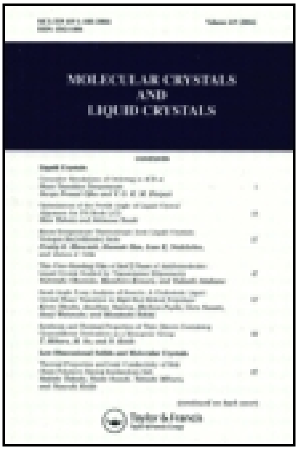


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Chemical Reactions in Perovskite-Type Layer Structures

Bernd Tieke [a]

[a] Institut für Makromolekulare Chemie der Universität Freiburg, Hermann-Staudinger-Haus, Stefan-Meier-Straße 31, D-7800, Freiburg, West-Germany

Version of record first published: 17 Oct 2011.

To cite this article: Bernd Tieke (1983): Chemical Reactions in Perovskite-Type Layer Structures, Molecular Crystals and Liquid Crystals, 93:1, 119-145

To link to this article: http://dx.doi.org/10.1080/00268948308073523

Mol. Cryst. Liq. Cryst., 1983, Vol. 93, pp. 119–145
0026-8941/83/9304–0119/$18.50/0

Printed in the United States of America

CHEMICAL REACTIONS IN PEROVSKITE-TYPE LAYER STRUCTURES

BERND TIEKE
Institut für Makromolekulare Chemie der Universität Freiburg, Hermann-Staudinger-Haus,
Stefan-Meier-Straße 31, D-7800 Freiburg,
West-Germany

Abstract The use of organic inorganic double halides as a matrix for solid state reactions has been investigated. It was found that unsaturated primary amines R-NH_2 with trans, trans-butadiene units and butadiyne units can be polymerized. Highly ordered polyelectrolytes are obtained, if the crystals are exposed to UV- or high energy radiation. The solid state polymerization is characterized by spectroscopic methods and by x-ray diffraction.

INTRODUCTION

In the recent years a large number of polymerization reactions in the solid state has been described, which in some cases lead to highly ordered products with a stereospecific arrangement of the substituents. Among those are reactions in the bulk phase [1,2], in mono- and multilayers [3-5] and in inclusion compounds [6,7]. The solid state polymerization in perovskite-type layer structures, which are organic inorganic double halides by its nature, represents a novel method which allows us to obtain highly ordered polyelectrolytes.

The perovskite-type layer structures of the stoichiometric composition $(R\text{-}NH_3)_2MX_4$ consists of an alternating sequence of single layers of corner sharing MX_6 octahedra with divalent metal ions M^{2+} in the centers, surrounded by the halide ions X^-, and bilayers of $R\text{-}NH^+$ cations in a head-head-tail-tail-head arrangement[8,9]. Hence the inorganic layers can be looked at as a matrix, which forces the $R\text{-}NH_3^+$ ions into specific packing patterns. Thus incorporation of photoreactive units into the side groups R allows for the use of the layer perovskites as a matrix for solid state reactions.

Recently preliminary results on the polymerization of aminodienes and -diynes have been reported [10-14]. In the following a number of unsaturated primary amines is described, which are all able to form layer perovskites and which were investigated concerning their reactivity upon UV- or high energy irradiation as well as annealing.

RESULTS AND DISCUSSION

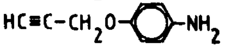
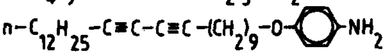
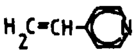
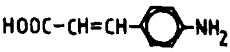
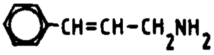
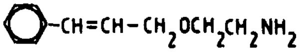
Previous studies on perovskite type layer structures mainly dealt with their physical properties. They are considered as model systems for the study of two-dimensional magnetic phenomena and of structural phase transitions as they also occur in lipid bilayer membranes. Thus only organic inorganic double halides of amines with saturated unbranched alkyl chains of 1 to 18 carbon atoms in R were investigated in detail 8,9,15,16).

However, besides the aminoalkanes a variety of unsaturated amines as well as amines with further polar groups such as carboxy groups or ether and ester linkages can be crystallized in the form of layer perovskites (see Tab. 1). It was also found that a variety of p-substituted anilines or pyridines are able to form complex crystals of similar stoichiometries.

Efforts to synthesize the layered complexes of amines containing bulky substituents such as anthracene moieties failed, probably due to their large size. The layer perovskites listed in Tab.1 were investigated concerning their photochemical and thermochemical reactivities. For this purpose the crystals were either exposed to UV light for a period of 3 days using a 240 W medium high pressure mercury lamp, or irradiated by high energy radiation with a maximum dose of 5×10^7 rad using a ^{60}Co-γ-source, or annealed at 120°C for two days. Chemical reactions were detected by UV- and/or IR-spectroscopy.

Reactivity upon UV- or γ-irradiation was found for various derivatives, as indicated in the last column of Tab. 1 and described in detail below. Thermal reactivity except decomposition at termperatures above 450 K was found for none of the derivatives.

TABLE I List of unsaturated compounds forming organic inorganic double halides *)

	organic compound	matrix MX_2	reactivity upon UV- or ^{60}Co-γ-radiation	
1	$HC{\equiv}C-CH_2NH_2$	$CdCl_2$, $CdBr_2$	(+)	
2	$HC{\equiv}C-(CH_2)_4-NH_2$	"	–	
3	$HC{\equiv}C-CH_2O-CO-(CH_2)_{10}-NH_2$	" , $CuCl_2$	–	
4		"	–	
5	$n-C_{12}H_{25}-C{\equiv}C-C{\equiv}C-(CH_2)_9-NH_2$	$CuCl_2$	+	10)
		$CdCl_2$	(+)	10)
6	$n-C_4H_9-C{\equiv}C-C{\equiv}C-(CH_2)_3-NH_2$	$MnCl_2$	+	10)
7		$CdCl_2$	(+)	
8	$H_2C{=}CH-CH_2NH_2$	$CdCl_2$	–	
9	$H_2C{=}CH-CH{=}CH-CH_2NH_2$	"	+	
10	$CH_3-CH{=}CH-CH{=}CH-CH_2NH_2$	"	+	
	$ROOC-CH{=}CH-CH{=}CH-CH_2NH_2$			
11	with R = H	$CdCl_2$, $MnCl_2$, $FeCl_2$	+	
	H	$CuCl_2$, $CdBr_2$	–	
12	CH_3	$CdCl_2$	+	
13	$CH(CH_3)_2$	"	+	
14	$CH_2CH(CH_3)_2$	"	+	
15	$n-C_4H_9$	"	+	
16		$CdCl_2$, $CdBr_2$	–	
17		$CdCl_2$	–	
18		$CdCl_2$, $CuCl_2$	–	
19		$CdCl_2$	–	

+ high reactivity, (+) low reactivity

*) Besides these derivatives also p-amino benzophenone and p-aminoacetophenone were found to form complex crystals with $CdCl_2$ in a 2:1 stoichiometry

REACTIONS OF THE ACETYLENE AND DIACETYLENE DERIVATIVES

In the series of the acetylene derivatives 1-4 only 1 exhibits chemical reactivity. While the $CdCl_2$- and $CdBr_2$-complexes remain unchanged upon UV irradiation, as previously reported by Day and Ledsham [13,14], they turn golden-brown and finally black upon γ-ray doses higher than 5 x 10^6 rad (Fig. 1a).

However, a polymerization of the triple bonds with formation of a polyene structure $\leftarrow CH{=}CR \rightarrow_x$ with $R{=}CH_2NH_3^+$ could not be detected, neither changes in the infrared spectra nor in the melting behaviour or in the γ-ray powder patterns. Thus the colour changes can only be due to the formation of traces of a polyene structure or to different radiochemical processes.

In general, the diacetylene derivatives 5-7 are photoreactive, as can be easily detected by the purple or red colour of the crystals, which immediately appears upon UV- or γ-irradiation of the crystals. This indicates a 1,4-addition of adjacent diacetylene units under formation of a fully conjugated polymer backbone with alternating double and triple bonds, as described for various disubstituted diacetylenes in the literature [2].

However, the coloration of the cadmium comlex of 5 occurs much slower as that of the corresponding copper complex. This indicates a control of the reactivity by the nature of the inorganic octahedra layers, in agreement with previous

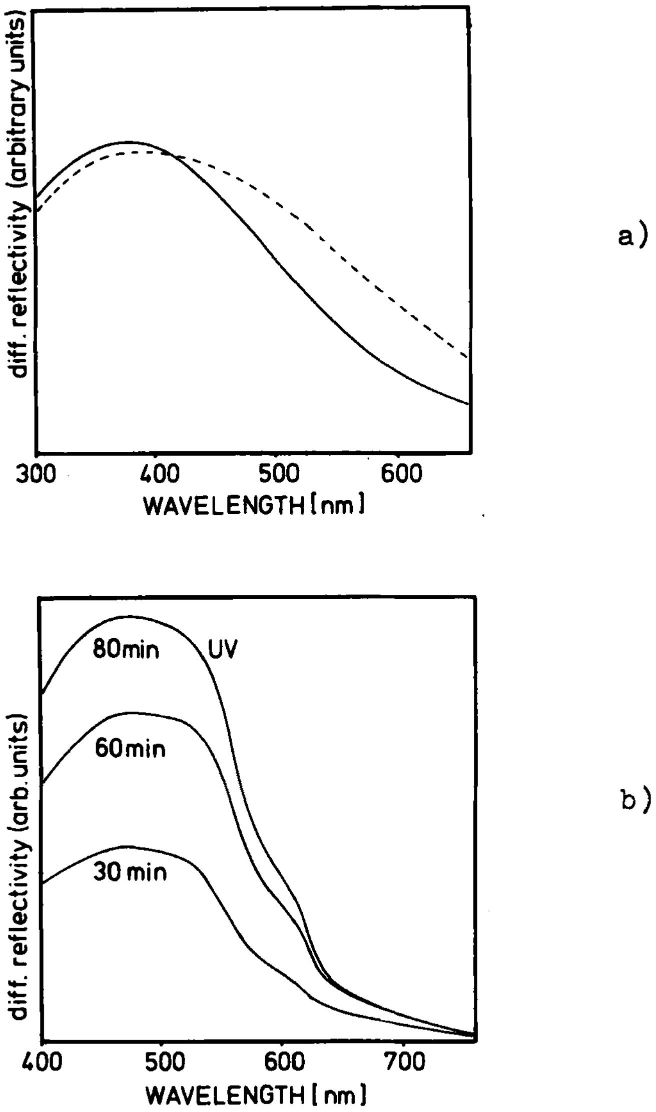


FIGURE 1. Diffuse reflection spectra of (a) the $CdCl_2$-complex of 1 (—),and the $CdBr_2$-complex of 1 (---), after exposure to a γ-ray dose of $1.5x10^7$ rad, and of (b) the $CdCl_2$-complex of 7 after various UV-irradiation times

observations 10,13,14). A diffuse reflection spectrum of the UV-polymerization of the $CdCl_2$-complex of 7 is shown in Fig. 1b. The reactivity of this derivative is fairly low. After exposure to a γ-ray dose of 2×10^7 rad less than ten percent of the monomer are converted into insoluble polymer.

REACTIONS OF THE BUTADIENE DERIVATIVES

All butadiene derivatives 9-15 exhibit chemical reactions, if exposed to γ-irradiation. Infrared spectra of the $CdCl_2$-complexes of 9, 10, 11 and 15 are shown in Fig. 2, for example, either as monomers or after exposure to a γ-ray dose of 3×10^7 rad. In addition, the compounds 11-15 are reactive on exposure to UV-light. This is caused by their strong UV absorption band near 260 nm, originating from the butadiene chromophor, which is extended by the C=O unit.

Typical spectral changes observed for all derivatives are the decrease of the C=C wagging mode intensity at about 1000 cm^{-1} and the appearance of a new mode at 960-980 cm^{-1}, which can be attributed to an isolated trans C=C bond, indicating a reaction of the butadiene unit. The C=C stretching modes at 1650 and 1620 cm^{-1}, which are very intense for 11 and 15, disappear as well(see Figs. 2c and d).

The reaction product of 11 is soluble in strong bases such as 1N KOH or 2.5 % aqueous $N(CH_3)_4OH$, and can be characterized by ^{13}C-NMR-

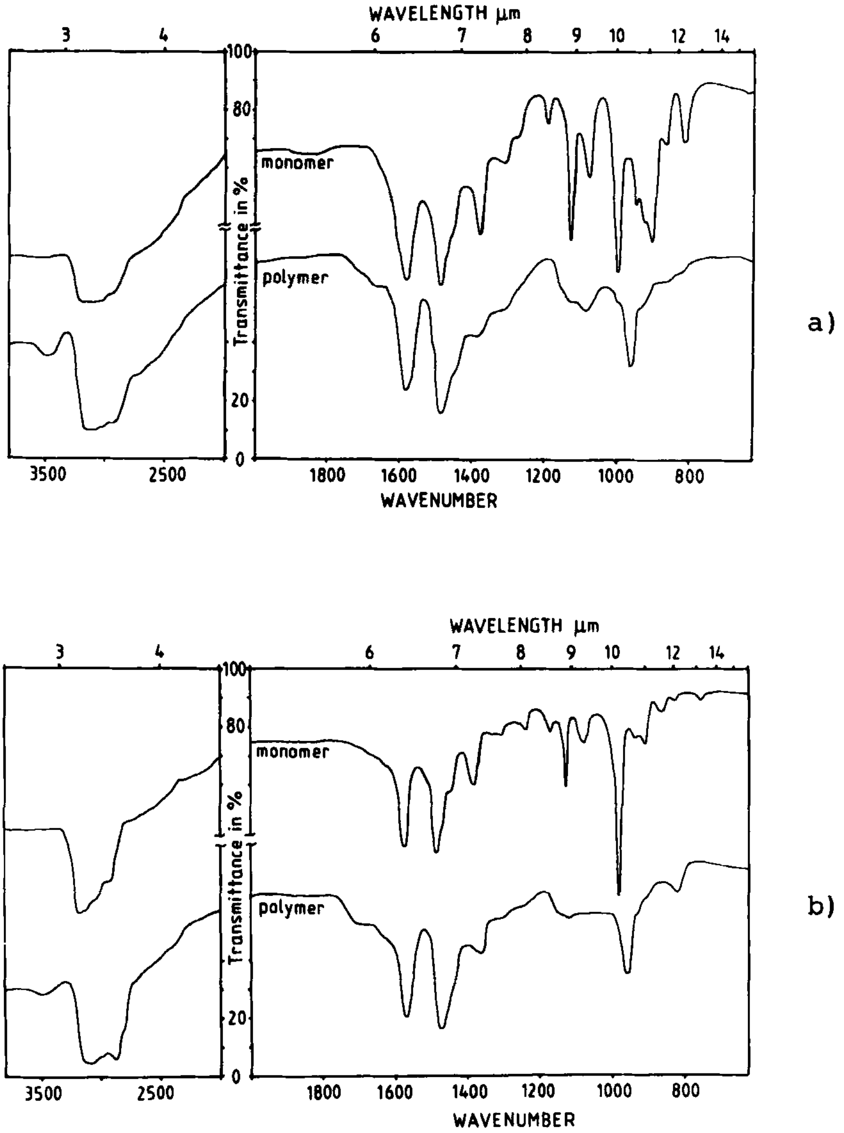


FIGURE 2. Infrared spectra of the $CdCl_2$-complexes of (a) compound 9 and (b) compound <u>10</u> as monomers and polymers (after exposure to a γ-ray dose of $3x10^7$ rad).

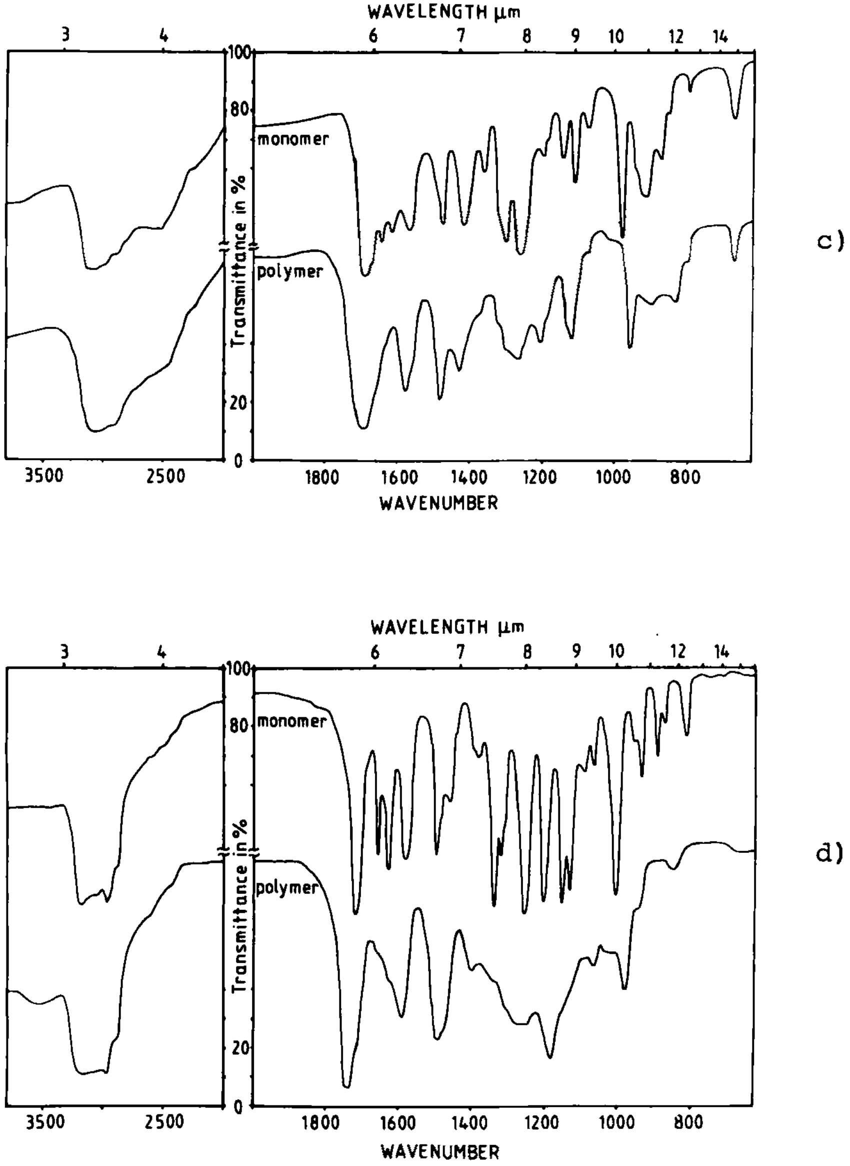


FIGURE 2. (continued) Infrared spectra of the $CdCl_2$-complexes of (c) compound 11 and (d) compound 15 as monomers and polymers (after exposure to a γ-ray dose of $3x10^7$ rad).

spectra. As recently demonstrated [12), the spectra indicate the formation of a 1,4-polybutadiene structure with the trans C=C unit (δ=135.4 and 134,2), and the aliphatic carbon atoms, created upon the reaction (δ=49.8 and 45.2). The signals of the carboxylic and aminomethyl end groups occur at δ=184.2 and 59.2. The corresponding spectrum of the monomer exhibits signals of the butadiene unit (δ=143.8, 143.6, 130.6 and 129.3), the carboxylic and the aminomethyl group at δ=178.7 and 44.9. There was no evidence for the formation of cyclobutane units, which would indicate a four-center type dimerization that has been described for a large number of trans, trans-butadiene derivatives 17).

Conversion vs. dose curves of various derivatives are shown in Fig. 3. The conversion has been determined by an evaluation of the intensity of the 960-980 cm^{-1} trans C=C wagging mode of the reaction product.

Fig. 3a shows the influence of the substituent R of various butadiene derivatives R-CH=CH-CH=CH-$CH_2NH_3^+$ on the polymerization properties. Compound <u>9</u> (R=H) exhibits the highest reaction rate, whereas compounds <u>11</u> and <u>12</u> with R=COOH and $COOCH_3$, respectively, are less reactive. However, in all cases a nearly complete conversion to polymer is observed.

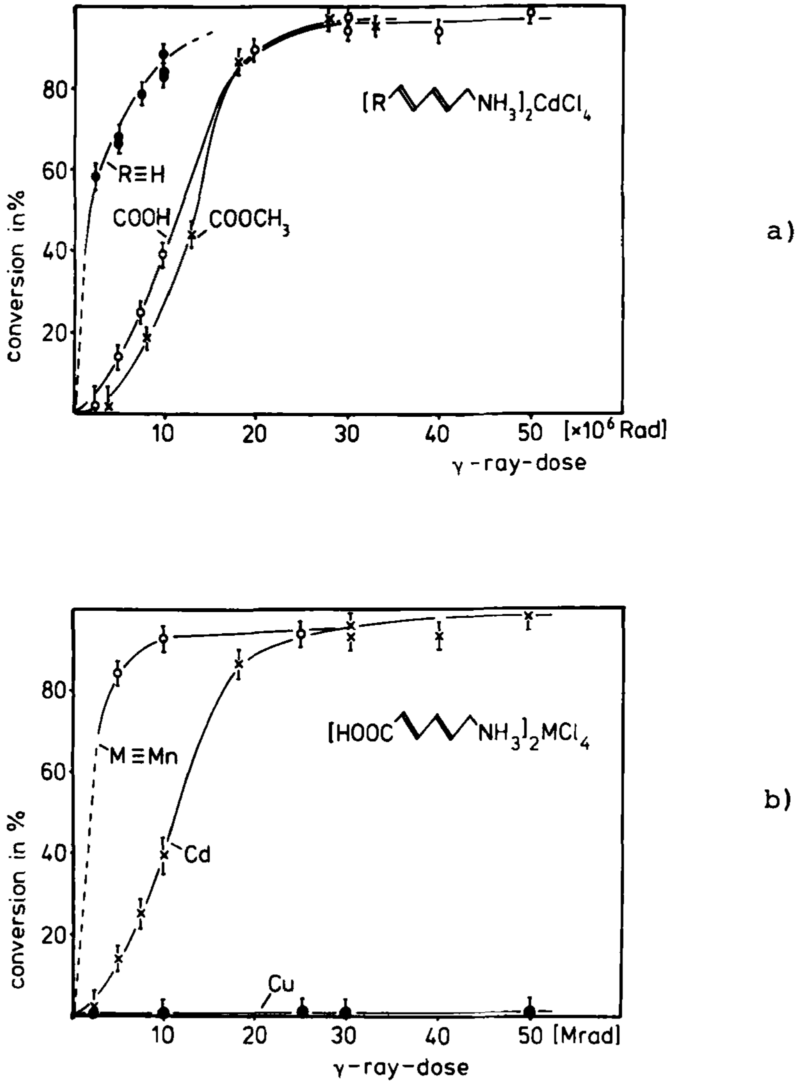


FIGURE 3. Conversion vs. dose curves of (a) $CdCl_2$-complexes of butadiene derivatives with various substituents R and (b) various metal halide complexes of compound <u>11</u>.

Fig. 3b shows the influence of the transition metal cation M^{2+} on the polymerization properties of 11. The exchange of the cadmium ions by manganese ions, for example, strongly increases the reaction rate, whereas the copper complex is completely unreactive. This behaviour may have its origin in a Jahn-Teller distortion of the $CuCl_6$ octahedra, influencing the packing of the organic cations, and is similarly observed for the $CuCl_2$-complex of compound 12. However, it should also be noted that the $CdBr_2$-complex of 11 is photoinactive as well.

STRUCTURAL CHANGES DURING POLYMERIZATION

The complex crystals of the butadiyne derivatives 5-7 could only be obtained as microcrystalline powders, whereas the butadiene derivatives form single crystals of a size up to 0.1 x 0.2 x 0.02 mm, as shown in Fig. 4. The crystals are typically obtained as platelets exhibiting a layered structure and a characteristical twinning.

Structural changes during the solid state polymerization were investigated by x-ray diffraction methods. Fig. 5 shows Debye powder patterns of the $CdCl_2$ complexes of 11, 13 and 15, as monomers and after exposure to a γ-ray dose of 3×10^7 rad. For all examples crystalline products are obtained.

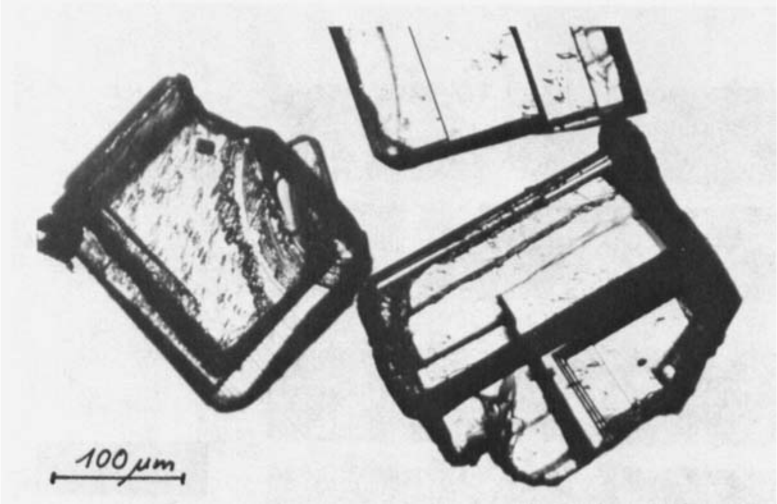


FIGURE 4. Polymeric layer perovskites. Crystals of the $CdCl_2$-complex of <u>11</u> after exposure to a γ-ray dose of 3×10^7 rad.

As Fig. 4 indicates, crystals of the $CdCl_2$-complex of <u>11</u> actually remain unchanged in their appearance. This is mainly due to the relatively small dimensional changes, as the unit cell parameters indicate and as listed in Tab. 2.

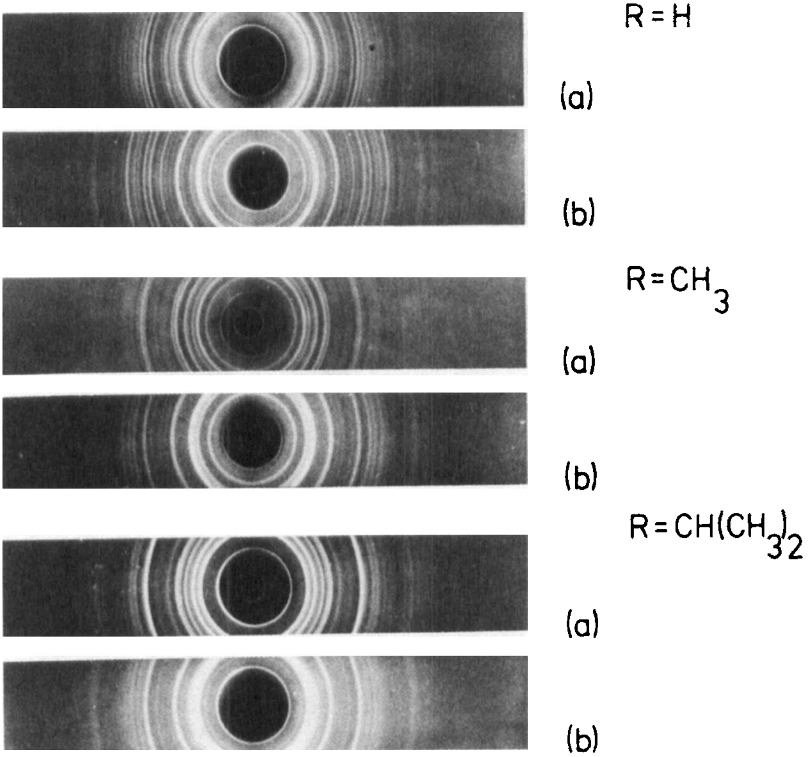


FIGURE 5. Effect of γ-ray polymerization on the x-ray diffraction patterns of the CdCl$_2$-complex of various compounds ROOC-CH=CH-CH=CH-CH$_2$NH$_3^+$. (a) monomers and (b) polymers (after a γ-ray dose of 3.5 x 10^7 rad)

TABLE II Crystallographic data of the $CdCl_2$-complex of 11

monomer		polymer (γ-dose 2.5×10^7 rad)
a [Å]	10.52	9.67
b [Å]	10.84	10.70
c [Å]	17.03	17.79
α	89.1°	93.3°
β	89.0°	90.0°
γ	87.5°	90.0°
V [Å³]	1939.7	1837.7
D_x[g/cm³]	1.75	1.84
Z	4	4
triclinic, space group $C\bar{1}$		triclinic, space group $C\bar{1}$

The interlayer spacing (c-axis) increases by 0.8 Å, as similarly observed for most of the butadiene derivatives [12]. The a-axis shortens by about 0.9 Å. Its final value of 9.67 Å agrees very well with twice the repeat unit of poly-trans-butadiene [18], which is a strong indication that the polymer chains are extended in this direction, thus implying a one-dimensional chain growth.

Structural models in two different projections are shown in Fig. 6. As the 001-projection onto the plane of the inorganic octahedra layer indicates, the polymer chains are most likely extended in the direction diagonal to the edges of the MX_6 octahedra (Fig. 6a). In this direction the distance between adjacent monomer units is about 5 Å, which agrees very well with the distance that is required for the observed photoreactions of either the butadiene or butadiyne derivatives [2,18].

Fig. 6b schematically represents the 1,4-addition reaction of the butadiene derivatives. Similarly to the solid state polymerization of disubstituted butadiynes [2] the polymerization proceeds under formation of extended polymer chains in a one-dimensional chain growth. As a consequence, the polymeric layer perovskites are cleavable only along the crystal axis parallel to the polymer chain direction (a-axis). This is demonstrated in Fig. 7. The electron diffraction pattern of such a fiber, shown as an insert of Fig. 7, demonstrates its crystalline perfection. The position of the reflections allows the conclusion that the polymer chain direction coincides with the fiber axis.

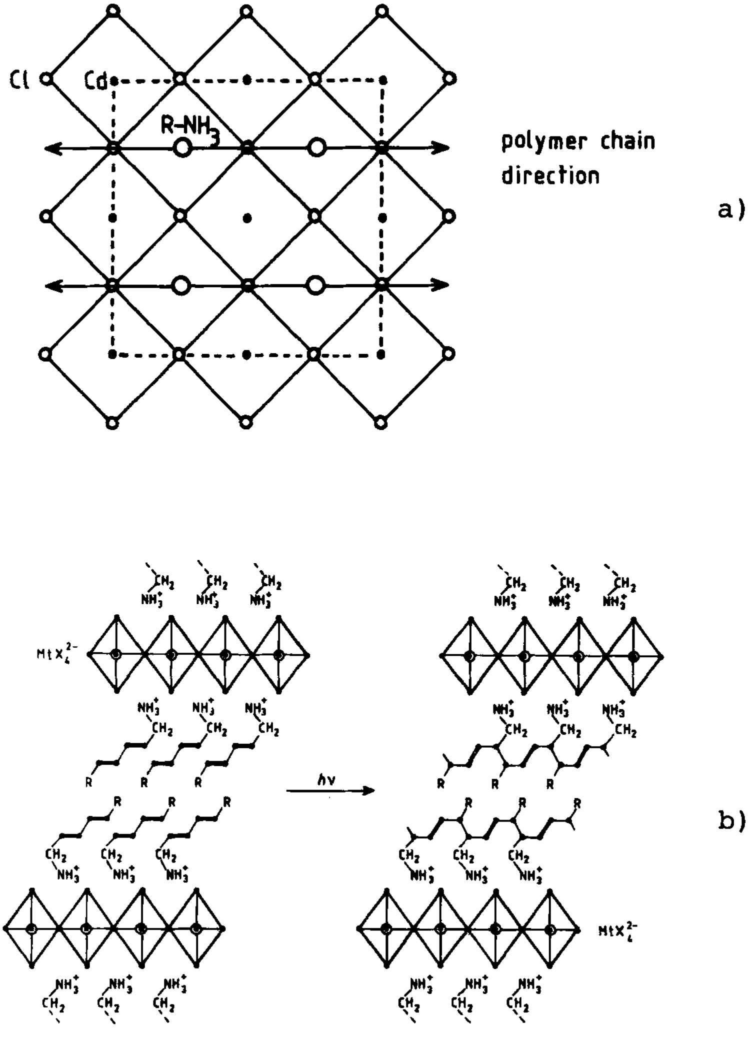


FIGURE 6. Schematic representation of the polymerization in layer perovskites. (a) Model of the 001-projection onto the inorganic MX_6 octahedra layer. (b) Model of the 010-projection ($M=Mn^{2+}$, Cd^{2+}, $X=Cl^-$, R see Tab. 1)

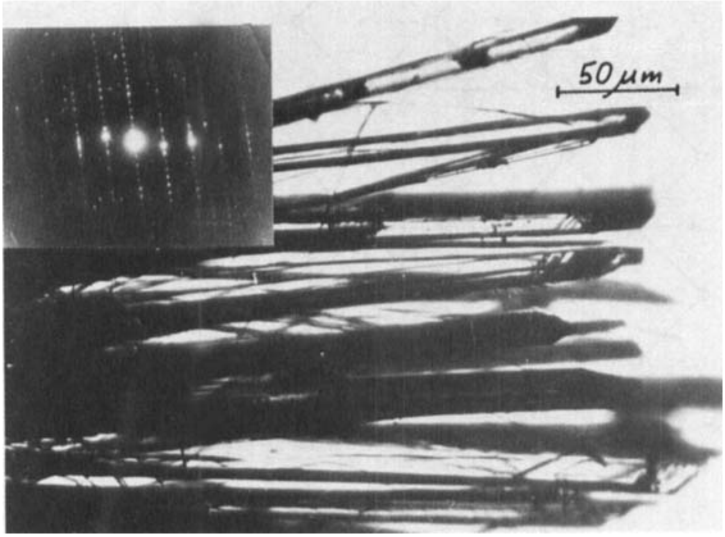


FIGURE 7. Fibrous structure of polymeric layer perovskites, as obtained upon cleavage of the crystals shown in Fig.4. Insert: Electron diffraction pattern of a polymeric fiber.

STEREORGEULARITY AND CHIRALITY OF THE POLYBUTADIENES

In principle, 1,4-disubstituted butadienes may crystallize in two different stacks, which are symmetry-related by a mirror plane, as shown in Fig. 9. As a consequence, in both stacks a growing chain end will attack the next monomer unit from different sides. This causes the formation of two different polymer chains, which are again

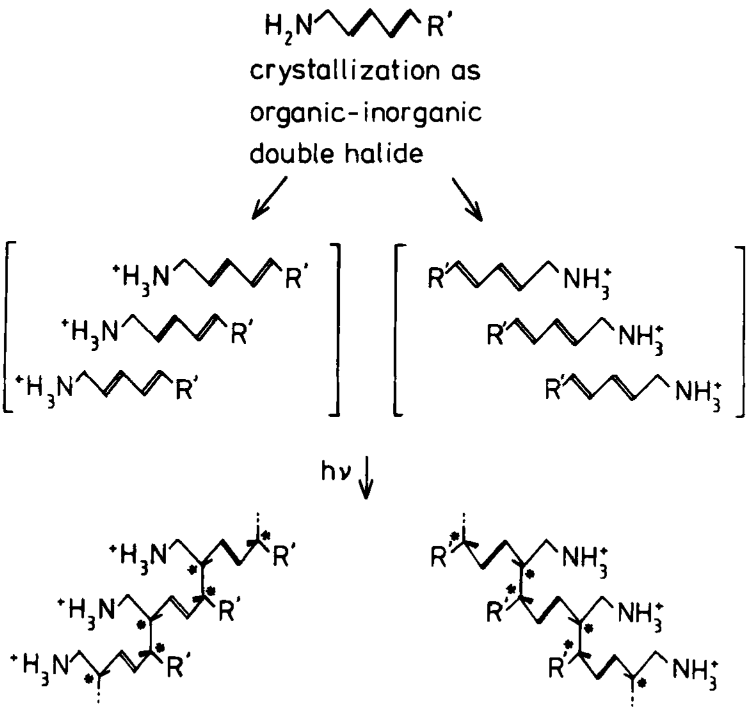


FIGURE 8. Schematic representation of the two polymeric enantiomers as formed upon a topochemical reaction without conformational changes during the chain growth. The formation of the enantiomers depends on the stacking of the monomer units (for R' see Tab. 1).

symmetry-related to each other by a mirror plane. Since the polymerization induces two centers of chirality per monomer unit the two polymer chains are enantiomeric with regard to each other.

Due to the centrosymmetry of the unit cells of the layer perovskites both types of chains are actually formed and a racemat is obtained. Consequently solutions of the polymer do not show optical activity.

The formation of non-centrosymmetric crystals by the use of chiral monomers may therefore offer a possibility for obtaining one of the enantiomers in excess.

Provided that the polymerization proceeds without conformational changes of the substituents, the polymer must exhibit an erythro-diisotactic arrangement of the substituents, as shown in Fig. 8.

THERMAL PROPERTIES

In Tab. 3 the thermal stabilities of various organic inorganic double halides are summarized, as determined by DSC. The layer perovskites usually melt under decomposition in the temperature range between 450 and 550 K. Melting and decomposition of the copper complexes usually occurs 50 to 80° below that of the cadmium complexes. Many of the complex crystals exhibit phase transitions in the temperature range between 270 K and their decomposition point. However, in case of the butadiene derivatives, neither the monomers nor the polymers show any transitions.

The polymerization of the butadiene derivatives increases their melting and decomposition points to temperatures higher than 600 K, as shown for the $CdCl_2$-complexes of <u>11</u> and <u>12</u> in Fig. 9. The polymers are fairly high temperature stable materials, due to their high crystallinity and the inorganic matrix, in which they are embedded.

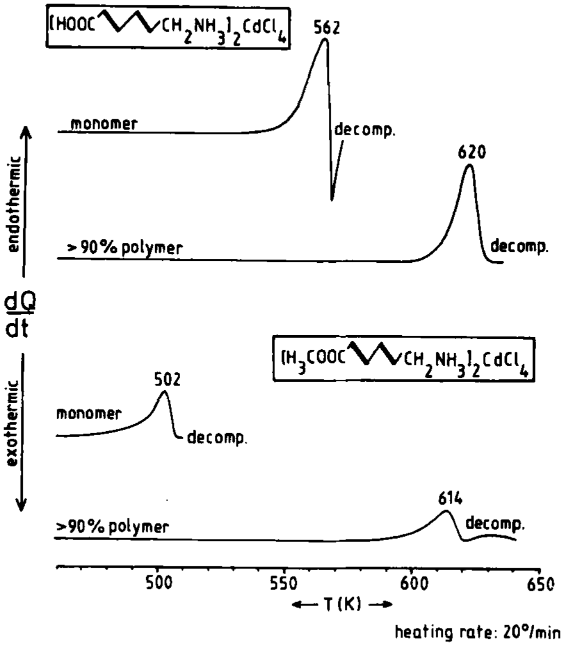


FIGURE 9. DSC-diagrams of monomeric and polymeric layer perovskites

TABLE III Melting behaviour of various layer perovskites

organic compound	inorganic compound	phase transition temp. in |K|	melting and decomp. in |K|
<u>1</u>	$CdCl_2$	370 and 410	520
	$CdBr_2$	-	444
<u>2</u>	$CdCl_2$	363	514
<u>3</u>	$CdCl_2$	347	510
	$CuCl_2$	347	440
<u>7</u>	$CdCl_2$	375,380,435	490
<u>8</u>	$CdCl_2$	-	535
<u>11</u>	$CdCl_2$	-	562
<u>12</u>	$CdCl_2$	-	502
	$CuCl_2$	-	420
<u>15</u>	$CdCl_2$	-	420
<u>16</u>	$CdCl_2$	-	510
<u>17</u>	$CdCl_2$	432	482
<u>18</u>	$CdCl_2$	515	561
<u>19</u>	$CdCl_2$	409	470

SUMMARY AND CONCLUSIONS

The packing of the organic cations $R\text{-}NH_3^+$ with butadiyne or trans, trans-butadiene units in R in layer perovskites was found to be suitable for a 1,4-addition polymerization. This type of photoreactivity has not been observed for 1,4-disubstituted butadienes in the crystalline state so far 18).

However, unsaturated amines with isolated double and triple bonds, or cinnamic acid units were found to be photoinactive. This originates most likely from the 5 Å distance of the adjacent monomers. This distance is just favourable for solid state reactions of the butadiynes and butadienes, but is too large for the other derivatives.

In general, the polymerization in layer perovskites opens a novel method to obtain highly ordered polyelectrolytes.

EXPERIMENTAL PART

Materials

The compounds 1, 8, 16 and 17 are commercially available (Merck, Aldrich). The synthesis of the butadiene derivatives has been described previously 12). 1-Amino-5-hexyne (2) was obtained from the corresponding alcohol 19) as described previously for 9 and 10 [12]. The ester 3 was obtained by heating the corresponding acid in propargylic alcohol under reflux for 2 hours in a stream of dry gaseous HCl. The anilines 4 and 7 were obtained from 4-formaminophenol and the corresponding alkylbromide by heating 1 mole of either compounds together with 1 mole of potassium carbonate in acetone under reflux for 6 hours. The formyl group was cleaved off by refluxing 0.05 moles of the corresponding compounds in 150 ml of a 5:1 mixture of ethanol and concentrated aqueous HCl for 5 hours. 5 and 6 were obtained by reduction of the corresponding acid amides with $LiAlH_4$ [10]. The synthesis of 18 is described in the literature [20] 19 was obtained from cinnamyl bromide by etherification with ethanol amine [21].

The layer perovskites were obtained as described previously [11,12].C- and H-analyses are listed in Tab. 4.

Measurements

Infrared spectra were recorded on KBr dispersions. UV/VIS spectra were obtained from powdered samples using a Perkin Elmer Hitachi 200 spectrometer. DSC-measurements were performed in the temperature range between 270 and 650 K (Perkin Elmer DSC-2). Debye-Scherrer photographs were taken with a camera having a diameter of $\frac{360}{\pi}$ mm using Ni-filtered Cu-K_α-radiation.

TABLE IV C and H analyses of the monomeric layer perovskite crystals $(R-NH_3)_2MX_4$ (data of the butadiene derivatives 9-15 were described previously)[12].

$R-NH_2$	MX_2	Calc.		Found	
		C	H	C	H
1	$CdCl_2$	19.76	2.74	19.54	3.05
1	$CdBr_2$	13.37	2.35	13.24	2.21
2	$CdCl_2$	31.97	5.33	31.56	5.22
3	$CdCl_2$	45.75	7.08	45.51	7.16
4	$CdCl_2$	39.24	3.63	37.83	3.17
5	$CdCl_2$	61.56	9.56	61.46	9.45
5	$CuCl_2$	64.81	10.00	64.75	9.74
6	$MnCl_2$	50.30	6.91	49.92	7.20
7	$CdCl_2$	64.23	8.63	62.71	7.43
8	$CdCl_2$	19.65	3.28	19.55	4.05
16	$CdCl_2$	36.02	3.43	34.45	3.57
17	$CdCl_2$	37.09	3.43	36.98	3.66
18	$CdCl_2$	41.35	4.59	41.09	4.50
18	$CuCl_2$	45.62	5.07	44.37	5.14
19	$CdCl_2$	41.10	4.98	40.87	4.98

ACKNOWLEDGEMENT

Dr. V. Enkelmann is acknowledged for the determination of the unit cell dimensions and Dr. G. Lieser for the electron diffraction experiments. Useful discussions with them and Prof. Wegner are gratefully acknowledged. The Stiftung Volkswagenwerk supported this work financially.

REFERENCES

1. H. Nakanishi, F. Nakanishi, Y. Suzuki, and M. Hasegawa, J. Polymer Sci. A1, 11, 2501 (1973)
2. G. Wegner, Pure and Appl. Chem., 49, 443 (1977).
3. R. Ackermann, D. Naegele, and H. Ringsdorf, Makromol. Chem., 175, 699 (1974).
4. S. A. Letts, T. Fort jr., J. B. Lando, J. Colloid Interf. Sci., 56, 64 (1976).
5. M. Breton, J. Macromol. Sci. - Rev. Macromol. Chem. C21, 61 (1981).
6. K. Takemoto, and M. Miyata, J. Macromol. Sci.- Rev. Macromol. Chem. C18, 83 (1980).
7. M. Farina, Makromol. Chem. Suppl. 4, 21 (1981).
8. H. Arend, W. Huber, F. H. Mischgofsky, and G. K. Richter van Leeuwen, J. Crystal Growth, 43, 213 (1978).
9. R. Kind, S. Plesko, H. Arend, R. Blinc, B. Zeks, J. Seliger, B. Lozar, J. Slak, A. Levstik, C. Filipic, V. Zagar, G. Lahajnar, F. Milia, and G. Chapuis, J. Chem. Phys., 71, 2118 (1979).
10. G. Wenz, Diplomarbeit, Freiburg 1979.
11. B. Tieke, andG. Wegner, Angew. Chem. Int. Ed. Engl., 20, 687 (1981).
12. B. Tieke, and G. Wegner, Makromol. Chem. Rapid Commun., 2, 543 (1981).
13. R. D. Ledsham, and P. Day, J.C.S. Chem. Comm. 1981, 921.
14. P. Day, and R. D. Ledsham, Mol. Cryst. Liquid Cryst., 86, 163 (1982).
15. H. Arend, H. von Känel, and P. Wachter, phys. stat. sol. (b), 74, 151 (1976).
16. G. F. Needham, and R. D. Willett, J. Phys. Chem., 85, 3385 (1981).
17. G.M.J. Schmidt et al., Solid State Photochemistry, Monographs in Modern Chemistry, Vol. 8, D. Ginsberg Ed., Verlag Chemie, Weinheim 1976.
18. S. Ywayanaki, I. Sakurai, and T. Sakurai, J. Macromol. Sci., B2 , 163 (1968).
19. E.R.H. Jones, G. Eglington, and M.C.Whiting, "Organic Syntheses", Vol. 3, p. 698, Wiley, New York 1955

20. T. Posner, Ber. dt. chem. Ges., 26, 1856 (1893).
21. W. Kern, S. Iwabuchi, H. Sato, and V. Böhmer, Makromol. Chem., 180, 2539 (1979).