New Linking Reactions for the Synthesis of Head-to-head Vinyl Polymers

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WE have recently described[1] a technique for making vinyl-type polymers with head-to-head linkages instead of the conventional head-to-tail bonds. The process involves the synthesis of disodium salts of dianions of type (I) or (II)

$$\mathrm{Na_2^+[\bar{C}RR'\cdot CH_2\cdot CH_2\cdot \bar{C}RR']} \qquad \text{(I)}$$

$$\mathrm{Na_2^+[\bar{C}RR'\cdot CH_2\cdot CRR'\cdot CH_2\cdot CH_2\cdot CRR'\cdot CH_2\cdot \bar{C}RR']}$$
(II)

and their subsequent coupling, by a controlled reaction with iodine. The disadvantages of this synthesis are that the molecular weight of the product appears to depend on the purity of the iodine and on the precision of its addition, and that it tends to produce thermally weak terminal carbon–iodine bonds. We have therefore looked for other linking methods and have used the disodium salt of α-methylstyrene tetramer as a substrate for testing the reactions. The tetramer is relatively easy to prepare[2] and has the structure (II; $R = Me$, $R' = Ph$).[3] The maximum amount of head-to-head bonding obtainable is therefore 50%.

Iwakura *et al.*[4] have shown that the α-methyltetramer dianion reacted with certain ketones on heating to give a polymer and ketyls. We have found two novel linking reactions which proceed at ambient temperature.

In the first reaction, a solution of triphenylmethyl bromide in tetrahydrofuran solution was added to a similar solution of the dianion. The characteristic red colour of the carbanion was immediately discharged and on adding the solution to excess methanol a polymer was precipitated. The ^1H n.m.r. and i.r. spectra of the product were identical with those of the polymer produced from the iodine reaction.[1] The polymer formed regardless of how great an excess of the triphenylmethyl bromide was used.

In the second reaction, a tetrahydrofuran solution of the tetramer, to which mercury had been added, lost its red colour on shaking overnight. The polymer, precipitated by admixture with methanol, had identical ^1H n.m.r. and i.r. spectra to the other polymers. The polymer was formed independently of the degree of excess of the mercury.

The triphenylmethyl bromide reaction is an example of the effect of steric hindrance on the course of the reaction. Normally, carbanions are metathetically alkylated by alkyl halide, inorganic halide being eliminated.

$$\mathrm{R\,Na} + \mathrm{R^1X} \rightarrow \mathrm{R} - \mathrm{R^1} + \mathrm{NaX}$$

However, the polymer from this reaction gives an n.m.r. spectrum with an aliphatic to aromatic hydrogen ratio of 1 : 1·05, showing that very little triphenylmethyl radical has been incorporated in the polymer. It is thought that in the reaction, two free radicals are produced initially which are unable to combine because of steric hindrance. Two polymeric radicals may however dimerise because the steric conditions are less stringent

i.e.

$$\overset{+}{\mathrm{Na}}\,\mathrm{T}^{2-}\,\overset{+}{\mathrm{Na}} + \mathrm{Ph_3CBr} \rightarrow \overset{+}{\mathrm{Na}}\,{}^{-}\mathrm{T}\cdot + \mathrm{Ph_3C}\cdot + \mathrm{NaBr}$$

$$2\,\overset{+}{\mathrm{Na}}\,{}^{-}\mathrm{T}\cdot \rightarrow \overset{+}{\mathrm{Na}}\,{}^{-}\mathrm{T{-}T}^{-}\,\overset{+}{\mathrm{Na}} \text{ and so on}$$

where T^{2-} = tetramer dianion. This mechanism therefore accounts for the formation of polymer in the presence of excess alkyl bromide.

The reaction with mercury is analogous to that of certain other organometallic compounds. For example, the disodium salt of the dimer of 1,1-diphenylethylene, (I; R = R′ = Ph) reacts with mercury to regenerate the monomer[5]. A similar reaction occurs with iodine,[6] where the reaction proceeds by the stages

$${}^{-}\mathrm{D{-}D}^{-} + \tfrac{1}{2}\mathrm{I_2} \rightarrow {}^{-}\mathrm{D{-}D}\cdot + \mathrm{I}^{-}$$

$${}^{-}\mathrm{D{-}D}\cdot \rightarrow {}^{-}\mathrm{D} + \mathrm{D}$$

$${}^{-}\mathrm{D} + \tfrac{1}{2}\mathrm{I_2} \rightarrow \mathrm{D} + \mathrm{I}^{-}$$

where D = $\mathrm{Ph_2C{\cdot}CH_2}$ and the middle reaction is the rate-determining step. The radical anion dissociates rather than polymerises because of steric hindrance. When the hindrance is less, as with the α-methylstyrene tetramer, polymerisation takes place as follows

$$\overset{+}{\mathrm{Na}}\,\mathrm{T}^{2-}\,\overset{+}{\mathrm{Na}} + \mathrm{Hg} \rightarrow \overset{+}{\mathrm{Na}}\,{}^{-}\mathrm{T}\cdot + \mathrm{Na(Hg)}$$

$$2\,\overset{+}{\mathrm{Na}}\,{}^{-}\mathrm{T}\cdot \rightarrow \overset{+}{\mathrm{Na}}\,{}^{-}\mathrm{T{-}T}^{-}\overset{+}{\mathrm{Na}} \text{ and so on}$$

with the formation of sodium amalgam as by-product.

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