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PHASE TRANSFER CATALYSIS IN THE CHEMICAL MODIFICATION OF POLYMERS. PART II [1] .

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Summary: A soluble partly chloromethylated polystyrene has been successfully modified by compounds containing labile hydrogen and by NaCN or NaSCN, under PTC conditions.

Phase transfer catalysis (PTC) has been widely used in organic chemistry [2]. This method has received little attention in the field of the chemical modification of polymers. Roovers [3] has adapted a process using crown ethers to solubilize and activate potassium acetate in non-polar solvents for the acetylation of partly chloromethylated polystyrene. More recently Frechet et al [4,5] have studied the reaction of 1,4- butanedithiol and of malononitrile with cross-linked chloromethylpolystyrene under PTC conditions. This prompts us to publish some of our results in this field [6]. We have already reported the reaction of different amines with several soluble and cross-linked chloromethylated polymers, using phase transfer catalysts [1]. The best solvent is DMF for this type of reaction. Quantitative yields of substitution are obtained with chloromethylated polystyrene.

In this paper, we want to report some of our results concerning the application of PTC to the transformation of a soluble partly chloromethylated polystyrene [7] (PCMS) with alcohols, phenols, thiols, phthalimide, phenylacetonitrile, indene, propionic acid, NaCN and NaSCN. Phase transfer catalysts are tetrabutylammonium hydrogensulfate (TBAH) and the cryptand |222|. The polymer PCMS (10^{-2} mole) is dissolved in 150 ml DMF. The substituent ($1.5\ 10^{-2}$ mole) and a 50% aqueous solution of NaOH (4 ml) (except in the case of NaCN and NaSCN) are then introduced. After addition of a given amount of catalyst, the heterogeneous mixture is stirred, generally at 60°C, for a few hours and then filtered after cooling. The modified polymer is recovered after precipitation in methanol or water and further purified by several dissolutions in chloroform or THF and precipitations. It is then dried under high vacuum and analyzed by IR and ^{1}H NMR spectroscopy. Composition of the polymer is determined by elemental analysis and the degree of substitution of chloromethylated groups is calculated from the percentages of Cl and of N or O, S and C . Analysis of a PCMS sample treated in DMF with a 50% aqueous solution of NaOH in the presence of 5% molar of TBAH, at 60°C for 3 h. , does not show any significant change.

The results are shown in Table I. High yields of substitution are observed which are of the same order of magnitude those obtained in organic chemistry in solvents of much lower polarity [2]. When chloromethylated polystyrene is allowed to react with a carboxylic acid, such as propionic acid, under PTC conditions, esterification takes place but hydrolysis of ester functions simultaneously occurs due to the presence of OH^- in the medium. In our conditions a quantitative transformation of CH_2Cl groups is observed. This reaction is very interesting since direct hydrolysis of poly-p-chloromethylstyrene is impossible. Introduction of hydroxymethyl groups into polystyrene requires two long steps [8]. The resulting styrene /-p-vinylbenzyl alcohol copolymer (90/10) is still soluble in benzene but not in methanol whereas our modified sample (66/34) which contains more CH_2OH groups is soluble in methanol.

TABLE 1

Chemical modification of PCMS by PTC in DMF.

Run	Substituent	Catalyst [a]	T°C	Reaction time (h)	Degree of substitution (%)
1	N,N-diethylethanolamine	TBAH	60	1.5	75
2	p-methoxybenzylalcohol	TBAH	60	2	100
3	2,6-dimethylphenol	TBAH	60	2	93
4	2-mercaptopyrimidine [b]	TBAH	60	0.75	82
5	phthalimide	TBAH	60	2	87
6	phenylacetonitrile	TBAH	70	2	82
7	indene	TBAH	70	2	70
8	propionic acid	TBAH	70	3	100
9	sodium cyanide	TBAH	80	2	95
10	sodium thiocyanate	|222|	60	2	76

a) 5 mol % of the chlorine content of polymer except for run 7 and 8 (10 mol %) and for run 9 (15 mol %). b) run made with NaOH 5 N.

Molecular weights of modified PCMS have been measured by osmometry ($\overline{M}_n$) and by GPC. There is a good agreement between measured and calculated $\overline{M}_n$ as shown in Table 2.

TABLE 2.

Molecular weights $\overline{M}_n$ of modified polymers.

Run	Substituent	$\overline{M}_n$ osm.	$\overline{M}_n$ theor. [a)]
0	-	170,000	-
2	p-methoxybenzylalcohol	192,000	220,000
3	2,6-dimethylphenol	267,000	209,000
4	2-mercaptopyrimidine	198,000	200,000
6	phenylacetonitrile	260,000	202,000
10	sodium thiocyanate	150,000	178,000

[a)] calculated from $\overline{M}_n$ osm. of unmodified PCMS and the degree of substitution.

This means that no appreciable degradation occurs under PTC conditions. The slight increase of measured $\overline{M}_n$ compared to the theoretical value observed with 2,6-dimethylphenol and phenylacetonitrile might be due to a small amount of C-alkylation and dialkylation respectively. This is confirmed by GPC diagrams. A detailed paper will be published elsewhere.

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