

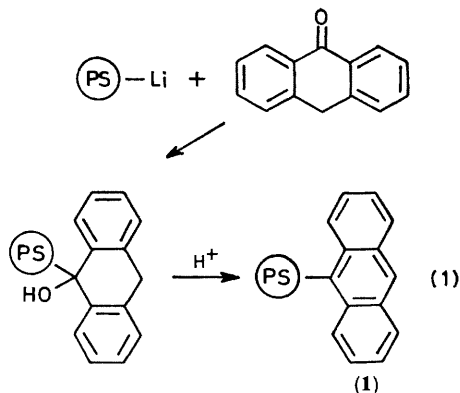
Polymer-bound Alkali Metal Aromatic Radical Anions

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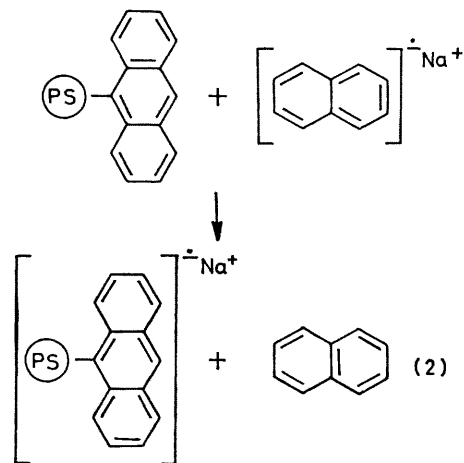
Summary Polystyrene-bound anthracene has been prepared and found to react with sodium-naphthalene to give a polymeric radical anion whose chemistry is analogous to that of soluble alkali metal aromatic radical anions.

FUNCTIONALIZED organic polymers containing reactive pendant groups are proving to be useful in both polymer chemistry and organic synthesis.¹ In this report we describe the first synthesis of an alkali metal aromatic radical anion bound to an organic polymer. In addition, examples of reactions of this polymeric organometallic reagent with organic and inorganic substrates are detailed.



A functionalized polymeric precursor to a polymeric aromatic radical anion is readily prepared by addition of an ethereal solution of anthrone to lithiated macroreticular

polystyrene. Subsequent treatment of the polymer bound tertiary alcohol with toluene-*p*-sulphonic acid in hot benzene yielded polystyrylanthracene (equation 1). Reduction of this polymeric polycyclic aromatic compound with a tetrahydrofuran (THF) solution of sodium-naphthalene according to equation (2) yields the polymeric radical



anion. Formation of this metallated polystyrene radical anion is accompanied by rapid decoloration of the THF solution of sodium-naphthalene and concomitant development of a dark blue-green colour on the polymer. Gas chromatographic analysis of the clear supernatant liquid over this coloured polymer shows that all the naphthalene originally added is present in solution. Aqueous quenching

of an aliquot of this solution also shows the absence of soluble base. These data are all in accord with quantitative formation of the polymeric radical anion and are not unexpected based on the relative reduction potentials of similar arenes in solution.² Based on the reactions of polymer (1) with alkyl halides (*vide infra*) there is an estimated 0.5 mmol of reducing agent per g of polymer using these synthetic procedures for (1).

Preliminary experiments have shown that polymeric alkali metal aromatic radical anions like the one prepared in equation (2) can be synthetically useful and mechanistically interesting. For example, aromatic radical anions are known to be useful reducing agents for the generation of anionic transition metal complexes.³ Using the polymeric radical anion prepared in equation (2) and π -cyclopentadienyldicarbonyliron dimer, we generated a solution of a nucleophilic iron complex which was trapped *in situ* with 2% divinylbenzene crosslinked chloromethylated polystyrene. The resulting polymeric organoiron compound was characterized by i.r. spectroscopy and by the characteristic rust colour of the polymer. Since the solution of the nucleophilic iron complex could be readily separated from the insoluble polymeric reducing agent, the polymeric organoiron reagent obtained using this procedure was not contaminated by spent reducing agent or by by-products derived from the reducing agent.

Aromatic radical anions are also known to be reactive reducing agents toward organic halides.^{2,4} The polymeric alkali metal aromatic radical anions we have prepared undergo qualitatively similar reactions. Alkyl iodides, bromides, and chlorides are partially reduced to hydrocarbons and in some cases i.r. evidence has been obtained which shows that alkylation of the polymeric aromatic radical anions has occurred. For example, reaction of sodium polystyrylanthracene with 1-iododecane leads to formation of 25% of n-decane and 4% of n-icosane. The remainder of the starting 1-iododecane which reacts apparently binds to the polymer as suggested by changes in the i.r. spectrum of the product polymer. Ethyl 11-iodoundecanoate reacts similarly with sodium polystyrylanthracene to give a polymeric product containing a strong carbonyl absorption at 1740 cm⁻¹. Our observation of formation of both reduced alkyl halide products (*ie* alkanes) and alkylated polymer products parallels known chemistry of sodium-naphthalene.

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