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Solid State Chemistry of Polymethines

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Solid State Chemistry of Polymethines

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The solid state chemistry of bis(dimethylamino) polymethine salts (n = 1,2,3,4) was investigated using thermogravimetry, difference thermal analysis, mass spectroscopy, UV/VIS spectroscopy and HPLC to analyze the extruded gaseous products and the residue.

The observed pathway is nonamethine → heptamethine → pentamethine → trimethine → insoluble residue extruding dimethylamine and ethylene.

The temperature of the strong exothermal process and the thermal behaviour in detail depend on the chain length, the anion and the crystal structure.

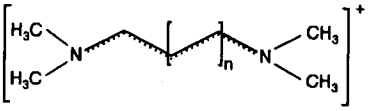
Keywords: Polymethine dyes, solid state chemistry, thermal analysis

1. INTRODUCTION

Polymethine dyes have an immense importance for sensitization of the photographical process.[1] Polymethines in the solid state show further unusual properties as, for example, large shifts of excitation energy, photoconductivity and enlargement of nonlinear optical properties.[2] Solid state reactions of unsaturated organic compounds in the crystalline state are important for the design of new materials with nonlinear optical properties e.g. polydiacetylene.[3]

We studied the solid state chemistry of polymethine dyes using formula (1):
The compounds **1a, 2a, 3a, 4a** differ in chain length of the polymethinium cation. The heptamethine salts **3a–3e** are characterized by different crystal structures.[5–7] The compounds **3d** and **3e** are isomorphous and isotypic to bis(dimethylamino) heptamethine-chloride tetrahydrate.

It was found that crystals of bis(dimethylamino) heptamethine-chloride tetrahydrate undergo a solid state reaction in vacuo at 115°C while keeping the crystal shape.[8] Further investigations of this compound by TG and DTA measurements have shown a solid state reaction under normal pressure with strong exothermal effects. During this



(1)

X	Trimethine n = 1	Pentamethine n = 2	Heptamethine n = 3	Nonamethine n = 4
ClO_4	**1a**	**2a**	**3a**	**4a**

X	ClO_4	BF_4	I	Br · 4 H_2O	N_3 · 4 H_2O
Heptamethine	**3a**	**3b**	**3c**	**3d**	**3e**

reaction new compounds are formed, probably, with new interesting properties.[9] Therefore we investigated the thermal behaviour of further polymethines (see Table 1) by thermogravimetry (TG) and by difference thermal analysis (DTA).

In order to clarify the thermal behaviour, the products existing after the first TG step were investigated by mass spectroscopy, HPLC and UV/VIS spectroscopy.
The compounds were investigated up to their decomposition temperature at linear heating rates of 2 K/min in a dried inert gas flow.

2. RESULTS

Thermal Analysis

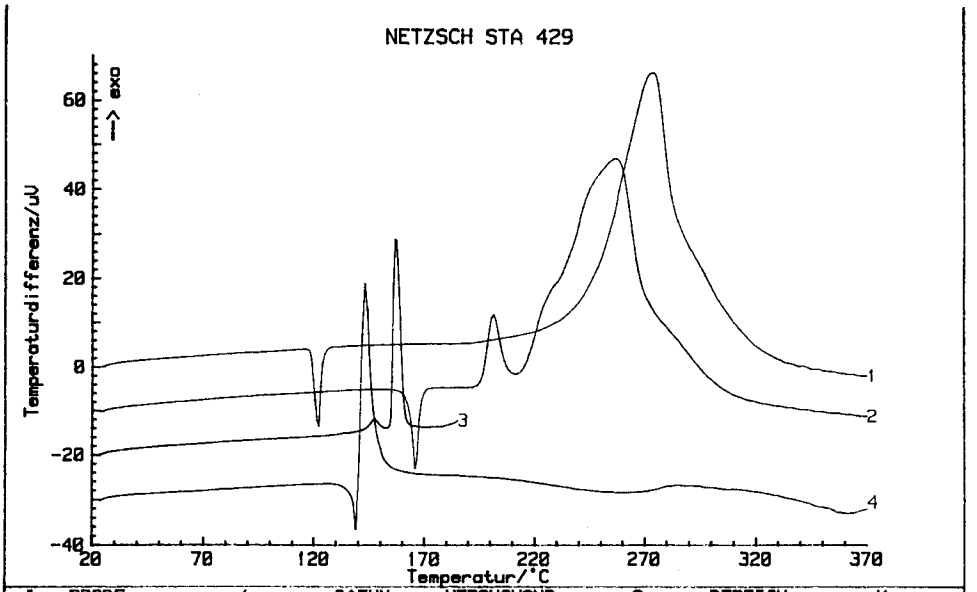
The dependence of cation chain length was studied (**1a, 2a, 3a, 4a**). The influence of the anion on the thermal behaviour should be investigated regarding substances **3a–e**.

The DTA curves of compounds **1a, 2a, 3a** and **3b** are shown exemplarily in Figure 1. The four curves compared reflect the different types of DTA curves of the investigated compounds. The types are:

- melting and one-step reaction of the melt (**1a**)
- melting and multi-step reaction of the melt (**2a**)
- multi-step solid state reaction (**3a**)
- melting under decomposition (**3b**)

The results of thermal analysis are summarized in Table 1.
With prolonging the cation chain length in the case of **1a** and **2a** the melting temperature increases but the decomposition temperature decreases in all cases.

The mass losses could not match quantitatively with the theoretical values of possibly extruded molecules or fragments.



#	PROBE	/mg	DATUM	VERSUCHSNR.	Seg.	BEREICH:	Kor.
1	BDT+ClO4-	9.0	13 Jan 1993	127	1:	20/ 2.00/ 410	
2	BDP+ClO4-	9.4	12 Jan 1993	126	1:	20/ 2.00/ 410	
3	BDH+ClO4-	8.7	11 Jan 1993	125	1:	20/ 2.00/ 410	
4	BDH+BF4-	8.7	15 Jan 1993	129	1:	20/ 2.00/ 410	

FIGURE 1 Comparison of different types of DTA curves 1: melting and one-step reaction of the melt 2: melting and multi-step reaction of the melt 3: multi-step solid state reaction 4: melting under decomposition.

Mass Spectroscopy

In order to clarify the nature and composition of the products involved during the thermal decomposition of **3a** and its isotypic compounds of **3d** and **3e** the gas phase was investigated by mass spectroscopy. The same experimental conditions as in the thermal analysis were applied.

Under constant heating (3K/min) the gas phase was continuously analyzed by mass spectroscopy. The evolution of the decomposition of **3a** in the mass spectrometer depending on temperature is shown in Figure 2.

In the case **3a** two emission effects could be detected. The maxima of gas emission (maximum of total ion current) are at 132°C and 147°C. All detected ions (44, 45, 28, 18 and 71) have their intensity maximum at these temperatures. Due to the much higher sensitivity of the MS analyzer and the lower pressure the emission effects begin at a lower temperature than at the thermal analysis measurement. Ions with mass 44 and 45 (dimethylamine), 28 (ethylene) and 71 (dimethylethylenamine) were found. The mass number 18 could be assigned to water.

These results show that dimethylamine and a C_2H_4 fragment were generated during the solid state reaction.

The dehydration of the compounds **3d** takes place in vacuo ($1.3 \cdot 10^{-4}$ Pa) at 80°C. After dehydration under constant heating (3 K/min) the gas phase was analyzed. The

TABLE I

Results of thermal analysis

Compound	T_{on}^{ex}/°C	T_p/°C	Δm/%	DTA	Comments
	118	122		endo vs	melting
1a	242	273	68.1	exo s	decomposition of the melt without steps
	161	166		endo vs	melting
	186	201	2.2	exo s	first reaction in the liquid phase
2a		256	58.8	exo b	second reaction in the liquid phase
	211				more than two steps (shoulder at 229°C)
	142	147	3.4	exo I s	both reactions in the solid state
3a					$\Delta_R H$ (I) $<<$ $\Delta_R H$ (II)
	154	156	5.2	exo II s	DTG (II): two steps
4a	106	127	7.4	exo s	one step solid state reaction
	129	139		endo vs	melting under decomposition
		143	5.7	exo vs	
3b			30.4	exo vb	unspecific decomposition
			31.3	exo vb	
	156	166		endo vs	melting under decomposition
3c		168	9.5	exo vs	
			57.4	exo vb	unspecific decomposition
		50	22.5	endo m	complete dehydratation (theoretical value: 22.3 %)
3d	145	150	12.8	exo vs	solid state reaction
			42		unspecific decomposition, no characteristic effects
		45	25.6	endo m	dehydratation analogous to **3d** theoretical value: 25.3 %)
3e	127	138		exo w	first two DTA effects are connected with one mass loss (one DTG peak),
		146	42.2	exo m	third DTA effect can be characterized as a different one
		152		exo s	(soft shoulder of DTA curve)

vw very weak vb very broad m medium vs very strong
w weak b broad s strong

composition of detected ions of **3d** in the gas phase as function of the temperature is exemplarily shown in Figure 3.

In this case, **3d**, besides the mass numbers 44 and 45 a product with mass 134 could be detected. The maximum of the total ion current is reached at 147°C ($m/e = 44/45$) and 152°C ($m/e = 134$). Although comparable experimental conditions were applied, the emission takes place without the very sharp exothermal effect at $T_p = 150$°C, which was found at the thermal analysis measurement.

Analysis of Thermolyzed Residue

a) UV/VIS Spectroscopy

In order to identify the products of the thermal analysis the heating was terminated at different temperatures and the solid residue was analyzed. We investigated the

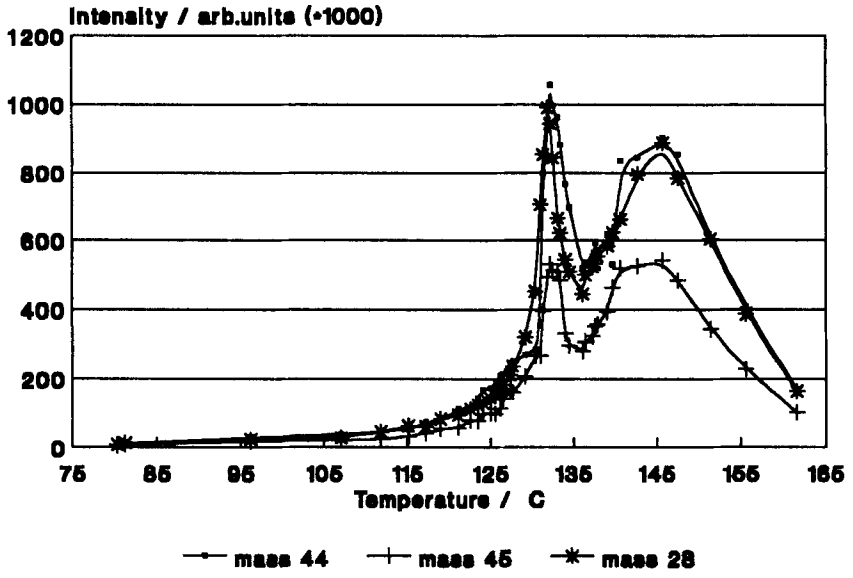


FIGURE 2 MS analysis of **3a**. Evolution of *m/e* intensities with increasing temperature (heating rate 3 K/min; pressure $3 \cdot 10^{-4}$ Pa).

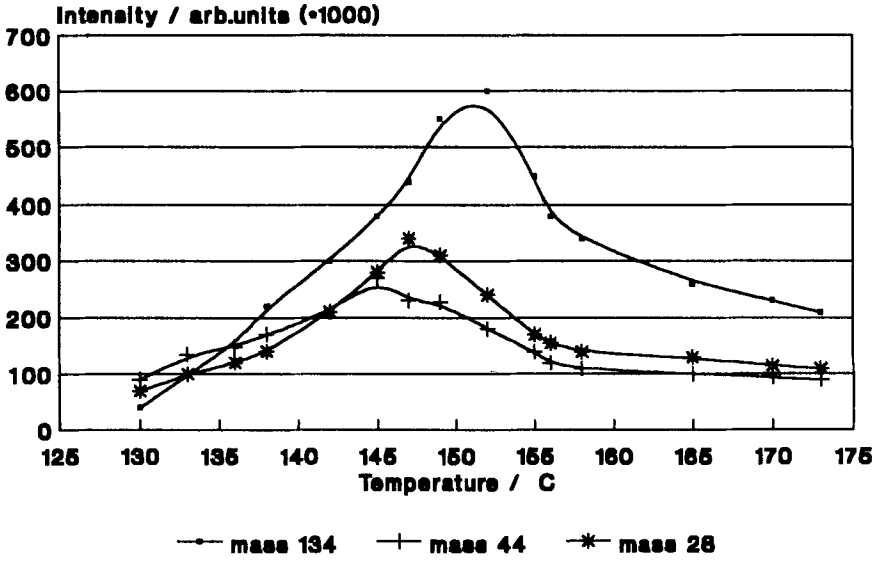


FIGURE 3 MS analysis of **3d**. Evolution of *m/e* intensities with increasing temperature (heating rate 3 K/min; pressure $3 \cdot 10^{-4}$ Pa).

compounds **3a, 3e** and **4a.** In all cases the residue was dissolved both in ethanol and dichloromethane.

3a was heated until the first exothermal effect started. The heating was stopped at 142°C and the sample was quenched to room temperature. No further mass loss could be detected. The obtained UV/VIS absorption spectrum of the product dissolved in ethanol is shown in Figure 4. The substance is soluble in ethanol and in dichloromethane, too.

Curve A shows the spectrum of **3a** in ethanol. The absorption maximum is at 512 nm in ethanol. Curve B shows the absorption spectra of decomposed compound **3a** at different concentrations. Besides the absorption band of the starting material these spectra contain two new absorption bands at 410 and 310 nm, respectively. The coincidence of these absorption maxima of the decomposition products with those of pure compounds is obvious.[9]

The residue of **3a** was investigated after the second exothermal effect. In this case the thermolyzed substance was only partially soluble. The insoluble residue, about 75%, was a black carbon-like substance. The spectrum of the soluble product mixture is similar to that of Figure 4, but the concentration of tri-and pentamethine dye is much higher than after the first exothermal effect.

4a was dissolved in ethanol after heating up to the exothermal effect. The UV/VIS spectra are presented in Figure 5.

Curve A gives the absorption spectrum of **4a**. The absorption maximum is at 612 nm in ethanol. Curve B shows the absorption spectra of the decomposition products. Two new absorption bands appear at 510 nm for the first and at 410 nm for the second one.

The corresponding penta-and heptamethine dyes (**2a, 3a–e**) have their absorption maxima at exactly the same wavelengths.[10]

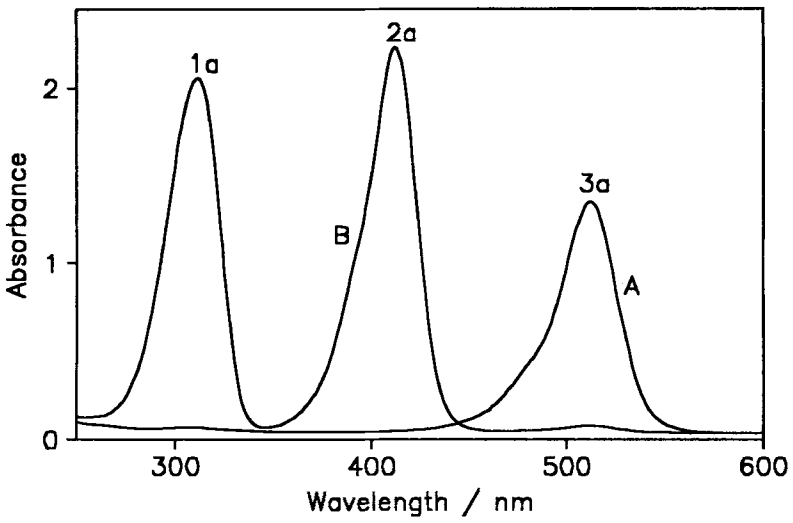


FIGURE 4 Absorption spectra of **3a** and the dissolved residue (**2a** + **1a**), solvent ethanol.

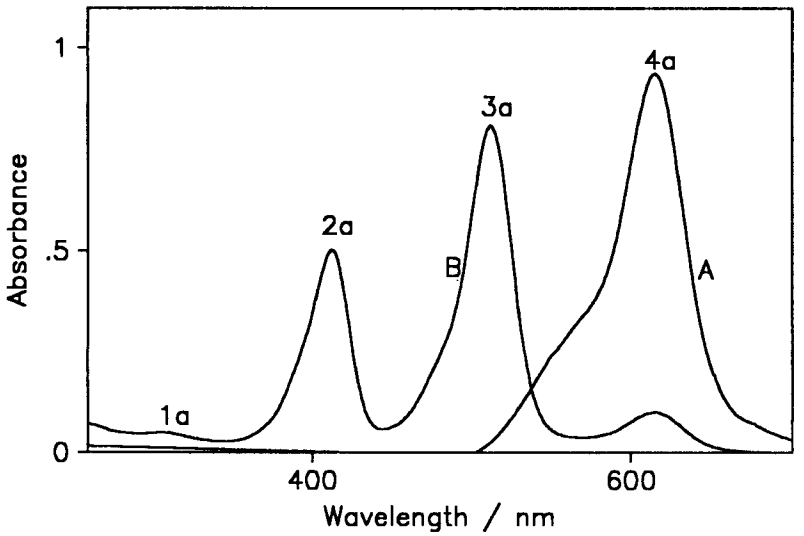


FIGURE 5 Absorption spectra of **4a** and the dissolved residue (**3a** + **2a** + **1a**), solvent ethanol.

b) HPLC

Knowing the results from the UV/VIS spectroscopy analysis of compound **3a** it was necessary to identify the dyes detected after the thermal experiment. High performance liquid chromatography (ion-pair chromatography) was applied. The detection wavelength was selected in relation to the UV/VIS spectra. We detected at the absorption maxima at 510, 410 and 310 nm and at 254 nm as well. The detected compounds could be identified by comparing the retention times t_R of the pure reference compounds (trimethine dye **1a** $\{t_R = 14.5\,\text{min}\}$ and pentamethine dye **2a** $\{t_R = 16.2\,\text{min}\}$) with the measured retention times of the decomposition products of **3a** ($t_R = 19.0\,\text{min}$).

The compounds of decomposition of **4a** were identified in the same way as in the case of **3a** using the retention times of pure heptamethines and pentamethines as reference (**4a**: $t_R = 24.5\,\text{min}$).

3. DISCUSSION

The thermal analysis (TG, DTA) of all investigated polymethine compounds shows three different effects: dehydration of the tetrahydrates (**3d, e**), melting (**1a, 2a, 3b, 3c**) and chemical reaction. The dehydration of **3d,e** takes place without chemical reaction. Crystallographic investigations show that the crystal structure becomes disordered.[11] When prolonging the chain length the melting point increases but the temperature of decomposition decreases, consequently **1a** and **2a** show the chemical reaction after melting, **3a** and **4a** give the same reaction in the solid state before melting. Therefore the results of the solid state reactions of **3a, 3d, 3e** and **4a** were investigated in more detail.

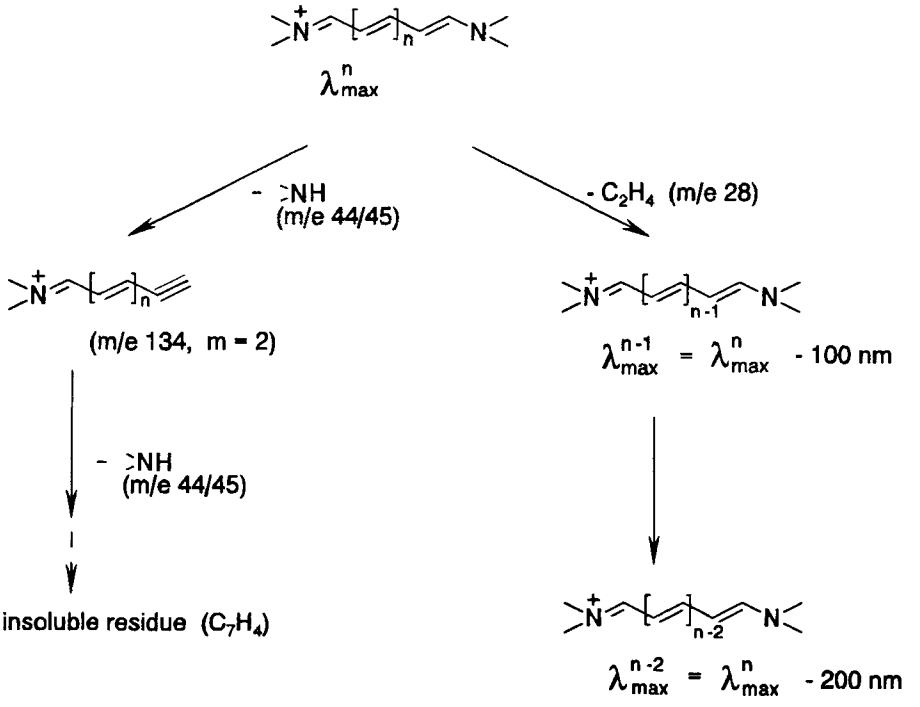
All compounds show exothermal reactions with very sharp DTA effects. The mass losses could not match quantitatively with the theoretical values of possibly extruded molecules.

The following pathway can be propounded, summarizing the results of mass spectroscopy of the gas phase during the exothermal solid state reaction, the results of UV/VIS spectroscopy and the HPLC data of the residue of the thermal analysis.

NONAMETHINE → HEPTAMETHINE + PENTAMETHINE + TRIMETHINE + INSOLUBLE RESIDUE

HEPTAMETHINE → PENTAMETHINE + TRIMETHINE + INSOLUBLE RESIDUE

In order to clarify the reaction mechanism of the solid state reaction all applied methods were combined. The following reaction scheme 1 can be assumed, it explains all results obtained:

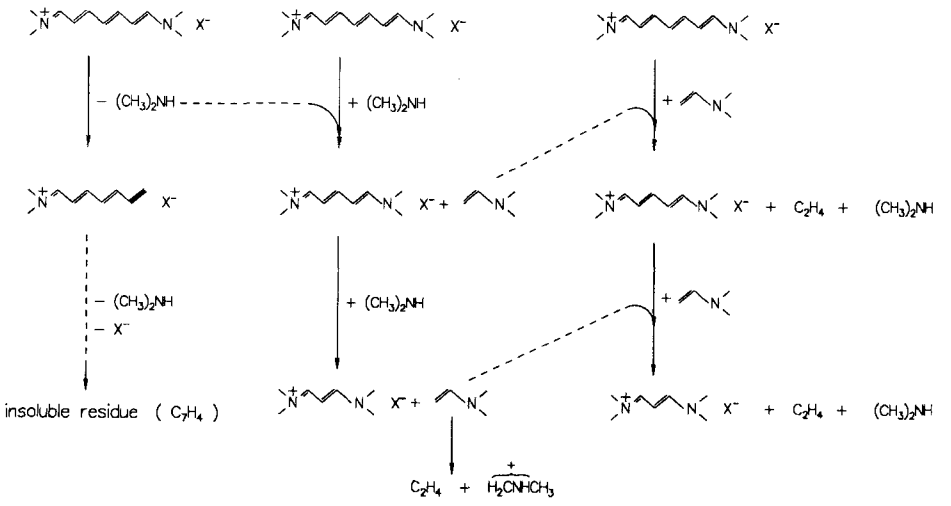


SCHEME 1

The MS analysis of the gas phase in all cases shows a separation and emission of dimethylamine (*m/e*: 44/45), which was detected before it causes a remarkable mass loss at TG. Subsequently, the dimethylamine reacts with the anion, e.g. forming the corresponding hydrohalide (Figures 1, 2). The reactions are incomplete in all cases, the mass loss in the TG curves never corresponds to a complete separation of one mole dimethylamine. Further heating after the exothermal effects forms the insoluble residue which is X-ray amorphous. This amorphous product has been also obtained if **3d** was

stored in vacuo at 115°C for 6 hours. The expected molar weight of the residue is about 88 g/mol (C_7H_4). A fragment with mass number 28 was also detected. This correlates with a C_2H_4- fragment, whose extrusion causes the chain-shortening. The pathway of fragmentation is characterized by the intermediate formation of a cation fragment with mass number 134 in the cases of **3d** and **3e**.

When the heating was terminated after the first exothermal effect and the compound was quenched to room temperature in all cases products with a shorter chain-length were found (Figures 3, 4, 5). The product was totally soluble. The UV/VIS spectrum shows only the absorption bands of the next shorter vinylogous polymethine dyes. Dimethylamine has no absorption bands within the detection range. HPLC investigations also prove the existence of the shorter polymethine cations.



SCHEME 2

The scheme 2 is divided into three parts. The molecules in the upper line are molecules in a crystal of a heptamethine salt (e.g **3d**). The mechanism is presented as *branched out chain reaction.*

The first step of the chain reaction is explained as elimination of dimethylamine by solid state reaction caused by the break of the most unstable C—N bond. This fact is supported by detecting dimethylamine in all cases and further by a detection of an ion with mass number 134 in the case of simple heptamethine halides. Dimethylamine has never been extruded completely. Therefore it can react with a neighbouring molecule of a polymethine cation. Such reactions starting with a nucleophilic attack are described for polymethines in solutions.[12] Products of this nucleophilic substitution are the corresponding next shorter polymethine and an enamine (*m/e*: 71). The proof of this step is given by the results of UV/VIS spectroscopy. In all cases the next shorter polymethines were found. A further ramification of the chain reaction is shown in the right part of the mechanism (Scheme 2). In this case the enamine formed in the second

step attacks another polymethine cation. This nucleophilic substitution proceeds in the same manner as the nucleophile attack of a polymethine by dimethylamine. The resulting next shorter polymethines (compare UV/VIS spectra), an ion with mass number 28 and dimethylamine are the products of this reaction. All these reactions are also possible with the first formed degradated polymethines. The result is a further chain shortening of polymethine cations and the formation of amines (dimethylamine or enamine). A continuation of the chain reaction is possible by nucleophilic attack of all kinds of polymethines by amines formed in previous reactions.

There are three possibilities to terminate the chain reaction. An extrusion of dimethylamine and further chemical solid state reactions such as forming of dimethylamine hydrohalides in the case of heptamethine halides give an insoluble residue with a sum formula of C_7H_4. Another possibility is the decomposition of the formed enamine during a nucleophilic substitution. The products have mass numbers of 28 (ethylene) and 44 (N-methyl-immonium). The third possibility to stop the solid state reactions is a split off of dimethylamine from the polymethine cation with the shortest chain length (trimethine). This decomposition gives also an insoluble residue.

SUMMARY

All kinds of investigated polymethines show the same solid state reaction mechanism. The differences of reaction enthalpy, the number of exothermal peaks and the temperature of the exothermal reaction are caused by the different crystal structures e.g. in the case of heptamethines as a function of the corresponding anion. The dependence of the chain length is established by different temperatures for the exothermal solid state reaction.

EXPERIMENTAL

a) Synthesis of Polymethines

— Bisdimethylamino-nonamethine-perchlorate (**4a**) was synthesized using the modified common synthesis of open chain polymethines.[13,14]
— Bisdimethylamino-heptamethine-chloride (**3d**) and Bisdimethylamino-pentamethine-perchlorate (**2a**) were synthesized using a Vilsmeier–Haack synthesis.[13]
— Bisdimethylamino-trimethine-perchlorate (**1a**) was sponsored by W. Grahn, TU Braunschweig.

The other anions of heptamethines (**3a** and **3e**) were obtained by anion exchange reactions. Heptamethine-chloride was dissolved in methanol and the solution of sodium salts in water of the corresponding anion was added. The products were purified by multiple recrystallization.

b) Thermal Analysis

The thermal analysis measurements were carried out in a Simultaneous Thermal Analyzer STA 429 from NETZSCH Gerätebau GmbH. The heating rate was 2 K/min

in an inert gas flow (dried argon) with volume flow v = 150 cm^3/min. A Pt crucible was used. The sample weight was in the range between 7–10 mg and as reference material Al_2O_3 was used.

c) Mass Spectroscopy

The mass spectra were obtained with a 5995 A Mass Spectrometer (Hewlett Packard). The ionization energy was 70 eV. The heating rate was 3 K/min.

d) UV/VIS Spectroscopy

The UV/VIS spectra were obtained using a HITACHI spectrophotometer U 3410.

e) HPLC

HPLC pump 422/422S with HPLC mixer M 494 (Kontron Instruments), mobile phase: methanol/water with octansulfonic acid, isocratic 70:30, flow 0.5 ml/min, Model 7125 Syringe Loading Sample Injector (Rheodyne Inc.), column: LiChrosorb RP 18 (5 μm) 250 mm x 4 mm (Knauer), LCD 502 detector (Gamma Analysen Technik GmbH), detection wavelength 254 nm.

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