Solid-state Photo-polymerization of Unsaturated Organic Cations in Layer Perovskite Halide Salts

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Summary U.v. and *X*-ray irradiation causes polymerization of amino-diacetylene cations $R^1NH_3^+$ and $H_3NR^2NH_3^{2+}$ where $R^1 = ClCH_2C{\equiv}C{-}C{\equiv}CCH_2{-}$ and $R^2 = ({-}CH_2CO_2CH_2C{\equiv}C{-})_2$ in the solid salts $(R^1NH_3)_2CdCl_4$ and $(H_3NR^2NH_3)CdCl_4$ with the layer perovskite structure; under the same conditions tetrachlorocadmate salts $(RNH_3)_2CdCl_4$ ($R = CH_2{=}CHCH_2{-}$ and $CH{\equiv}CCH_2{-}$) do not react.

Recently there has been much interest in the physical properties of polymers with conjugated backbones such as polyacetylenes,[1] polydiacetylenes,[2] and polypyrrole-[3] and poly-*p*-phenylene-derivatives[4] because doping with electron acceptors may result in metallic conductivity. In most cases the polymers are either fibrillar[1] or amorphous.[4] It would be a great advantage if they could be prepared in oriented form or even as single crystals and in this note we report preliminary experiments on the photopolymerization of organic cations containing unsaturated sidechains held in rigid arrays between the infinite two-dimensional inorganic anions in layer perovskite halide salts.

In many compounds $(RNH_3)_2MX_4$ and $(H_3NR'NH_3)MX_4$ (M = Cr, Mn, Fe, Cu, Cd; X = Cl, Br) the metal and halide ions form infinite layers of corner-sharing octahedra separated by the organic cations, which are hydrogen-bonded to the axial halide ions.[5] We have prepared new compounds with R and R′ containing a variety of unsaturated functional groups which potentially might undergo ultraviolet photolysis in the solid state to yield conjugated polymers.† Samples were sandwiched in thin layers between quartz plates sealed to prevent atmospheric oxidation. They were irradiated by a water-cooled 1 kW hydrogen discharge lamp with a sapphire window, producing a continuum to wavelengths shorter than 200 nm. All the salts employed were tetrachlorocadmates because the $CdCl_4^{2-}$ ion has no absorption down to 200 nm.

After a preliminary experiment to show by i.r. spectroscopy that the well known[6] solid-state dimerization of *trans*-cinnamic acid took place rapidly under the conditions of our experiment the first tetrachlorocadmate salts photolysed were those with $R = CH_2{=}CHCH_2{-}$ and $CH{\equiv}CCH_2{-}$. In neither case was there any change in the i.r. spectrum or visible colour after 48 h irradiation. Next we synthesised tetrachlorocadmate salts of diacetylenic cations, since many substituted diacetylenes polymerize readily in the solid state.[7] Two synthetic routes to the required amino-diacetylenes, both starting from hexa-2,4-diyne-1,6-diol, were selected so that all reactions could be carried out as far as possible at room temperature or below, and in the dark. The first route involved the conversion of the diol into the corresponding dichloride with $SOCl_2$–pyridine, followed by conversion into $[ClCH_2C{\equiv}C{-}C{\equiv}CCH_2NH_3]Cl$ ($R'NH_3Cl$) by hexamethylenetetramine in $CHCl_3$ and HCl in MeOH.[8] In the second route the hydroxy-groups were coupled to the carboxy-group of glycine using dicyclohexylcarbodi-imide in ether,[9] after first protecting the amino-group with a t-butoxycarbonyl group,[10] later removing it with 40% CF_3CO_2H in CH_2Cl_2, and conversion into the hydrochloride salt with HCl

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† New compounds were characterized analytically and/or spectroscopically.

in MeOH, to give $(H_3NCH_2CO_2CH_2C{\equiv}C\text{–})_2Cl_2$ $[H_3NR^2NH_3]Cl_2$. Attempts to couple hexa-2,4-diyne-1,6-diol to 6-aminocaproic acid, $H_2N[CH_2]_5CO_2H$, and octa-3,5-diyne-1,8-diol to glycine by the same method failed because the products polymerized very rapidly to black tarry materials. In contrast both white R^1NH_3Cl and pale brown $(H_3NR^2NH_3)Cl_2$ darkened only very slowly at room temperature in daylight. The tetrachlorocadmate salts were prepared by evaporation from aqueous ethanolic solutions containing stoicheiometric amounts of the amine hydrochlorides and $CdCl_2$.

Photolysis of $(R^1NH_3)_2CdCl_4$ gave a deep red product after 1 h, with i.r. bands at 1620 and 500 cm^{-1}, the former in the region assigned to the polydiacetylene backbone. A similar colour change occurred in that part of a powder sample exposed to Cu-K_α X-irradiation. In contrast 5 h exposure of $(H_3NR^2NH_3)_2CdCl_4$ to u.v. radiation produced only a light orange–brown colouration and no detectable change in the i.r. spectrum. We conclude that, as in other photolytic reactions in organic molecular crystals, details of intermolecular orientation which may be difficult to predict *a priori* are crucial to the rate of the reaction. In the present case we conjecture that the extra flexibility conferred on the organic cation by binding it to the inorganic layer through one end only, rather than at both ends, may be the factor which leads to the enhanced reactivity of $(R^1NH_3)_2CdCl_4$ compared with that of $(H_3NR^2NH_3)_2CdCl_4$. Many more experiments will be needed to optimize the conditions for photopolymerization in these salts, but we believe it has been demonstrated that inorganic layer salts have the potential to act as templates for producing oriented conjugated organic polymers.

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