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Synthesis of dye containing epoxide-amine addition polymers and investigation of their thermal and optical properties

39. Uncross linked epoxide-amine addition polymers*

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Summary

N-alkylated epoxide-amine addition polymers as well as epoxide-amine addition polymers containing carboxylate groups are used for an ion exchange by various anionic dyes such as diamine green, crocein or cationic dyes, respectively like rodamine and malachite green. The polymer-dye salts **1** and **2** are soluble in DMF, DMF/ 2-methoxy ethanol and other solvents and can be cast into transparent coloured films from these solutions. The glass transition temperatures were found between 90 and 165 °C (**1**) and between 85 and 112 °C (**2**), respectively. The thermal decomposition of polymers **1** and **2** takes place at 300 - 370 °C. Furthermore, non-linear optical properties (third harmonic generation) of the polymer-dye salts **1** and **2** were expected and calculated to be 10^{-12} - 10^{-13} esu.

Introduction

For the last three decades an intensive investigation of polyelectrolytes has arisen because of their outstanding mechanical, dielectric, optical and ion-exchanging proper-ties [2-4]. Polyelectrolyte complexes possess a high dielectric constant, a high loss factor and a high electroconductivity (about 10^{-2} to 10^{-5} S/cm^2). They are highly permeable to water, gases and dissolved low molecular weight substances.

Recently, Wegner and Meyer reported on linear and non-linear optical properties of Ionenes [5], containing dyes as counterions.

In the present work we report on the preparation and the properties of dyes containing cationic and anionic epoxide-amine addition polymers.

Experimental

Polymer **1a**: 1,00 g (1,80 mmol) crocein were added to 2,00 g (3,48 mmol) of the cationic polymer **1** [6] (X^-= Cl^-) dissolved in 20 ml DMF. After stirring the solution for 1h it was precipitated in 200 ml water, filtered, washed with distilled water and dried at 80 °C and 0,01 Torr. 1,90 g (68,7 % of th.), $\lambda_{max.}$= 530 nm.

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$[(C_{35}H_{40}NO_4)^+ .1/2(C_{22}H_{14}N_4O_7S_2)^{2-}]_n$ $(794,0)_n$

calc.	C 69,59	H 5,97	N 5,29	S 4,04
found	C 69,68	H 5,91	N 4,66	S 3,59

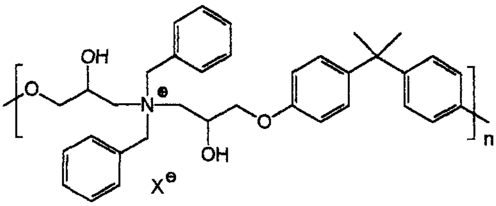
In the same manner further six dyes containing cationic polymers **1b-1g** were prepared:
1b-methaniline yellow, **1c**-diamine green, **1d, 1**g-Evan's blue, **1e, 1f**-mordant brown. Polymers **1f** and **1g** were prepared by addition polymerisation of bisphenol-A diglycidyl ether and N,N´-dibenzylethylenediamine followed by quaternization with benzylchloride and ion exchange with dyes.

Polymer **2a**: 1,33 g (2,77 mmol) rodamine b were added to 1,00 g (1,39 mmol) of polymer **2** [7] containing carboxylate groups ($Z^+ = K^+$) dissolved in 20 ml DMF. After stirring the solution for 1h it was precipitated in 200 ml water, filtered, washed with distilled water and dried at 80 °C and 0,01 Torr. $\lambda_{max.} = 555$ nm.
In the same manner further three dyes containing anionic polymers **2b-2d** were prepared: **2b**-tetranitrotetrazolium blue, **2c**-neutral red, **2d**-malachite green.

Thermal properties: The thermogravimetric decomposition were measured under a nitrogen atmosphere with a heating rate of 20 K/min using a Mettler DSC-30. The glass transition temperatures were determined with a Perkin Elmer DSC-7 analyser using a heating rate of 20 K/min. In every case the second run was used for the Tg estimation.
The flowing ranges T_f were measured using a Boëtius apparatus using a heating rate of 4 K/min.

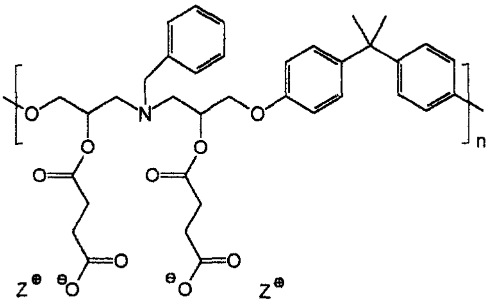
Results and Discussion

Dyes containing epoxide-amine addition polymers **1** were prepared by ion-exchange of halogenid anions by anionic dyes such as diamine green, mordant brown, crocein and Evan's blue.



1

Cationic dyes containing polymers **2** were prepared in the same manner by ion-exchange. Starting polymers are epoxide-amine addition polymers which were modified at the hydroxyl groups by cyclic carboxylic anhydrides.



2

The formation of the polymer-dye salts were carried out in DMF solution, in which they are completely soluble. After the exchange the polymer solution was precipitated in water, filtered, washed with distilled water until no dye was extracted and dried in vacuum. All polymer-dye salts **1** and **2** are soluble in polar solvents like DMF and 2-methoxy ethanol. They form transparent films with a good adhesion to glass surfaces by casting from these solutions.

The ion exchange by dyes to polymers **1** and **2** is proved by elemental analysis, UV-Vis-spectra, ^{1}H-NMR and ^{13}C-NMR spectra.
UV-Vis-spectra of 1c and 2a are shown in Fig.1. If all charges in polymers **1** and **2** are compensated, the dye content by weight in **1** and **2** varied from 40 to 50 % depending on their molecular mass and the number of ionic groups in polymer and dye.

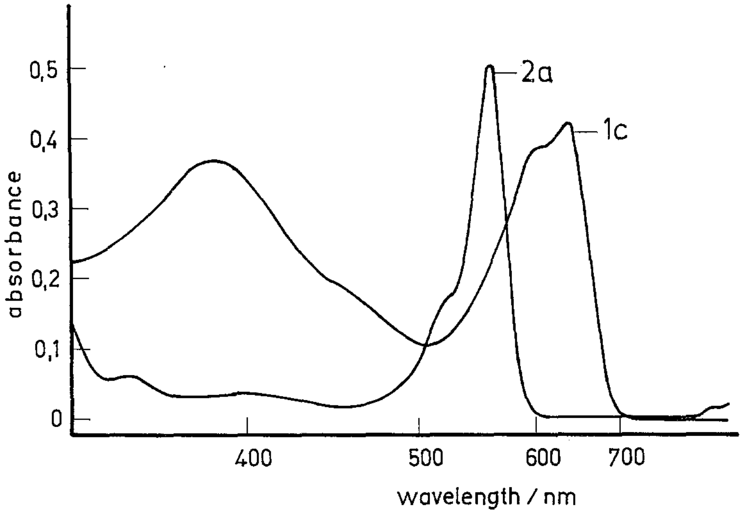


Fig.1 UV-Vis-spectra of polymers **1c** and **2a**

The third order nonlinear optical susceptibility $\chi^{(3)}$ $(-3\omega,\omega,\omega,\omega)$ is shown to be depending on absorption coefficients and $\lambda_{max.}$ for conjugated polymers [8,9], according to $\chi^{(3)}/\alpha_{max} \approx \lambda^{6}_{max}$.

Knowing the discrepancy between one-dimensional semiconductors and two-dimensional p-systems of dyes, we applied this correlation to the polymer-dye salts **1** and **2**. The $\chi^{(3)}$-values calculated to be 5.10^{-12} to 5.10^{-13} esu (**1**) and 5.10^{-13} to 2.10^{-14} esu (**2**), respectively (tab.1). The efficiency of the THG of **1** and **2** should increase with the concentration of the NLO-active dye, to be seen in examples **1e/1f** and **1d/1g** . However, the calculated values are two decades lower than those of conjugated polymers (polydiacetylene: $\chi^{(3)}\sim 3.10^{-10}$ esu, PPV: $\chi^{(3)}\sim 4.10^{-10}$ esu).

Table 1 Optical properties of Polymer-dye salts **1** and **2**

Polymer	dye[a)]	$\lambda_{max.}$ /nm	α/l.mol-1.cm-1	$\chi^{(3)}$(calc)
1a	C	530	26913	$1 . 10^{-12}$
1b	MA	420	30420	$6 . 10^{-12}$
1c	DG	620	29391	$5 . 10^{-13}$
1d	EB	470	10614	$1 . 10^{-12}$
1e	MB	465	13899	$1 . 10^{-12}$
1f[b)]	MB	465	26574	$3 . 10^{-12}$
1g[b)]	EB	470	22374	$2 . 10^{-12}$
2a	R	555	25119	$9 . 10^{-13}$
2b	TB	640	1440	$> 10^{-14}$
2c	NR	530	2930	$1 . 10^{-13}$
2d	MG	615	29976	$6 . 10^{-13}$

a) C-crocein, MA-methaniline yellow, DG-diamine green, EB-Evan's blue, MB-mordant brown, R-rodamine b, TB-tetranitrotetrazolium blue, NR-neutral red, MG-malachite green,
b) The amine in the polymer main chain is N,N'-Dibenzylethylendiamine.

Table 2: Thermal properties of polymer-dye salts **1** and **2**

Polymer	dye[a)]	T_g/°C	Δcp/$Jg^{-1}K^{-1}$	T_{TGA}[c)]/°C	T_f/°C
1a	C	132,3	0,26	250/325	178-185
1b	MA	115,0	0,33	250/340	165-176
1c	DG	99,5	0,27	340	183-195
1d	EB	140,0	0,25	275/350	-
1e	MB	121,6	0,35	250/350	159-172
1f[b)]	MB	115,1	0,39	300	141-154
1g[b)]	EB	163,6	0,24	275/350	190-205
2a	R	99,5	0,42	320/360	-
2b	TB	87,9	0,19	200/300	-
2c	NR	85,9	0,48	370	-
2d	MG	94,5	0,40	230/350	-

a) and b) see Tab.1, c)Temperature of the maximum of the first derivative of the TGA curve.

The thermal properties of **1** and **2** differ characteristically from the high molecular-weight epoxide-amine addition polymers. The glass transition temperatures of polymer-dye salts **1a-1g** are 10 to 80 °C higher than the Tg of polymer **1** containing chlorine as counterion (X=Cl) having T_g= 90,8 °C.

Furthermore, the Δcp-values of **1** and **2** are lower as compared to the corresponding amorphous addition polymers. Especially the polymers with the longest dye counter-ions exhibit the lowest Δcp-values, for instance **1c**, **1d**, **1g** and **2b**. Also the flowing range of these polymers are the most extendest ones. Obviously, the entropy increase at Tg in these polymers is minimised by a stiffing effect of the dyes. This assumption is also supported by the fact that the T_f-values of the same compounds are the highest in our series of polymers.

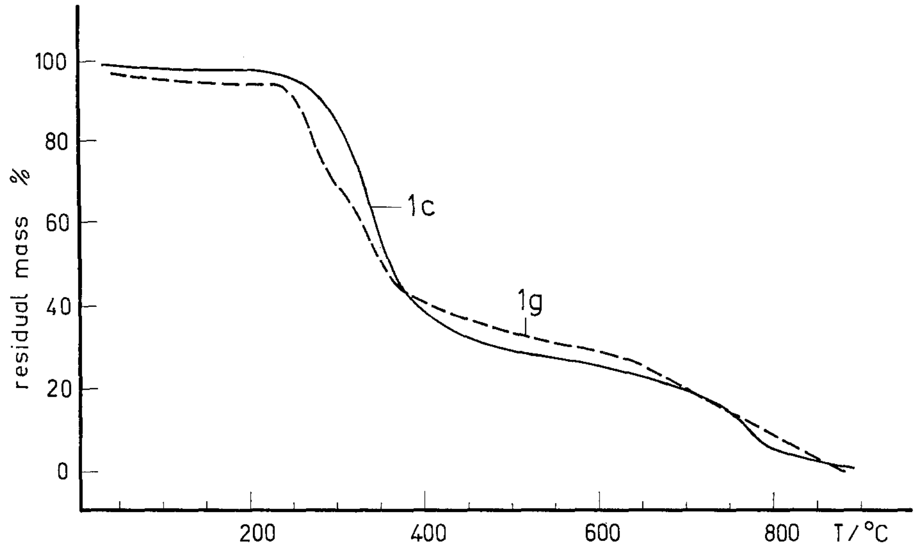


Fig.2 Thermal decomposition of polymers **1c** and **1g**

The thermal decomposition of **1** and **2** (Fig.2) takes place between 200 and 370 °C and is lower than those of epoxide-amine addition polymers (370-390 °C) as expected for poly-quarterly ammonium salts.

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