are given in *Table 1*.

The percentage yield of anilide obtained from acetyl oximinobenzoate (**6c**) is 65% where as the corresponding aldoximinobenzoate (**4c**) gave 62% yield. The extent of benzoylation obtained from benzoyl oximinobenzoate (**8c**) is only 58% and that of *p*-nitrobenzoyl oximinobenzoate (**10c**) is 55%. A higher extent of acyl group transfer from the acetyl oximinobenzoate is probably due to the presence of an electron releasing methyl group on the carboximino carbon. The lower extent of conversion from the benzoyl and *p*-nitrobenzoyl reagents may be partially due to the steric factors and partially due to electronic factors.

The acyl transfer reaction was tried on different amines using the polystyrene supported oximino esters as the acylating agents. The details of acyl transfer reaction are given in *Tables 2–4*. Percentage yield given in the table is the actual percentage of isolated pure product. Polystyrene oximino esters are selective for acylating an amino group in the presence of a hydroxyl group or carboxyl group. The resins on prolonged reaction with *o*-aminophenol produced only *o*-hydroxy benzanilide and with glycine gave only benzoyl glycine. The resins did not react with ethanol to give the respective esters (*Tables 2–4*).

Acylation of aniline using polystyrene supported aldoximinobenzoate gave 62% yield, corresponding aldoximinoacetate gave only 51% and aldoximino-*p*-nitrobenzoate gave 65% yield. *p*-Nitrobenzoyl group is found to be a better leaving group compared to benzoyl and acetyl groups. Thus the extent of acyl transfer is higher for the *p*-nitrobenzoyl esters.

Effect of a neighbouring nitro group

From the studies on acyl transfer reactions using the polystyrene supported aldoximino esters, it is observed that the extent of acyl transfer is higher in the case of resins having a nitro group at the 3-position of the phenyl residue of the polystyrene backbone. The results are given in *Tables 1–4*.

The nitro group is supposed to enhance the electrophilic character of the carbonyl carbon of the oximino esters. This may arise from the electron withdrawing inductive effect of the -NO_2 group. Similar cases have been reported where the presence of a nitro group increases the extent of acyl group transfer with polystyrene supported dithiocarbamic anhydrides[17].

Effect of reaction conditions on the extent of acyl transfer reactions

The acylation reactions using polymer bound oximino esters were found to be affected by the various conditions of the reaction like solvent, temperature, duration of reaction and the effective concentration of the reagent function. It has been observed that only when there is an effective interaction between the reagent function attached to the macromolecular matrix, the substrate and the reaction medium, the reaction takes place with a reasonable extent of functional group conversion.

Effect of solvent

A major factor influencing the efficiency of the polymer supported reaction is the type of solvent used for the reaction. The reactions using the polymeric acylating reagents are heterogeneous in nature, taking place in two distinct phases. The compatibility of the two phases is an important factor which controls the extent of the reactions[6,18]. The acylating reagents are macroscopically insoluble in almost all solvents. But the substrates, amines, are taken as solutions in some organic solvents. If reaction is to take place, strong interaction between the substrate in solution and the solid polymeric reagent must occur. Thus solvents which are capable of swelling the polymer network, which are also able to dissolve the low-molecular substrates, are found to be suitable for carrying out the acylation reactions. In order to investigate the effect of the nature of the solvent on the reactivity of the acylating reagents, the acyl transfer reaction with aniline was conducted using polymer supported aldoximinobenzoate in solvents like chloroform, dichloromethane, carbon tetrachloride, acetonitrile and dioxane. The percentage conversion after a specified period was noted and the results obtained are given in *Table 5*.

Table 5 Effect of solvents on acylation of aniline using polystyrene bound aldoximinobenzoate resin (**4c**)[a]

	% Yield of anilide formed in				
Acylating reagent	CH_2Cl_2	$CHCl_3$	CCl_4	CH_3CN	Dioxane
Polystyrene supported aldoximinobenzoate resin	65	62	60	52	45

[a] Substrate to resin ratio, 1 : 2; temperature, 30°C; time, 3 h

The highly polar solvents like acetonitrile and dioxane have not much effect on the extent of acylation reaction using polystyrene supported oximino esters. The yield of anilide obtained was comparably low in dioxane (45%). In chloroform, a reasonable amount of benzanilide was formed from aniline on acyl transfer. The work up of the reaction mixture is comparably easy with chloroform as the solvent, since it swells the polymer only to a reasonable extent. Both dichloromethane and chloroform are equally good for polystyrene supported aldoximinobenzoate resins in carrying out the acyl transfer reactions.

Effect of temperature

A second major factor influencing the rate of the polymer supported acylation reaction is temperature. In order to study the effect of temperature on the reactivity of polystyrene supported oximino esters, acylation of aniline was conducted at various temperatures, with chloroform as the solvent. The percentage conversion obtained using polystyrene aldoximinobenzoate after a definite period of time was noted and the results are given in *Table 6*.

Table 6 Effect of temperature on acylation of aniline using polystyrene bound aldoximinobenzoate resin (**4c**)[a]

	% Yield of anilide formed at				
Acylating reagent	20°C	30°C	40°C	50°C	60°C
Polystyrene supported aldoximinobenzoate resin	50	62	65	65	65

[a] Substrate to resin ratio, 1 : 2; solvent, chloroform; time, 3 h

The percentage yield of anilide obtained increased gradually and remained constant at temperatures beyond 40°C. Further increase in temperature did not affect the percentage yield.

Effect of duration of reaction

The acylaton reaction with aniline was carried out at room temperature in chloroform using polystyrene

Table 7 Acylation of aniline using polystyrene bound aldoximinobenzoate resin (**4c**) at various time intervals[a]

	% Conversion after				
Acylating reagent	1 h	2 h	3 h	4 h	6 h
Polystyrene supported aldoximinobenzoate resin	45	55	62	62	62

[a] Substrate to resin ratio, 1 : 2; solvent, chloroform; temperature, 30°C

Table 8 Acylation of aniline using polystyrene bound aldoximinobenzoate resin (**4c**) with different resin to amine ratio[a]

	% Conversion when the molar ratio is				
Acylating reagent	1 : 1	2 : 1	3 : 1	4 : 1	5 : 1
Polystyrene supported aldoximinobenzoate resin	36	62	64	72	86

[a] Solvent, chloroform; temperature, 30°C; time, 3 h

Table 9 Regeneration of the acylating reagent, polystyrene supported aldoximinobenzoate (**4c**)

No. of cycles	Capacity (meq g^{-1})	Acylation yield (%)[a]
1	1.6	62
2	1.6	62
3	1.52	58
4	1.45	56

[a] Acyl transfer to aniline in chloroform at room temperature. Yield noted after 3 h. Aniline to resin ratio, 1 : 2

supported aldomixinobenzoate. The percentage yield of the anilide obtained was determined at fixed time intervals. The results are given in *Table 7*.

The acyl transfer reaction was allowed to go to completion and the time for complete conversion was noted. No further change was noticed irrespective of the additional time for which the reaction was run. It was observed that the reaction proceeded rapidly in the initial stages until more than half of the substrate was converted to the product. Afterwards the speed of the reaction was found to decrease gradually as more and more of the acylating function was consumed.

Effect of molar ratio

To study the dependence of the reactivity of acylating function on their effective concentration, the acylation reaction with aniline was conducted at different reagent to substrate ratios. In the present study, the relative concentrations investigated were 1 : 1, 2 : 1, 3 : 1, 4 : 1 and 5 : 1. When the molar equivalent was used, the reaction did not go to completion in any case, irrespective of the duration of the reaction. The details of the acylation of aniline at room temperature in chloroform using the polystyrene supported aldoximinobenzoate with different resin to amine ratios are presented in *Table 8*.

With an increase in resin to amine ratio, there was a corresponding increase in the percentage yield of the anilide formed.

Recyclability of the polystyrene bound oximino esters

The polymeric byproduct obtained after the acyl group transfer reactions was found to be polystyrene oxime, the precursor of the acyl transfer reagent, by spectral and chemical analysis. Thus it could be converted to the original oximino ester resin by simple treatment with the acyl halide. The polystyrene byproduct obtained after the acyl transfer reactions were collected together and washed free of any low molecular weight contaminants was treated with the respective acyl halide in presence of pyridine. The regenerated resins were found to be equally good in transferring their acyl groups to amines in solution as in the original case. The acyl transfer capacity of the resins were found to be practically unaffected even after several recycling steps. The change in the capacity of the resins in the course of the recycling steps using the aldoximinobenzoate resin (**4c**) is presented in *Table 9*. The only loss observed during all these processes was mechanical due to powdering of the resins, unavoidable during magnetic stirring and due to repeated handling of the polystyrene samples.

The foregoing observations indicate that polystyrene based oximino ester resins fulfil the requirements of an efficient polymeric solid phase acylating reagent for the acylation of amino groups. The reagent has the advantages of increased shelf-life, operational simplicity, possibility of regeneration and reuse. The crosslinked polystyrene support system also offers the possibility of studying the effects of crosslink density and other structural parameters of the polymer matrix on the reactivity of the attached reagent functions.

EXPERIMENTAL

General

Infrared spectra were recorded on a Perkin-Elmer 397 spectrometer with KBr pellets. Solvents were purified and dried following literature procedures. The resin support used was 2% divinyl benzene crosslinked polystyrene, prepared by suspension copolymerization or purchased from Fluka. Melting points were determined on a hot stage melting point apparatus and are uncorrected. Microanalyses were performed at the Regional Sophisticated Instrumentation Centre, IIT, Madras.

Friedel crafts reaction of polystyrene (1) with chloromethyl methyl ether: preparation of chloromethyl polystyrene (2)

Polystyrene beads (10 g), pre-swollen in dichloromethane (20 ml) were added to a well stirred mixture of anhydrous $SnCl_4$ (3 g) and chloromethyl methyl ether (10 ml) at 0°C. The temperature was allowed to rise to 30°C during a period of 1 h. The mixture was then stirred for 10 h. Finally, the reaction mixture was cooled, filtered at the pump and washed successively with dioxane : water (1 : 1), dioxane–water–HCl, water and methyl alcohol. The resin was dried in vacuum. Yield: 14.5 g. Chlorine content: 4.2 meq g^{-1}.

*Preparation of polystyrene based ketones (**6a, 8a, 10a**)*

Polystyrene beads (10 g) were allowed to swell in carbon tetrachloride (20 ml) for 10 h. Acyl chloride (acetyl, benzoyl or *p*-nitrobenzoyl) (25 ml) was taken in a RB flask fitted with a reflux condenser and cooled in an ice bath. Anhydrous $AlCl_3$ (15 g) was added in small portions over a period of 30–45 min to the acyl chloride with stirring. After the addition was over, the pre-swollen polymer was gradually added to the reaction mixture with continuous stirring. The mixture was then heated under reflux for 10 h and kept overnight at room temperature. The reaction mixture was poured into aqueous ethanol to break the Lewis acid complex. The resin was filtered and washed with water, ethanol, acetone, dried in vacuum to constant weight. Yield: 19.5 g.

*Preparation of 3-nitro 4-chloromethyl polystyrene (3) and 3-nitro 4-keto polystyrene resins (**7a, 9a, 11a**)*

Chloromethyl polystyrene (**2**) or acetyl, benzoyl or *p*-nitrobenzoyl polystyrene resin (**6a**, **8a**, **10a**) (10 g was added to fuming nitric acid (150 ml) in a RB flask and the reaction mixture was stirred at 0°C for 1 h. The temperature was allowed to rise to 30°C during a period of 2 h. The contents were poured into water (300 ml) containing crushed ice. The resin was collected by filtration, washed with water, water–dioxane, ethanol and finally with methanol, drained and dried in vacuum. Yield: 13 g.

*Preparation of polystyrene based aldehydes (**4a, 5a**)*

Chloromethyl polystyrene (**2**) or 3-nitro 4-chloromethyl polystyrene (**3**) (10 g) was heated with dimethyl sulfoxide (150 ml) in presence of sodium bicarbonate (15 g) at 135°C for 15 h. The reaction mixture was cooled and filtered at the pump. The resin was washed successively with dimethyl sulfoxide, hot water, dioxane: water (1 : 1), dioxane, ethanol and methanol. The resin was dried in vacuum to constant weight. Yield: 8.5 g.

*Preparation of polystyrene based oximes (**4b–11b**)*

The aldehyde (**4a**, **5a**) or keto (**6a–11a**) resin (10 g) was mixed with hydroxyl amine hydrochloride (25 g) and pyridine (30 ml) in chloroform (50 ml). The mixture was refluxed at 80°C for 20 h. The resin was filtered and was washed successively with chloroform, water, ethanol and methanol. The resin was then dried in vacuum to constant weight. Yield: 11 g.

*Acylation of polystyrene based oximes: preparation of polystyrene oximino esters (**4c–11c, 4d and 5d, 4e and 5e**)*

The oxime resin (**4b–11b**) (10 g) was suspended in acetonitrile: chloroform mixture (1 : 1 v/v, 50 ml) and a 3-fold molar excess of acyl halide, (acetyl chloride, benzoyl chloride or *p*-nitrobenzoyl chloride) was added to the suspension. Pyridine (5 ml) was added and the mixture was stirred for 8 h. The reaction mixture was filtered at the pump to collect the resin particles, washed with acetonitrile, hot water, ethanol and methanol and dried in vacuum. Yield: 12 g.

Acyl transfer reactions using polystyrene oximino esters: general procedure

The polystyrene oximino esters (**4c–11c**, **4d** and **5d**, **4e** and **5e**) (1 mmol) was suspended in chloroform (20 ml) and the amine (0.5 mmol) was added to it. The mixture was stirred at room temperature for a definite period when maximum conversion was obtained as indicated by t.l.c. The mixture was then filtered and washed with chloroform. To the filtrate, dilute HCl (25 ml) was added and shaken well to remove the excess amine. The organic layer was collected and chloroform was evaporated off to get the amide. Results are shown in *Tables 2–4*.

Recycling of the spent oximino ester resins

The polystyrene oximino ester resins, obtained after the acyl transfer reactions, were collected together and washed free of any low molecular weight contaminants. The resin (2 g) was shaken with benzoyl chloride (5 ml) in acetonitrile: chloroform (1 : 1 v/v, 10 ml) mixture for 8 h. The product resin was filtered, washed with chloroform, acetonitrile, hot water, ethanol and methanol and dried. Yield: 2.2 g.

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