

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 salts⁴ 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 system⁵. The polymer (1% crosslinked, 1.8 mequiv Cl/g, 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° 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 conversion.



