Cationic Polymerization of 9-Vinylacridine

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Summary 9-Vinylacridine (VAcr) was polymerized with ethyldichloroaluminium to give poly-9-vinylacridine (PVAcr).

IN a search for new vinyl polymers having large π-electron systems, we have been investigating the polymerization of VACr. Homer and Shinitzky[1] recently reported that radical polymerization of VAcr gave PVAcr, but that cationic and anionic polymerization gave no polymers. However, we have confirmed that cationic polymerization with $AlEtCl_2$ could give a polymer.

A solution of $AlEtCl_2$ in benzene (1—40 mol%/monomer) was added under dry nitrogen at room temperature to a benzene solution of VAcr (m.p. 89·0—89·5°), which was synthesized from 9-methylacridine by a Mannich reaction according to Tsuge's method.[2] A yellowish-brown precipitate (I) formed immediately, which was filtered and dissolved in methanol after 20—38 hr. and reprecipitated with benzene. PVAcr (II) was obtained by adding aqueous ammonia to the methanol solution of (I). The polymer (II) was separated by extraction with benzene into a benzene-soluble polymer (III) (reprecipitated with n-hexane) and a benzene-insoluble polymer (IV).

The i.r. spectrum of (I) was identical to that of the yellowish-brown precipitate obtained from (IV) on treatment with gaseous HCl in tetrahydrofuran, indicating that the benzene-insoluble precipitate (I) is the HCl salt of PVAcr.

The PVAcr thus prepared gave correct elemental analyses and its i.r. spectrum showed no vinyl absorption. The molecular weights of (III) and (IV) measured with a Mechrolab vapour pressure osmometer were about 2000—4000 and about 4000—6000, respectively. The polymer was soluble in tetrahydrofuran and chloroform, partly soluble and swelling in benzene, toluene and methanol, and insoluble in n-hexane.

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[1] R. B. Homer and M. Shinitzky, *Macromolecules*, 1968, **1**, 469.
[2] O. Tsuga, unpublished data.