

The Synthesis of Vinyl Polymers with Head-to-head Bonding

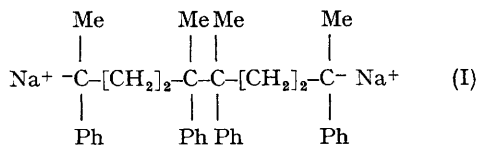
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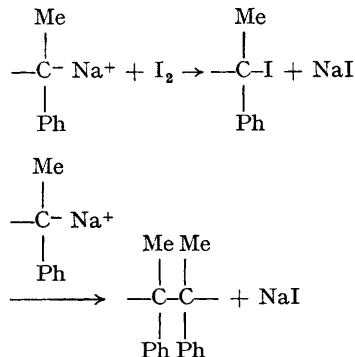
ALTHOUGH the polymerisation of vinyl compounds usually takes place by a head-to-tail addition,¹ under certain conditions such as high temperature the less energetically favourable head-to-head addition could become possible. For example, Grassie and Kerr² have observed a correlation between the number of thermally weak links in polystyrene and the temperature of its preparation. It is therefore of interest to prepare polymers in which head-to-head links predominate to study the effect of these on the physical and chemical properties of the polymer.

A possible synthesis of these polymers was suggested to us by the observation that the molecular weight of the polymer prepared by iodine termination of living anionic polystyrene was several times that of the polymer formed by killing the same polymer with water.

At concentrations less than the equilibrium monomer concentration for polymerisation, α -methylstyrene reacts with sodium in tetrahydrofuran solution to give the disodium salt of a tetramer which has been shown³ to have the structure (I)



If a solution of iodine in tetrahydrofuran is added very slowly to a solution of (I), there is a steady diminution of the characteristic deep red colour of the carbanion. Sodium iodide is eliminated in accordance with the reaction sequence



and the hydrocarbon residues are coupled in a head-to-head manner. The product can be precipitated by pouring the solution into an excess of methanol in the usual way. Its identity as a poly- α -methylstyrene is established by its microanalysis, infrared, and nuclear magnetic resonance spectra. However, there are features in the latter

two which differentiate it from normal poly- α -methylstyrene. For example, the methyl and methylene stretching vibrations which occur for the normal polymer at 2983 and 2891 cm^{-1} and 2933 and 2865 cm^{-1} (CS_2 solution) lie at 2969 and 2878 cm^{-1} and 2938 and 2859 cm^{-1} in the new polymer, and differ considerably in relative intensities. This indicates differing steric hindrance in the two compounds.⁴ Other bands in the rest of the spectrum also show displacements.

The n.m.r. spectrum (CS_2 solution) of the head-to-head polymer has absorptions at τ 3.05 (C_6H_5), several in the range τ 7.7—8.7 (CH_2) and at τ 9.09, 9.28, and 9.61 (CH_3). The corresponding values⁵ for normal poly- α -methylstyrene are near τ 3.05, 8.40, and 8.52 (CH_2) and 9.22, 9.74, 10.08 (CH_3), the differences being greater than possible experimental error.

Thermal degradation of the polymer at 284° gives less than 1% monomer but considerable amounts of viscous low-molecular-weight oils are also formed. Under similar conditions⁶ normal poly- α -methylstyrene yields more than 95% monomer.

So far, polymers with number-average molecular weights up to 3000 have been produced, the chief limitation of molecular size apparently being inadequate drying of the iodine solutions. The technique is now being applied to other vinyl monomers, which form stable carbanions by the action of electron-transfer agents, the reduction of the anion being accomplished by the addition of iodine or electrolytically.

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