

Polydiacetylene

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Polydiacetylene films and powders have been prepared from the AsF_5 -induced polymerization of butadiyne in both the solid and gas phases at low temperatures; the charge transfer interaction can be explosive if large quantities of the reactants are mixed.

Polymerization of butadiyne (diacetylene), C_4H_2 , can be induced with AsF_5 under controlled experimental conditions. The polymer is formed as either a thin or thick film on a glass substrate or as an amorphous powder. C_4H_2 in the gas or liquid state undergoes uncatalysed autopolymerization very slowly (months),¹ whereas typical catalysed (free radical, cationic, anionic, heat, and light) polymer formation in solution is reasonably rapid at room temperature. The resultant polymer always had a high degree of inorganic ash on combustion.² Likewise, Zeigler-Natta co-ordination catalysts have been found to produce polymer with high (30–40%) ash content.^{2,3} In contrast with such catalysts, AsF_5 , which, we recently reported, acts as a radical cation generator,⁴ causes essentially instantaneous polymerization at low temperature with a relatively low ash content.

Butadiyne has usually been synthesized from double dehydrohalogenation of 1,4-dichlorobut-2-yne in aqueous KOH.⁵ Contrary to a previous report,⁶ the content of the chlorinated impurity, $\text{C}_4\text{H}_3\text{Cl}$, could be reduced to no less than 2–3% as determined by mass spectroscopic analysis. Another preparative route involves the generation of gaseous C_4H_2 when bis(trimethylsilyl)diacetylene was added to an aqueous KOH⁷ or borax solution.⁸ Polymer formation after fractional distillation of C_4H_2 at low temperatures was

accomplished by first condensing a small amount of pre-purified AsF_5 at -196°C and then condensing C_4H_2 above the AsF_5 at this temperature on a vacuum line. It should be noted that even though the rate of polymerization is slow at -196°C , it is nearly uncontrollable at slightly elevated temperatures. AsF_5 is energetic enough to generate a substantial number of radical cation centres that react in such a manner as to detonate the entire reaction mixture. Several explosions occurred following a flash of light within the reaction vessel when large quantities of both reactants (*ca.* 200 mg) were allowed either to mix rapidly in the gas phase or to warm quickly from -196°C . To avoid explosions with such quantities, the -196°C AsF_5 - C_4H_2 mixture was surrounded as quickly as possible with a -78°C dry-ice slush bath. Apparently, the dissipation of heat from reaction at -78°C was sufficient to reduce the internal pressure build-up but did not prevent detonation. Caution is therefore advised when combining materials like $\text{C}_4\text{H}_2(\text{C}_2\text{H}_2)$ with catalysts such as $\text{AsF}_5(\text{PF}_5)$, SnF_4 , or $\text{BF}_3(\text{AlF}_3)$ in the solid or gas state.

The polymeric material which results is in the form of a thin film and amorphous-like aggregates. The polymer as a film adheres to a glass substrate and is blue-black in transmitted light and black in reflected light. The experimentally-

determined elemental atomic ratios were as follows: C/H = 1.9–2.2, C/As = 15.1–15.4, and F/As = 4.85. That the F/As ratio is different from 6.0 is owing to residual AsF₃ in the polymer that was not released during prolonged pumping under high (<10⁻⁴ Torr) vacuum and was detected by mass spectroscopic means when the polymeric material was heated. The film is sensitive to oxygen and moisture (owing to residual radical cation centres and bound AsF₃) and heat which, when applied to the substrate's surface, causes the film to peel (*via* contraction) and roll onto itself thus giving the appearance of cigar-like needles. This thermally-treated polymer is highly reflective, appearing either bronze or silver at various reflective angles. Preliminary differential scanning calorimetric studies revealed two exotherms: *ca.* 150 °C and *ca.* 550 °C. The transition at 150 °C is tentatively assigned to a structural modification for which the *cis-trans* isomerization is known to occur for polyacetylene at *ca.* 147 °C.⁹ The transformations at 550 °C involve charring (aromatization) since the ratios of C/H and C/As were found to increase to 3.4 and 2801, respectively.

Conductivity of the unheated film at room temperature was *ca.* 10⁻¹⁰ Ω⁻¹cm⁻¹, the order of magnitude being comparable with that reported for polyacetylene,¹⁰ poly-*p*-phenylene,¹¹ and substituted polydiacetylenes.¹² The conductivity of the film did not increase upon further exposure to AsF₅. Attempts to induce solid state topochemical polymerization¹³ of single crystals of C₄H₂ were performed *via* γ- or u.v.-irradiation. γ-Irradiation (6.3 Mrad/h; 3 h exposure; -78 °C) produced a brittle black material assumed to be polydiacetylene. In contrast, u.v.-irradiation (1000 W Xe-Hg lamp; 24–48 h) yielded trace amounts of a rusty-brown film. Azobisisobutyronitrile as a u.v.-sensitive free radical initiator was not effective under these conditions.

Previous i.r. studies characterising the polymer of butadiyne as aromatic were used to propose mechanisms of polymerization involving not only isotactic linearization *via* 1,2-addition at the triple bonds, but also cyclization (*via cis-trans* isomerization) with or without hydrogen migration.^{2a} I.r. absorptions^{2a} and X-ray^{2b} patterns of the heated polymer (400 °C) were viewed as suggestive of sheet-like carbonaceous macromolecules.

Although the polymerization mechanism of butadiyne is complex, it is apparent that AsF₅ is crucial in the initiation of the solid state polymerization and involves the charge transfer interaction which generates, *via* a one-electron transfer process, radical anions and cations (both detectable at 77–100 K).

The highly reactive radical cations, C₄H₂⁺, undergo auto-polymerization as described above. It seems reasonable that analogous AsF₅-induced polymerizations (C₂H₂;¹⁴ *p*-phenylene oligomers¹⁵) share the common radical cation initiation mechanism.

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