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Synthesis of photodegradable polymers by SH-En polyaddition

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Summary

The polyaddition reaction of the Michael donor 1.2-bis(2-mercaptoethoxy)ethane (Bis-SH) 2 as dithiol to various Michael acceptors such as divinyl sulfone (DVS) 1, N,N'-bismaleimido-4,4'-diphenylmethane 3, 4,4'-(N-maleimido)diphenyliodoniumchloride 4 and diallyl succinate 5 in the presence of tributylamine is described. Polymers were characterized by NMR-spectroscopy, elemental analysis, DSC and TG-analysis. In particular we synthesized a photosensitive polymer with 4,4'-(N-maleimido)diphenyliodonium chloride as comonomer, which eliminated analytical amounts of HCl during irradiation.

Introduction

The Michael-addition of divinyl sulfone as a highly reactive compound with diamines and dithiols is well known (1,2,3). In particular polyaddition with variable dithiol compounds is described by two different groups (4,5). The polymers are unsoluble and therefore less characterized.

In connection with our investigations in the field of photodegradable polymers we were interested in obtaining soluble polymers by Michael-addition. It is known that glycol units in the chain increase the solubility of polymers. The intent of the publication is the investigation of the Michael-type polyaddition of divinyl sulfone 1 and Bis-SH 2 and under addition of another En-compound 3, 4 or 5. The synthesis of prepolymers was not investigated.

$$CH_2{=}CH{-}SO_2{-}CH{=}CH_2 \quad + \quad HS{-}CH_2CH_2OCH_2CH_2OCH_2CH_2{-}SH \xrightarrow{Bu_3N}$$

1 2

$$\left[CH_2CH_2{-}SO_2{-}CH_2CH_2{-}S{-}CH_2CH_2OCH_2CH_2OCH_2CH_2{-}S\right]_n$$

Polymer A

The reaction is catalyzed by the addition of a tert. amine.

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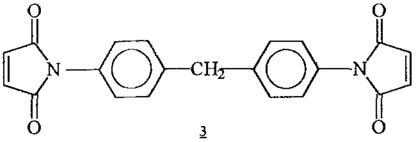
Especially we examined the thermal and photochemical properties of the polymers. We established, that the polymer with the iodonium salt group in the main chain forms transparent films on glass, decomposes under irradiation and it is quite possible, that the polymer is applicable for preparation of photo resist materials.



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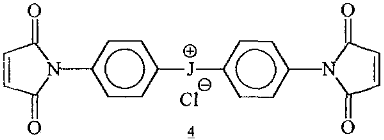

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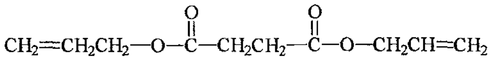


$$CH_2{=}CH_2CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_2CH_2{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2CH{=}CH_2$$

5

Experimental part

Materials

Divinyl sulfone (from FLUKA) and the solvents were freshly distilled before use. Bis-SH **2** was synthesized by (6). The compounds N,N'-bismaleimido-4,4'-diphenylmethane **3** and 4,4'-(N-maleimido)diphenyliodoniumchloride **4** were synthesized by the method of Crivello et al. (7). Diallyl succinate was prepared by esterification of succinic acid and prop-2-en-1-ol in the presence of p-toluene sulphonic acid (6).

A general preparation for base-catalyzed Michael-type polyaddition

A solution of 0.001 mol of 1,2-bis(2-mercaptoethoxy)ethane, 0.001 mol of divinyl sulfone and 3 drops of tributylamine were stirred at room temperature for 6-8 h. On addition of the catalyst the reaction temperature rose from 25 to 40-60°C. During polymerization increases the solution viscosity. If the polyaddition was carried out in solution, then the polymer was isolated by pouring the reaction mixture into methanol acidified with hydrochloric acid, washed with methanol and reprecipitated from chloroform. The precipitated polymers were washed only with methanol.
The copolymers were prepared by the same method, but the ratio of DVS: diene: dithiol is 1:1:2. Toluene, THF and m-cresol were used as different solvents.
Yield is 85-95% of theory.

Polymer A of DVS and **2**

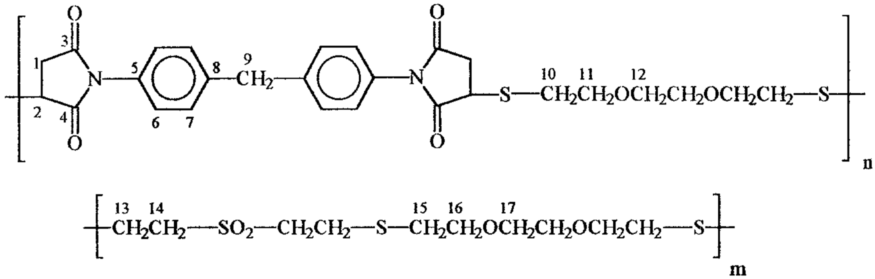
$(C_{10}H_{20}O_4S_3)_n$ (300.446 g·mol^{-1})				
	calc:	C 39.97	H 6.71	S 32.01
	found:	C 40.11	H 6.81	S 32.66

IR (KBr): 2951 and 2890 $(CH)_{Al}$, 1322 and 1124 (SO_2), 1113 (C-O-C) cm^{-1}
^{13}C NMR (62 MHz; d^6-DMSO; 80°C):23.4 C_1 ; 52.9 C_2; 30.9 C_3; 69.2, 69.8 C_4,C_5
T_m = 112 -115°C

Polymer B of DVS, BIS-SH and **3**

$(C_{27}H_{28}N_2O_6S_2)_n\ (C_{10}H_{20}O_4S_3)_m$ (420.484 g·mol^{-1})

calc:	C 52.84	H 5.75	N 3.33	S 19.06
found:	C 53.07	H 5.56	N 3.30	S 18.92



$$\left[\mathrm{CH_2CH_2{-}SO_2{-}CH_2CH_2{-}S{-}CH_2CH_2OCH_2CH_2OCH_2CH_2{-}S}\right]_m$$

IR (KBr): 3040 $(CH)_{Ar}$, 2970 and 2876 $(CH)_{Al}$, 1780 and 1710 (C=O), 1387 and 1179 (SO_2), 1112 (C-O-C) cm^{-1}
^{13}C NMR (62 MHz; $CDCl_3$): 36.3 C_1; 39.5 C_2; 173.9, 175.7 C_3,C_4; 140.9 C_5; 126.5 C_6; 129.5 C_7; 129.7 C_8; 40.8 C_9; 31.9 C_{10}; 71.1, 71.2 C_{11}, C_{12}; 24.5 C_{13}; 53.6 C_{14}; 31.36 C_{15}; 70.3, 70.8 C_{16}, C_{17}
M_n (VPO, $CHCl_3$): 5800 g•mol^{-1}
T_g = 36°C

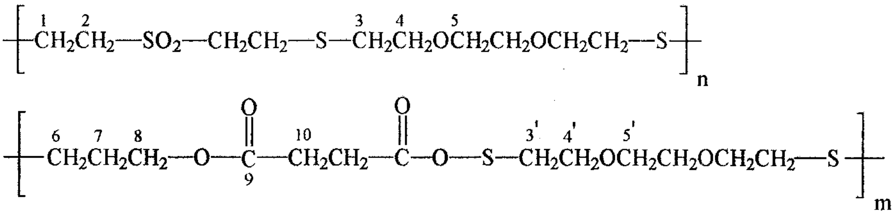
Polymer C of DVS, BIS-SH and 4

$(C_{26}H_{26}JClN_2O_6S_2)_n$ $(C_{10}H_{20}O_4S_3)_m$ (494.646 g•mol^{-1})

calc:	C 43.70	H 4.68	N 2.83	S 16.20
found:	C 43.62	H 4.95	N 2.95	S 15.97

IR (KBr): 3088 and 3028 $(CH)_{Ar}$, 2920 and 2858 $(CH)_{Al}$, 1789 and 1714 (C=O), 1378 and 1169 (SO_2), 1112 (C-O-C) cm^{-1}
^{13}C NMR (62 MHz; d^6-DMSO): 36.5 C_1; 39.8 C_2; 173.9, 175.6 C_3, C_4; 134.6 C_5; 129.5 C_6; 135.6 C_7; 119.9 C_8; 30.7 C_9; 70.2, 69.9 C_{10},C_{11}; 24.0 C_{12}; 53.3 C_{13}; 30.5 C_{14}; 69.5, 69.5 C_{15},C_{16}
T_g = 119°C

Polymer D of DVS; BIS-SH and 5



$$\left[\mathrm{CH_2CH_2{-}SO_2{-}CH_2CH_2{-}S{-}CH_2CH_2OCH_2CH_2OCH_2CH_2{-}S}\right]_n$$

$$\left[\mathrm{CH_2CH_2CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_2CH_2{-}\overset{O}{\overset{\|}{C}}{-}O{-}S{-}CH_2CH_2OCH_2CH_2OCH_2CH_2{-}S}\right]_m$$

$(C_{10}H_{20}O_4S_3)_n$ $(C_{16}H_{28}O_6S_2)_m$ (340.422 g•mol^{-1})

calc:	C 45.86	H 7.11	S 23.54
found:	C 45.57	H 7.01	S 24.02

IR (KBr): 2949, 2892 and 2869 $(CH)_{Al}$, 1733 (C=O), 1322 and 1126 (SO_2), 1112 (C-O-C) cm^{-1}
^{13}C NMR (100 MHz; d^6-DMSO; 80°C): 23.5 C_1; 53.0 C_2; 31.0 C_3; 69.3, 70.0 C_4, C_5; 27.8, 28.5 C_6,C_7; 62.4 C_8; 171.1 C_9; 28.3 C_{10}
T_m = 73°C

Photolysis of polymer C of DVS, BIS-SH and 4

A film was prepared from a definite solution of polymer C in chloroform on quartz glass. After drying in vacuum at 60°C the quartz glass was irradiated with light of a high pressure mercury lamp (250 W, without filter) for 30 min in a closed quartz tube. The quartz tube contains a solution of 2 ml 0.05 n KOH and 12 drops of saturated hydrazine sulphate solution to absorb eliminated HCl. The content of chloride in the film was determined by potentiometric titration with $AgNO_3$.
The degradation of the polymer C was measured with light of a high pressure mercury lamp (250 W; without filter). The distance between film and lamp was 5 cm.
The irradiation time was not optimized.

Characterization

^{13}C NMR spectra were recorded on a AC 250 and on a DRX 400 (BRUKER). UV-VIS spectra were obtained by means of a UV-VIS-NIR Lambda 19 (PERKIN ELMER) and IR spectra by means of a FT-IR Impact 400 (NICOLET). DSC measurements were carried out on a DSC 2 or DSC 7 (PERKIN ELMER). TG-curves were recorded on a selfmade thermobalance by Ludwig, Opfermann (8).

Results and discussion

For our investigations we used the dithiol 2 and divinyl sulfone 1 as diene in combination with dienes 3, 4 or 5. All polymers were synthesized at room temperature in solution or without a solvent with tributylamine as catalyst. The results are summarized in Tab. 1.

Polymer	Monomer	Solvent	Yield (%)	T_g or T_m (°C)	Thermal degrad. up[1)]	Remarks[2)]
A	1/2	without toluene	97 95	T_m 112-115	260	P P
B	1/2/3	THF	88	T_g 36	240	S
C	1/2/4	m-cresol	83	T_g 119	200	S
D	1/2/5	without toluene	85 83	T_m 73	260	P P

1) TGA under argon; heating rate 10 K•min^{-1}
2) P= precipitation during the polymerization; S = homogeneous solution

Tab. 1: Polyaddition of BIS-SH 2 with different diens

Polymerizations without a solvent to A and D are strong exothermic reactions and started even without the catalysator; after addition of amine the polymer precipitated 10-15 min later. The polymers A and D are soluble in hot DMF, DMSO or dioxane in contrast to the polymers B, C; the last two are soluble in common solvents, e.g. $CHCl_3$. Fig. 1 shows the ^{13}C NMR spectrum of polymer A in d^6-DMSO at 80°C.
The molar masses can only determined from the polymer B because the polymers A and D are soluble exclusively in hot solvents and precipitated rapidly at room temperature; the polymer C is a polyelectrolyt.

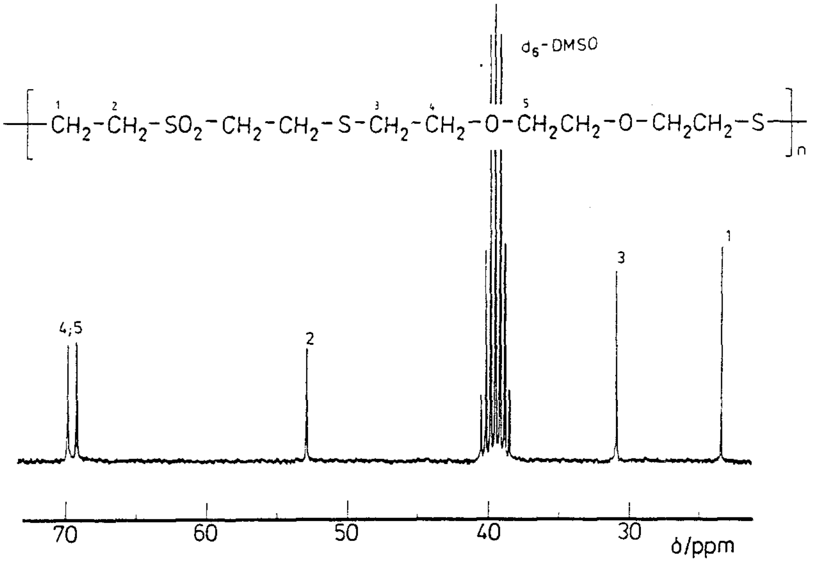


Fig. 1: ^{13}C NMR spectrum of polymer A (62 MHz; d^6-DMSO, 80°C)

In particular we investigated the polymer C, which has the iodonium salt structure in the main chain. It is known that such iodonium salts decompose under irradiation (9,10). The main products after the photolysis of an unsymmetrical substituted iodonium salt, for instance p-methoxydiphenyliodoniumchloride, are iodbenzene, iodanisole, anisole and HCl. Films on a quartz glass were prepared from a solution of polymer C in $CHCl_3$. These films are transparent and slightly yellow. UV-VIS spectrum shows an absorption maximum at $\lambda = 198$ nm and a shoulder at $\lambda = 242$ nm. During irradiation with a high pressure mercury lamp (250 W) this maximum and the shoulder decrease (Fig. 2). We assume, that the decrease of the absorption maximum at $\lambda = 198$ nm is in connection with the photochemical decomposition of the polymer in several fragments. The decrease of the shoulder at $\lambda = 242$ nm based on the decomposition of the iodonium salt structure.

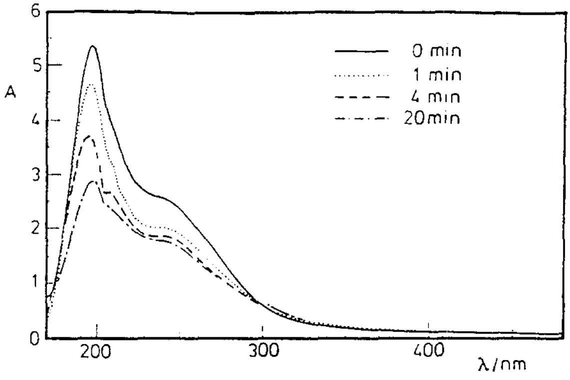


Fig. 2:
UV-VIS Spectrum
of polymer C (film)
in dependence on
the irradiation time

We also determined the content of chloride in the polymer by means of the photolysis (see experimental part). Potentiometric titration showed that the experimental value (2.48 % Cl) is different from the theoretical value (3.58 % Cl). We assume that the HCl doesn't diffuse completely through the layer.

The ^{13}C NMR spectrum of polymer C (Fig. 3) shows, that the polymer has vinyl sulfone as end group. The occurrence of the end group is an evidence for low molecular masses or for a broad destibution of molecular masses. Thermal degradation starts at 200°C (argon, heating rate 10 K•min^{-1}) and the is determinate through the decomposition temperature of the iodonium salt (decomposes at 200°C).

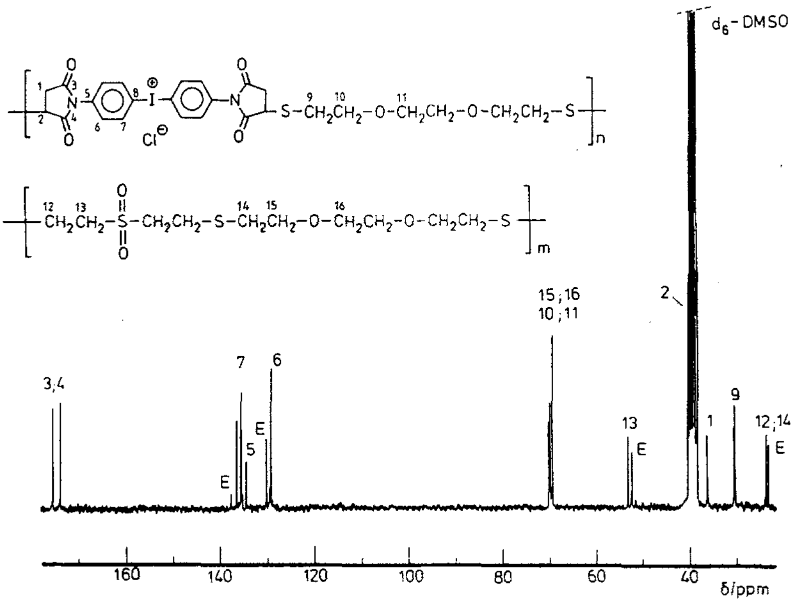


Fig. 3: ^{13}C NMR spectrum of polymer C (62 MHz; d^6-DMSO); E = end groups

Acknowledgement

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