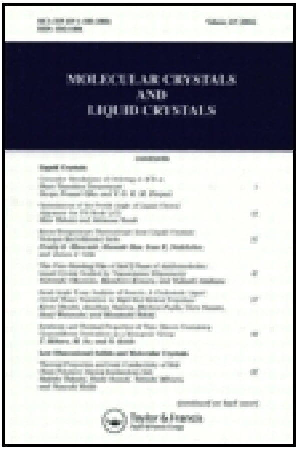

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Solid State Chemistry of Some Diacetylenic Acid Derivatives

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SOLID STATE CHEMISTRY OF SOME DIACETYLENIC ACID DERIVATIVES

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Abstract An example of chemical reactivity in LB films is described. α and ω diyne long chain fatty acids are synthetized and their polymerization in multilayers studied. The reactivity depends on the position of the diyne along the alkylchain and on the metallic ion so far as the α diyonic acid salt is concerned. In LB films the chemical reactions are followed by infrared spectroscopy and the spectra are compared to those of model synthetic analyzed compounds. Decarboxylation often takes place under UV radiation or heat and leads to unpolymerisable material. From an oxidative coupling of the copper salt a tetrayne formation is presumed and a fast polymerization under visible radiation is observed

INTRODUCTION

In our previous studies we examined the chemical reactivity in multilayers and we specially focused our attention on solid state polymerizations for ultimate photoresist applications (1).

After ω-tricosenoïc acid, we thought that the polymerization of diacetylene worked out by Wegner was well suited to LB film chemistry. Tieke and co-workers[2] performed their experiments with fatty acid salts where the polymerizable function was located in various places along the chain. We tried to find out new compounds with the diyne in the α or ω positions with respect to the carboxylic group.

In the first part of the paper the syntheses will be briefly described ; in the second part we shall deal with the chemistry of the α diyne because the reactivity is modified by the conjugation of the acid group to the diyne one.

Infrared spectroscopy proved to be a useful tool for studying ultrathin films by comparison of the spectra of the LB films to those obtained with the derivatives identified under usual conditions i.e elemental analysis.

SYNTHESES

2,4. Tricosadiynoïc Acid : $CH_3-(CH_2)_{17}-C\equiv C-C\equiv C-COOH$

Starting from commercial 1-eicosene, bromination followed by dehydro - bromination in concentrated alcoholic potassium hydroxyde solution yields a mixture of 1-eicosyne and 1-bromo-eicosene. Purification was performed through the silver acetylide, insoluble in any solvent, which extracts all the impurities. This acetylide reacts at once with an ethereal solution of iodine giving rise to very pure 1-iodoeicosyne (yield 60%) : $I-C\equiv C-(CH_2)_{17}-CH_3$. Coupling with propiolic acid under modified Chodkiewicz conditions (chloroform-alcohol-water (homogenious phase) as solvent) produces the 2-4 tricosadiynoïc acid in 80% yield.

22.24 Pentacosadiynoïc acid

The ω position for the polymerizable group had proved to promote easy polymerization in LB films since the strains are weakened in the vicinity of the plane between two layers The more freedom available to the polymerizable groups the better the reactivity. Nethertheless the synthesis is compelling : starting from ω-tricosenoïc acid, blocking the carboxylic acid group by esterification is the first step. Then the ethylenic function is worked up as above to generate the methyl, 23-iodo, 22-23 tricosynoate : $I-C\equiv C-(CH_2)_{20}$ $-COOMe$. A Chodkiewicz coupling as previously described produces the methyl, 23-carboxy, 22-23 pentacosynoate $COOH-C\equiv C-C\equiv C-(CH_2)_{17}COOMe$ - Decarboxylation in an ammoniacal copper sulphate-acetone solution an then hydrolysis of the ester yield the 22-23 Pentacosadiynoïc acid.

All the compounds at each step are characterized by their infrared spectra.

CHEMICAL REACTIVITY

Polymerization of the 2-4 diyne

It is followed by the infrared spectra on crystals as well as LB films. Under UV irradiation of crystals a blue polymer is obtained. Neither solvents nor heat generate a red form. It swells in chloroform. The acetylenic bond of the polymer absorbs at 2120 cm^{-1} instead of 2240 cm^{-1} for the monomer. The frequency of the conjugated carboxy group shifts from 1680 cm^{-1} to higher frequencies as a very broad band to 1760 cm^{-1}, implying that the carboxyl is no longer conjugated to the unsaturated polymer backbone. The rotation mechanism which provides this solid state polymerisation forces the chain to tilt as well as the COOH. It is to be noticed that, from the infrared bands this acid before polymerization is not dimerized (lack of the broad 950 cm^{-1} band = OH out of plane of the dimer).

In monolayers, on CaF_2, substrates, the same phenomena are observed. The yield of the polymer lies between 50 and 70% depending on the quality of the film ; the visible absorption reaches 610 nm. By prolonged UV irradiation decarboxylation occurs. Then, since there are no longer any polar groups causing adherence, the polymer is removed from the substrate by dipping in chloroform.

Polymerization of the 22-24 Pentacosadiynoïc acid

This molecule polymerizes readily in a red form only (λmax-500 nm). Neither solvents nor heat make a blue form appear. In monolayers the polymerization yield is nearly 100% (followed from the disappearance of the acetylenic C-H stretching of the monomer at 3310 cm^{-1}).

Metal Derivatives of The 2-4 Tricosadiynoïc acid :

This acid is the only compound where the vicinity of the diyne groupe can influence the chemical resistivity of the carboxylic group and vice versa. The polymerizations of various salts were studied. Among monovalent salts, silver and ammonium derivatives undergo an UV polymerization. Sodium and potassium salts do not. Morawetz[3] in the early sixties, already noticed the influence of the crystalline network in the solid state polymerization of acrylic salts. This can account for the fact that the monovalent salt may polymerize or not. But in this case of di-or trivalent salts, we never observe any polymerization (the Cadmium salt is reported to polymerize to an extent of 1% only and this may be due to an impurity, for instance domains of free acid which is known to polymerize). The lattice parameters could of course explain the failure of the polymerization but another argument is proposed : multivalent çations bind stiffly two or three monomers either in the same layer or in neighbouring layers. Then the motion required for the polymerization can be prevented as has been previously described by Bloor in various bulky substituted PTS.

The heavy metal salts, namely silver and copper, have an interesting chemistry as far as their acetylenic derivatives are concerned. Their reactivity in monolayers fits with the results obtained by the classical chemistry.

Silver salt :

1. In the crystalline state : We synthetized the silver salt from an acetone solution of silver nitrate and the α diynoïc acid. The hemihydrated salt is precipitated as proved by elementary analysis (IR ν_{COO^-} 1590 and 1570 cm^{-1} for the anhydrous and hydrated environment respectively - $\nu_{C\equiv C}$ at 2230 cm^{-1}). Heat effect on the powder generates the silver acetylide hemihydrate ($\nu_{C\equiv C}$ 2195 cm^{-1}). In presence of silver nitrate a complexe $R-C\equiv C-C\equiv C-Ag$, 1/2 NO_3Ag is obtained ($\nu_{C\equiv C}$ 1900 cm^{-1}). No polymerization is observed for either one or the other acetylides.

Under UV irradiation, the silver salt, at room temperature, produces a blue polymer, the carboxylate frequency of which is shifted to 1530 cm^{-1}. This value is close to that of silver behenate (1520 cm^{-1}) which is a saturated acid salt. Hence this shift could again mean that the carboxylate is no longer conjugated with the polymer backbone. Warming this polymer produces decarboxylation and breaking of conjugated bonds since discoloration takes place.

2. LB. films : The silver salt is obtained by diffusion of an aqueous silver nitrate solution through layers of tricosadiynoic acid deposited on a CaF_2 substrate. The only carboxylate frequency recorded is 1590 cm^{-1}. Under UV radiation the blue back polymer absorbing at 670 nm is formed and again the carboxylate frequency is shifted to 1530 cm^{-1} as in crystals. The yield reaches 70%. By further irradiation, decarboxylation occurs until complete disappearance of the 1530 cm^{-1} band. By heating at 100°C in air a yellow colour develops (absorption 410 nm). This is probably due to silver particles deposited in the structure by the rupture of the

bonds between the polymer backbone and silver atoms. An experiments which consisted of reducing layers of silver behenate by hydrazine vapors led to the formation of silver globules. The absorption was at 410 nm.

While heating films of the silver salt of the diynoic acid, bands of silver acetylide appear in the infrared spectrum. Here again, as in crystals, no polymerization was detected.

Copper salts

1 In the Crystalline state : When copper I salt is synthetized, it readily decarboxylates giving a yellow precipitate. Analysis gives the formula of the copper acetylide hemihydrate which does not polymerize. The C≡C stretching frequency is found as low as 1919 cm^{-1}. This frequency is also exhibited by the complexe : Copper I chloride-acrylonitrile where copper I has a strong interaction with the triple bonds. The copper acetylide obtained with the 2-4 tetracosanoïc acid is insoluble in all the solvents ; as a result we could not build any monolayers.

2. In LB. films : We synthetized "in situ" the monovalent coppersalt by dipping the substrate covered with layers of the acid in an aqueous reducing solution of copper I chloride ($CuC\ell$+NH_2OH, $HC\ell$). The colour is yellowish (λ=450 nm) and the carboxylate frequency is 1585 cm^{-1}. On standing the carboxylate band broadens, the C≡C stretching smoothens, and an important reorientation occurs. Under UV radiation no more change occurs. It may be due to a dismutation of $Cu_I \rightarrow Cu_{II} + CuO$ since the copper I in moist air is unstable.

Since copper acetylide is insoluble we thought that a soluble pirydine complex could be obtained. Actually, copper acetylide does dissolve in pyridine, but by slow evaporation of the solvent yellowish crystals deposit which contains no copper. The analysis corresponds to the formula :

$$\left[CH_3 - (CH_2)_{17} - C{\equiv}C{-}C{\equiv}C_n \right]$$

On the infrared spectra ν C≡C is formed at 2210 cm^{-1} but not C-H stretching appears at 3300 cm^{-1} which precludes n = 1 in the above formula. The only possibility is n ≈ 2, the dimeric form a diyne named tetrayne. The crystals undergo a very fast polymerization under daylight, giving a blue back compound insoluble in any solvent. By warming a suspension in chloroform the filaments turn red and come back to the blue form by cooling.

2 In LB films :

Pyridine vapors dissolve LB films of the unstable copper I salt. But with the copper II salt a reaction is observed : the carboxylate band on the infrared spectrum at 1565 cm^{-1} wanishes as the blue back color develops under daylight (λ max = 710 nm). We think that a Glaser coupling mechanism[4] is involved as above for the copper acetylide in crystals, leading to the same tetrayne and polytetrayne.

CONCLUSION

The method described here is convenient for following chemical reactions in LB films, i.e, comparison of the infrared spectra of known or analyzed compounds with those of reacted films. The results are roughly identical in both structures, but some intermediates, such as copper I salt, are stabilized for a while in monolayers.

The possibility of a tetrayne formation is to be noted for future polymerization work.

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