CHEMICAL MODIFICATION OF CROSSLINKED RESINS BY PHASE TRANSFER CATALYSIS: PREPARATION OF POLYMER-BOUND DINITRILES AND DIAMINES

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The preparation of insoluble functional polymers by chemical modification¹ is of current concern in view of the large number of applications which these resins possess. We have been interested mainly in the reactions of crosslinked polystyrene resins which are available commercially in convenient bead form, and are easy to functionalize by reaction on the aromatic rings. Resins containing multiple amine functions^{2,3,7} have been used extensively to prepare polymeric complexing agents which can selectively bind various metal ions. Although polymers containing malononitrile or similar dinitrile functionalities are likely to be useful in the preparation of such chelating resins, they have received little attention as their preparation results in low functional yields and in products which may be contaminated with undesired functionalities. The best published procedure² for the preparation of such polymers involves the reaction of a chloromethylated product with the anion of malononitrile in DMF using ethoxide ion as base. This method produces a polymer in which only 30% of the original chloromethylated sites have been transformed into the dinitrile. Our recent success in the use of phase transfer catalysis to prepare sulfur ylides on solid phase from the corresponding polymeric sulfonium salts 4 prompted us to test the application of phase transfer catalysis to the transformation of functional groups on insoluble polymers. Thus, alkylation of malononitrile with crosslinked polystyrene is achieved in almost quantitative yield using phase transfer catalysis in a three phase system³. The polymer (1% crosslinked, 1.8 mequiv Cl/q, Degree of Functionalization D.F. = 0.205) is swollen in o-dichlorobenzene containing an excess of malononitrile. After addition of a 50% solution of NaOH and a small amount of tetrabutyl ammonium hydroxide, the mixture was stirred at 80 $^{
m o}$ for 2-3 days. After washing thoroughly and drying, the polymer showed a very sharp CN absorption at 2200 cm⁻¹ in the infrared spectrum and contained 4.67% N (1.67 mequiv. dinitrile/g, D.F.=0.200) for a functional yield of 98%. The malononitrile polymer could be reduced easily by reaction with lithium aluminium hydride to yield the polymer-bound diamine in essentially quantitative conversi

$$(P)-CH_2C1 \xrightarrow{CH_2(CN)_2} (P)-CH_2CH_{CN} \xrightarrow{CN} (P)-CH_2CH_{CN} \xrightarrow{CH_2NH_2} (P)-CH_2CH_{CH_2NH_2} (P)-CH_2CH_2 (P)-CH_2NH_2 (P)-CH_2NH_2 (P)-CH_2NH_2 (P)-CH_2NH_2 (P)-CH_2NH_2 (P)-CH_2NH_2 (P)-CH_2NH_2 (P)-CH_2NH_2 (P)-CH_2NH_2 (P)-CH_2NH_2$$

A second, somewhat similar polymeric diamine was prepared using also a three phase reaction with phase transfer catalysis; for this reaction the polymer itself was used as nucleophile. The starting material was a readily available p-cyanomethylated polystyrene⁶ (1% crosslinked, 2.5mequiv CN/g, D.F. = 0.29) which was used in phase transfer reaction involving o-dichlorobenzene as swelling agent, with chloroacetonitrile, 50% aqueous sodium hydroxide and Adogen 464 (Aldrich Chem. Co.) as phase transfer catalyst. The product of the reaction contained 5.76% N (2.06 mequiv. dinitrile/g; D.F.=0.26) for an 88% functional yield. Duplicate experiments attempted under slightly different conditions gave almost identical results, indicating that the trinitrile which might conceivably form by abstraction of two acidic hydrogens from the starting polymer, was not obtained. The IR spectrum of the dinitrile included two sharp CN bands centered at 2200 cm⁻¹(strong) and 2250 cm⁻¹(medium). Conversion of the dinitrile to the diamine was accomplished easily by reduction of the polymer with LiAlH₄. The reduction was accompanied by the disappearance of the CN bands and the appearance of a new band at 3400 cm⁻¹.



<u>Acknowledgement</u>: Financial support by the National Science and Engineering Research Council of Canada is gratefully acknowledged.

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(Received in USA 7 November 1978)