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PREPARATION OF POLYMER-BOUND 1,2 - AND 1,3 - DIAMINES

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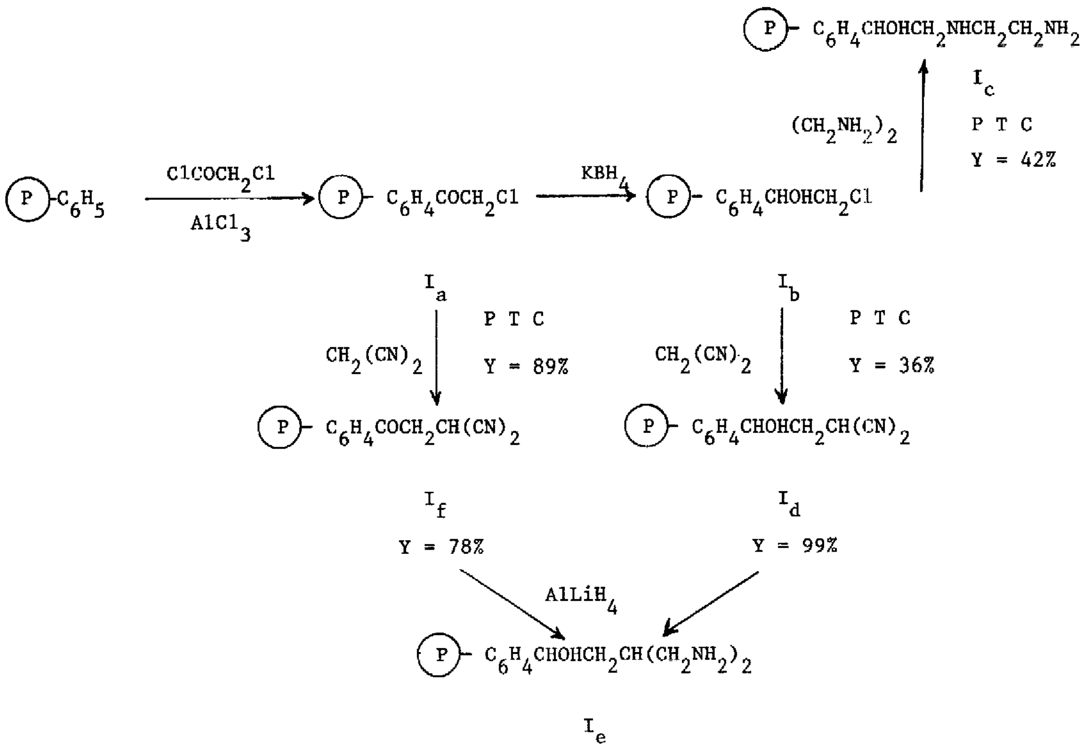
Two modified copolymers were used for the preparation of polymer bound symmetrical aliphatic diamines using phase transfer catalysis (P.T.C.). These compounds are potential ligands for transition metal ions.

A large number of functional polymers received wide applications as reagents in synthesis (1) or as supports of transition-metal catalysts (2). There are two major advantages over solution chemistry : a) an easier isolation of the desired product after reaction b) a quantitative regeneration of either the reagent or the catalyst bound to the insoluble polymer to its former activity in a convenient way.

We report the preparation of polymeric 1,3-and 1,2-diamines. Such polymeric ligands were proved to be suitable for the complexation of metal ions or the immobilization of crown compounds (3). Nevertheless a litterature survey shows that diamines attached to an insoluble polymer were poorly studied (4). Two types of insoluble supports were used. (I) is a functionalized 12% cross-linked divinylbenzene-styrene macroporous copolymer (5). This resin is flimsy, but has a good swelling property (160% in toluene) and a high specific surface (6). (II) a Merrifield copolymer (7), with good mechanical and poor swelling properties, has been extensively used as polymeric reagents.

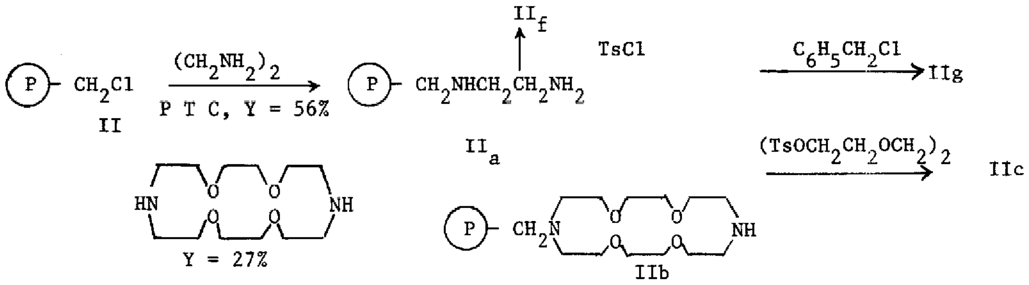
The Friedel-Crafts reaction of $ClCH_2COCl$ on (I) in the presence of a catalytic amount of $AlCl_3$ leads to (Ia) ($\nu_{C=O}$ 1685 cm^{-1} strong). Polymer (Ia) (2.1 m eq Cl/g) has a degree of functionalization of 0.26. (Ia) can be reduced with KBH_4 to (Ib) (ν_{OH} 3400 cm^{-1} broad). Using Triton B as phase transfer catalysis (Ib) reacts with an excess of ethylenediamine (8) leading to (Ic) (ν 3390 cm^{-1} broad) or with an excess of malononitrile giving (Id) (ν_{OH} 3370 cm^{-1} broad, ν_{CN} 2190 cm^{-1} strong). Reduction of (Id) by $AlLiH_4$ leads to the diamine (Ie). (Ie) can be obtained with a better degree of functionalization (70% of chloride sites were transformed) by a sequence of reactions which involves reaction of (Ia) with malononitrile using phase transfer catalysis, formation of (If) ($\nu_{C=O}$ 1700 cm^{-1} strong, $\nu_{C=N}$ 2190 cm^{-1} strong) and the subsequent reduction of (If) with lithium aluminium hydride in T.H.F.



Yields (Y) were calculated from microanalysis data (14)

The reaction of Merrifield resin (II) with ethylenediamine using phase transfer catalysis yields (IIa) and with cryptand 22 (IIb) (9). Reaction of (IIa) with the tosylate of 3,6 dioxaoctane 1,8 diol leads to (IIc). The activity of crown coumpounds (IIb) and (IIc) as phase transfer catalyst was tested with bromoheptane and KCN (10).

Resin (II) and an excess of 1,2-diamino benzene or 1,8-diamino naphtalene lead to (IId) or (IIe) (12).



Transformations of (Ib) into (Ic) and (II) into (IIa) were conducted with a large excess of diamines (8). It was shown that many symmetrical difunctional compounds can be monoblocked using an insoluble polymer and an excess of reactant(13). In this work, however the possibility of crosslinking between the diamine and two close chloride sites cannot be ruled out. Reaction of (IIa) with an excess of tosylchloride yields (IIf). The NH-Ts groups give to the resin some acid property. (IIa) with dichlorocarbene generated using phase transfer catalyst gives a resin containing isonitrile groups caracterized by IR spectroscopy (ν_{NC} 2180 cm^{-1} weak). These two reactions give evidence that one primary amine group is free but the fact that the ratio $\frac{eqN}{eqH^+} > 2$(obtained by the titration of compound (IIf)) shows that some ends of symmetrical diamines are attached themselves to the polymer.

(Ie), (IIa) and (IIc) can complex transition metal cations in water solution (eg : Co^{2+}, Rh^{3+}). This type of complex is under study as a catalyst. In this work, the use of phase transfer catalyst is an attractive way for the reaction of a hydrophobic polystyrene resine with a hydrophilic reagent like a diamine or a cryptand 2.2.

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5 Copolymer (I) was a gift from DIA-PROSIM (France)

6 - The specific surface of resin Ic measured by B.E.T. method is 630 m^2/g

7 - 2% crosslinked divinylbenzene-styrene copolymer (Merck) - (chloride content 1,1 - 1,4 meq/Cl/g resin).

8 - 1g resin Ib, 3 ml ethylenediamine (50 mmol) were stirred with 1g Triton B in 15 ml 25% NaOH at room temperature for 3h.

9 - Tetraoxa -1,7, 10, 16 diaza - 4,13 cyclooctadecane (Merck) purified by chromatography on Al_2O_3 with benzene.

10 - 5 10^{-3}M KCN in 2 ml water, 10^{-3} M C_7H_{15} Br in 1ml toluene and 50 mg of polymer are stirred at 90° for 17h. Analysis G.C. Column at 190°C, 10% silicone SE 30 on chromosorb GAW DMCS 80-100 mesh, lenght : 3m ; turn over IIb = 20, IIc = 50. Their catalytic activities seem to be lower than those described by S.L. Regen (11) and F.Montanari (3). However the experimental conditions and the concentration of the crown compound bound to the support are different.

11 - S.L. Regen, Angew. Chem. Int. Ed. Engl., 18, 421 (1979).

12 - The reactions are conducted under nitrogen atmosphere in order to avoid the rapid oxydation of the aromatic amines.

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14 - Microanalysis data.

	%Cl	%N	%S	$Cl_{meq/g}$	$N_{meq/g}$
Ia	7.58			2.10	
Ib	7.28			2.05	
Ic	2.53	2.45		0.70	1.74
Id	1.00	2.09		0.28	1.50
Ie from Id		2.08			1.48
Ie from If		3.96			2.80
If	1.38	5.22		0.38	3.72
II	5.08			1.40	
IIa	2.13	2.21		0.60	1.58
IIb	2.32	1.06		0.65	0.76
IIc		1.85	0.50		1.32
IIf		2.24	5.54		1.60

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