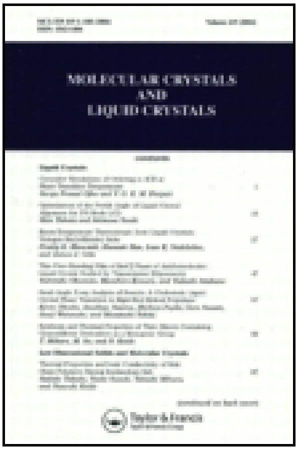

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Solid State Polymerization of Butadienes in Layer Structures

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SOLID STATE POLYMERIZATION OF BUTADIENES IN LAYER STRUCTURES

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Abstract The solid-state polymerization of 1,4-disubstituted trans, trans-butadienes has been investigated in perovskite-type layer structures and lipid layer structures. X-ray structure analyses of the complex salts

$[HOOC\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CH_2NH_3]_2\ CdCl_4$ (1) as polymer and
$[HOOC\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CH_2NH_3]_2\ CuCl_4$ (2) as monomer are

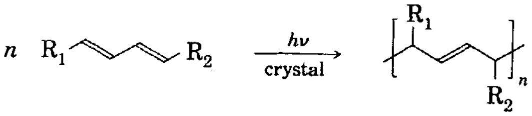
presented. Polymerization of 1 causes the formation of an erythro-diisotactic 1,4-trans-polybutadiene in a lattice controlled reaction. Crystals of 2 exhibit a Jahn-Teller-distortion of the $CuCl_6$ octahedra, which forces the monomer units into a packing geometry highly unfavourable for a solid state reaction.

Long chain butadienes such as 2,4-hexadienoic acid n-octadecylester (3) and 6-(n-octadecanoylamino)-2,4-hexadienoic acid (5) polymerize upon exposure to UV- and γ-irradiation. Studies by infrared and ^{13}C-NMR-spectroscopy indicate the formation of 1,4-trans-polymers in the crystalline state as well as in Langmuir-Blodgett-multilayers.

INTRODUCTION

Solid state polymerization represents a suitable method to obtain highly regular, in some cases nearly defect-free polymer single crystals. This has recently been demonstrated for a series of diolefin[1] and diacetylene derivatives[2]. 1,4-Disubstituted butadienes are also highly reactive in the solid state. Studies by G.M.J. Schmidt and coworkers[3] indicate that mainly dimerization occurs. Polymers are only obtained as a side product.

On the other hand, recent studies have shown that butadiene derivatives in layer structures undergo solid state polymerization. Initiated by UV- or γ-irradiation polymers are formed in Langmuir-Blodgett (L-B) multilayers[4], mono- molecular layers at the air-water interface[5], and perovskite-type layer structures[6]. In layer perovskites crystalline 1,4-trans-polymers are obtained[7] according to the reaction scheme



Purpose of the present paper is, firstly, to describe the crystal structure of the complex salt

$[HOOC\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CH_2NH_3]_2\ CdCl_4$ (<u>1</u>)

in the polymerized state. The structure analysis reveals the formation of a stereoregular polymer in a lattice controlled reaction. Secondly, the crystal structure of the photoinactive complex salt

$[HOOC\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CH_2NH_3]_2\ CuCl_4$ (<u>2</u>)

will be reported. Thirdly, the solid state reactivity of some long chain derivatives of sorbic and muconic acid will be described in the crystalline state and in L-B multilayers. The structure of the photoproducts has been analysed by infrared- and ^{13}C-NMR-spectroscopy.

RESULTS AND DISCUSSION

CRYSTAL STRUCTURE OF THE POLYMERIC COMPLEX SALT 1

Details of the crystal structure of 1 in the polymerized state have already been described previously[8]. In the following the most important results are briefly summarized. Crystal data are listed in Tab. 1.

TABLE I. Crystal data of 1

Formula	$(HOOC-CH=CH-CH=CH-CH_2NH_3)_2CdCl_4$ polymerized form
Molecular Mass	510.52
Crystal System	Triclinic
Space Group	$P\bar{1}$
a(Å)	7.2144(4)
b	7.2447(5)
c	18.5936(14)
α(°)	104.488(5)
β	96.631(5)
γ	95.706(5)
Z	2
$d_{(obs)}$ (g/cm^3)	1.84
$d_{(calc)}$	1.83
Radiation	Cukα, (λ = 1.5418 Å)

Crystals of 1 consist of two types of layers alternating in the third dimension. One type of layer consists of corner-sharing $CdCl_6$-octahedra, whereas the other type contains the organic polymer (Fig. 1). The polymer chains exhibit a 1,4-trans-structure with an erythro-diisotactic arrangement of the substituents. They are chiral, but due to the centrosymmetric crystal structure, a racemate is obtained. Each polymer chain is linked to its centrosymmetrical equivalent by hydrogen bonds (Fig. 2). There are two crystallographically independent monomer units linked together by C-C-single bonds. The conformation of the two parts is nearly identical, they differ only in the vicinity of the ammonium groups (Fig. 2 and 3).

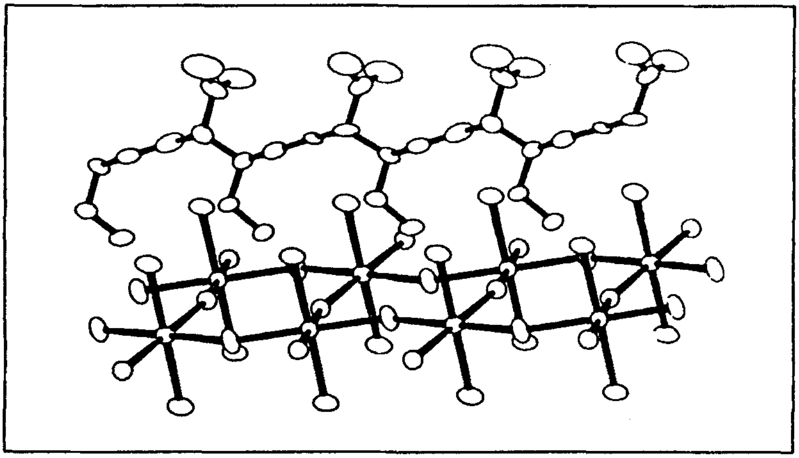


FIGURE 1. Perspective view of the inorganic and polymer layers

The Cl octahedra are distorted. Their packing deviates from a regular chessboard-like arrangement (Fig. 3) by a rotation of adjacent octahedra of nearly 30° about the normal to the layer. In the corresponding monomer crystal

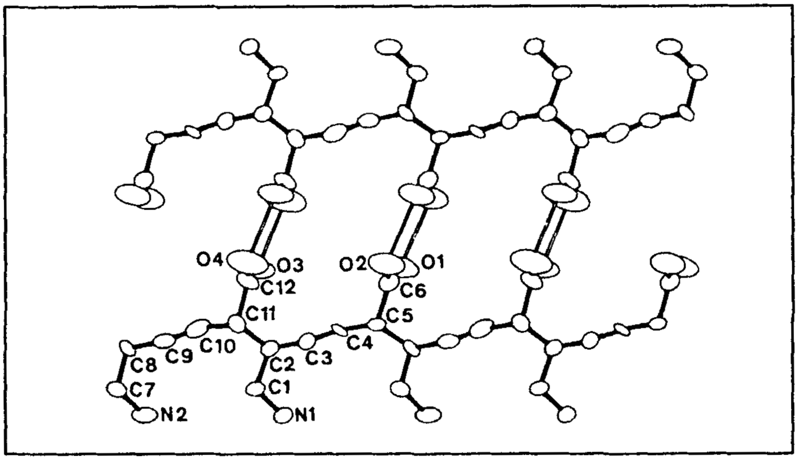


FIGURE 2. Representation of the polymer layer with H-bonded oxygen atoms linked by open bonds. The atoms of the two independent monomer units are identified on the figure.

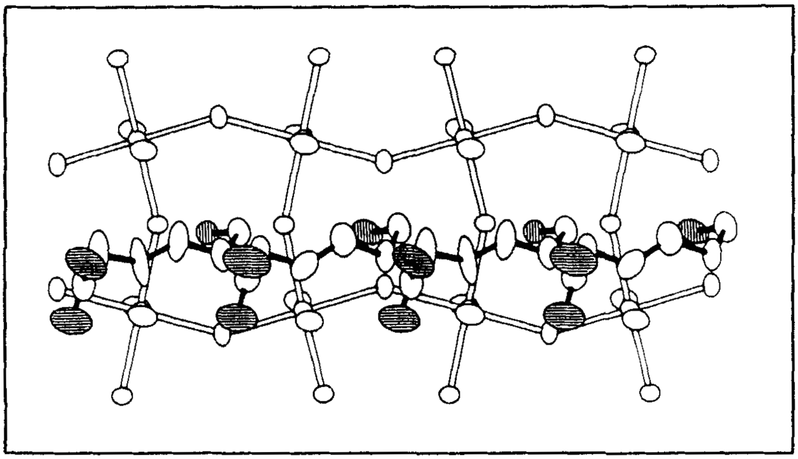


FIGURE 3. Projection of the crystal structure of 1 in the polymerized state onto the layer plane (the inorganic part is represented by open bonds).

this distortion is certainly lacking as the area of the unit cell in the layer is larger by nearly 8 %. Thus, the distortion and the contraction of the octahedra must be a consequence of the polymerization process. As a result, two crystallographically independent N atoms exist which are located in cavities with different surroundings. N(1) has four Cl atoms within a radius of 3.4 Å whereas N(2) has five Cl atoms within the same radius.

CRYSTAL STRUCTURE OF THE PHOTOINACTIVE COMPLEX SALT 2

Details of the structure analysis of 2 will be described elsewhere. Only the most important features will be reported in this article. Crystal data of 2 are given in Table II.

TABLE II. Crystal data of 2

Formula	$(HOOC\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CH_2NH_3)_2CuCl_4$
Molecular Mass	461.66
Crystal System	Triclinic
Space Group	$P\bar{1}$
a(Å)	10.422(1)
b	10.736(1)
c	17.340(2)
α(°)	87.95(1)
β	74.20(1)
γ	87.67(1)
Z	4
$d_{(calc)}$(g/cm^3)	1.64
Radiation	MoKα (λ = .71069)

This structure consists also of an alternating sequence of organic and inorganic layers. The Cu atoms are coordinated by four Cl-atoms with distances varying between 2.26 and 2.32 Å. Two additional Cl-atoms are separated by 2.99 Å. The coordination figure of the Cu-atom is an elongated tetragonal bipyramid with the axis laying parallel to the layer (Fig. 4 and 5).

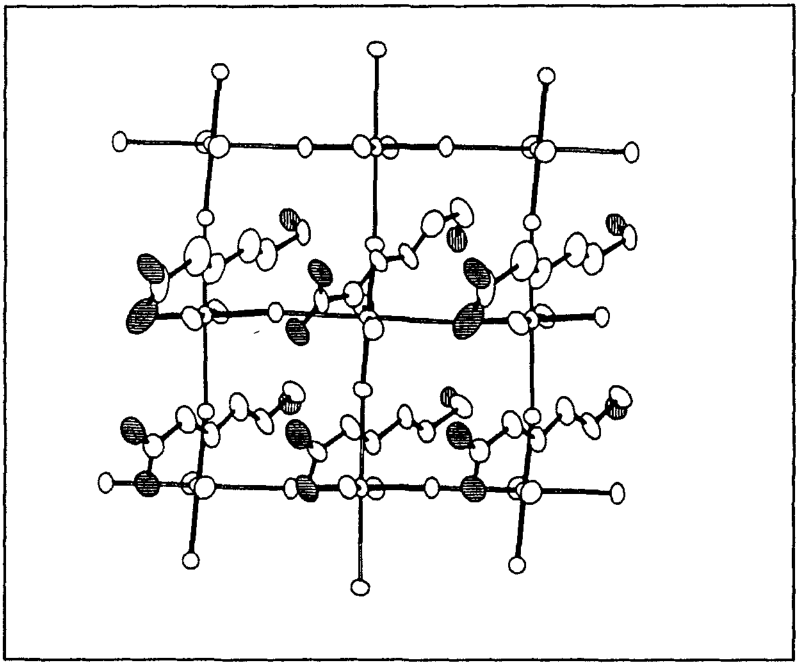


FIGURE 4. Projection of 2 perpendicular to the layer plane

The organic part consists of four independent monomer units attached to the inorganic layer by hydrogen bonds. The conformation of the four independent units is very similar if we consider the C- and O atoms. The main differences can be found in the torsion angles of the N-C-C-C bonds. The terminal part of each monomer tends to align in a single direction for packing optimization. The ammonium end is however subject to the orientation of each Cl-cavity which can only be accomodated by adapting locally the suitable N-C-C-C torsion angle.

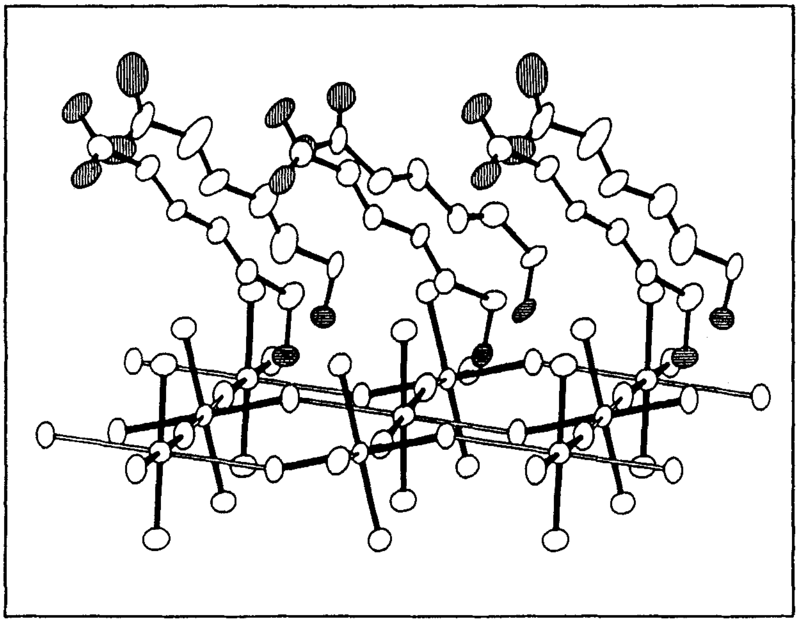


FIGURE 5. Perspective view of 2

The origin of the photoinactivity must be found in the packing of the monomer unit. In 1, each monomer lies in a plane defined by the normal to layer and the shortest translation period of the Cl-cavities. In this arrangement, the vicinity of the monomer is favourable for the polymerization process. In 2 however, the plane of the monomer does contain the next-shortest translation period which is longer by approximately $\sqrt{2}$. The distance between each monomer unit is thus too long to allow for polymerization.

LONG CHAIN BUTADIENES

Butadiene derivatives are not only photoreactive in layer perovskites, but a rapid polymerization has also been observed for long chain derivatives in the crystalline state and L-B type multilayers[9]. The compounds which have been investigated are listed in Table III.

TABLE III. List of long chain butadienes $R_1-CH=CH-CH=CH-R_2$ and some of their characteristic data

No.	R_1	R_2	m.p.(°C)	photo-react-ivity$^+$
3	$CH_3-(CH_2)_{17}-O\underset{\underset{O}{\|}}{C}-$	$-CH_3$	45	•
4	$CH_3-(CH_2)_{17}-\overset{\overset{H}{\|}}{N}-\underset{\underset{O}{\|}}{C}-$	$-CH_3$	99	+
5	$CH_3-(CH_2)_{16}-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{\|}}{N}-CH_2-$	$-COOH$	145	+
6	$CH_3-(CH_2)_{17}-O\underset{\underset{O}{\|}}{C}-$	$-\underset{\underset{O}{\|}}{C}O-(CH_2)_{17}-CH_3$	88-89	-
7	$CH_3-(CH_2)_{17}-\overset{\overset{H}{\|}}{N}-\underset{\underset{O}{\|}}{C}-$	$-\underset{\underset{O}{\|}}{C}-\overset{\overset{H}{\|}}{N}-(CH_2)_{17}-CH_3$	185-188	-

• upon ^{60}Co-γ-irradiation of UV-light (λ = 254 nm)

The sorbic acid derivatives 3 - 5 are highly reactive upon UV- and γ-irradiation, whereas the muconic acid derivatives

6 and **7** are completely photoinactive.

Infrared spectra of compounds **3**-**5** monitored after different γ-irradiation doses received by the crystals show a decrease in the intensities of the C=C-stretching and wagging modes at 1620 and 1000 cm^{-1}. This indicates a reaction of the butadiene moiety. Simultaneously a new mode appears at 960 cm^{-1}, which can be related to the wagging mode of an isolated trans C=C-unit, as it typically occurs in 1,4-trans-polybutadienes (see also Fig. 6).

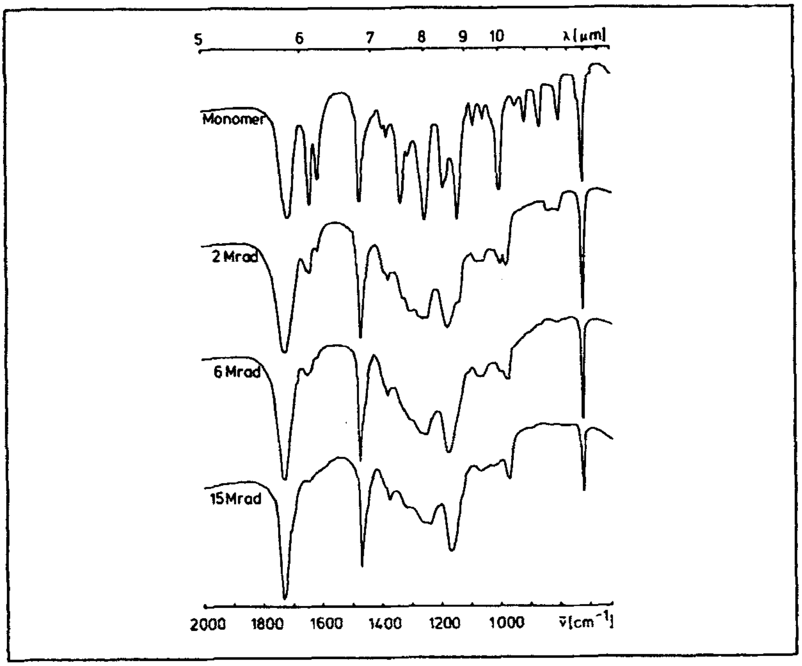


FIGURE 6. Section of IR-spectra of **3** as monomer and after various γ-ray doses

The photoproduct of **3** is completely soluble in chloroform. The ^{13}C-NMR-spectrum indicates the formation of a

1,4-trans-polymer by the occurrence of two signals at 137.1 and 126.8 ppm, which can be ascribed to the isolated trans-C=C-unit, and two signals at 56.0 and 39.4 ppm, which can be related to the aliphatic carbon atoms created by the reaction. No indications are found for the formation of [2+2]-cycloadducts (see also Fig. 7).

The acid 5 forms oriented monomolecular layers if spread at the air water interface. The π-A-isotherm measured at T=20°C indicates the formation of a solid condensed film with collapse pressure near 50 mN/m. UV-irradiation of the monolayer under constant pressure for a period of 30 min further increases the film stability probably due to polymerization (see also Fig. 8).

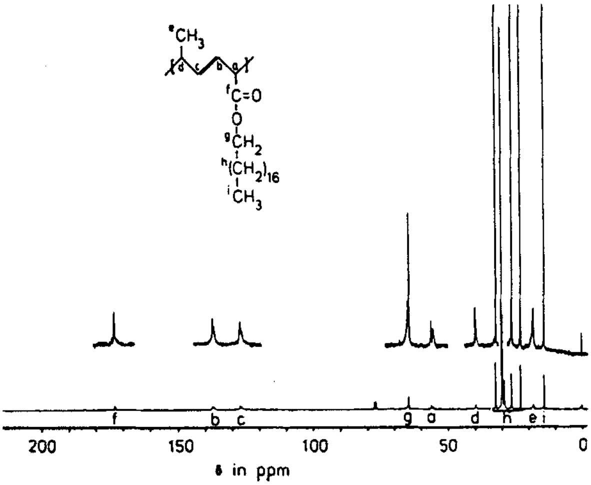


FIGURE 7. 90.556 MHz-^{13}C-NMR-spectrum of 3 after exposure of the crystals to a γ-ray dose of 15 Mrad and dissolution in $CDCl_3$.

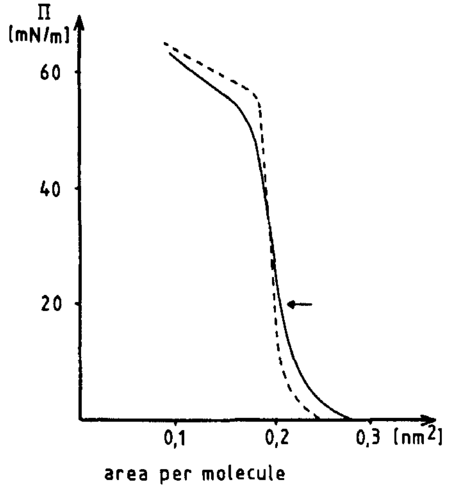


FIGURE 8. π-A-isotherms of 5 as a monomer (——) and polymer (--). Polymerization was carried out in UV-light under constant pressure (π=20 mN/m). Subphase : pure water, pH 5.8, T= 20°C.

Monolayers of 5 can be transferred onto hydrophobic substrates and L-B-type multilayers of variable thickness can be built up. UV- or γ-irradiation of the multilayers causes a rapid solid state reaction. Infrared spectra indicate the same 1,4-addition reaction as occurs in the crystalline state (Fig. 9). The C=C wagging mode at 990 cm^{-1} disappears. The inset of Fig. 9 shows that simultaneously a new mode appears at 970 cm^{-1}, which can be ascribed to an isolated trans C=C unit, indicating the formation of a 1,4-trans-polymer.

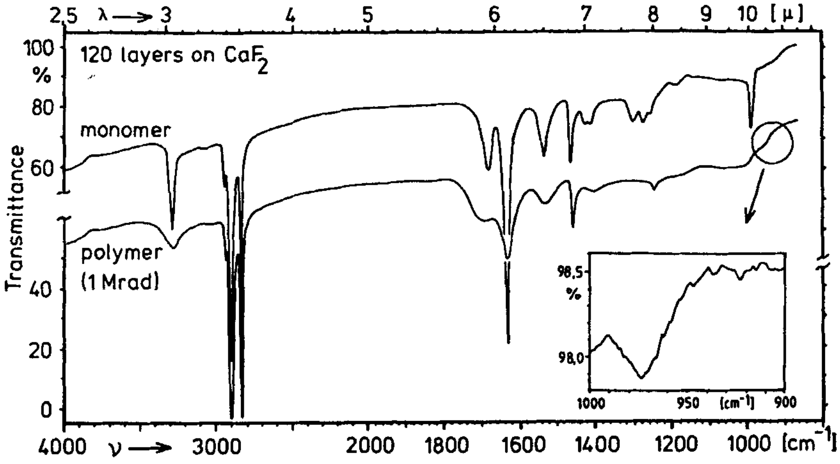


FIGURE 9. IR-spectra of a multilayer of 5 as a monomer and polymer (after exposure to a γ-ray dose of 1 Mrad). The inset shows the 1000 - 900 cm^{-1} section of the polymer spectrum obtained by accumulation of 10 scans and correction with the background spectrum of the window material.

CONCLUSIONS

The x-ray structure analysis of 1 in the polymerized state indicates the formation of a stereoregular 1,4-trans-polybutadiene in a layer perovskite.

Crystals of 2 are photoinactive due to a Jahn-Teller-distortion of the $CuCl_6$-octahedra which causes a monomer arrangement highly unfavourable for a solid state reaction.

Spectroscopic studies indicate that UV- and γ-irradiation of long chain derivatives of sorbic-acid lead to the formation of 1,4-trans-polymers in the crystalline state as well as in L-B-multilayers.

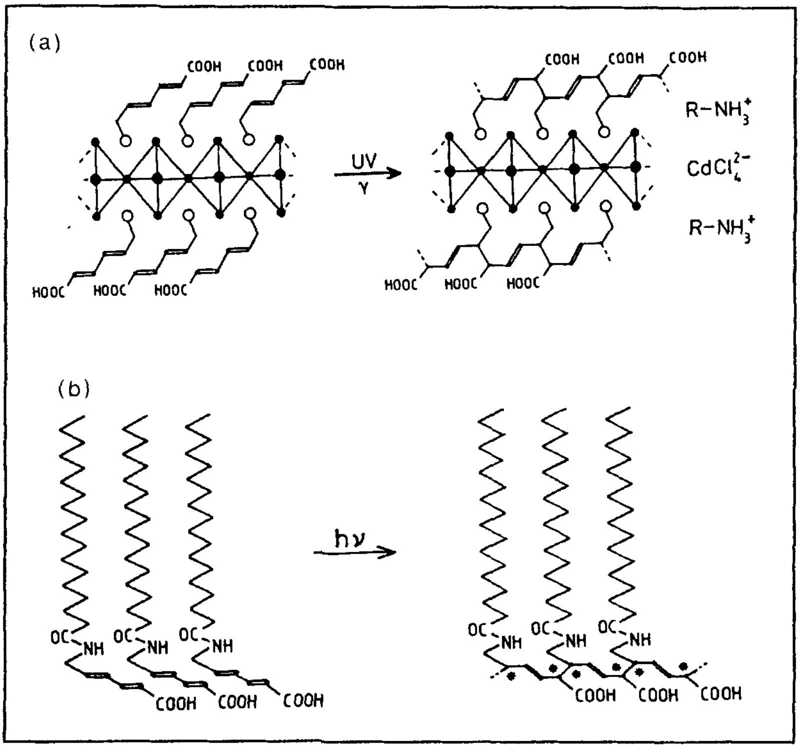


FIGURE 10. Schematic representation of the solid state polymerization of 1 (a) and 5 (b).

In Fig. 10 the polymerization reactions of 1 and 5 are schematically represented. The exclusive formation of a 1,4-trans-polymer originates

a) from the layer structure which reduces photoreactivity to two dimensions only, and

b) from large distances ≥ 0.5 nm between the monomers within the layer plane due to matrix effects by the inorganic ions as well as the packing of the paraffin chains. The large distances are just favourable for the 1,4-addition, but too large for the competing

[2+2]-cycloaddition of the butadiene units.

In addition, formation of a stereoregular polymer could be favoured by the strong hydrogen bonding of the substituents, rendering molecular diffusion or configurational rearrangements during polymerization difficult.

EXPERIMENTAL PART

The synthesis of the monomers 1 - 7 has been described previously[7-9]. Polymerization was carried out by subjecting the crystals or multilayers to ^{60}Co-γ-irradiation, or to a 6 W low pressure mercury lamp (λ = 254 nm). Monolayers were polymerized via the UV lamp at a distance of 30 cm. No efforts were made to exclude oxygen in any of the polymerization experiments.

Mono- and multilayers were obtained using a commercially available Langmuir-trough (MGW Lauda). Details of the preparation have been described previously[9].

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