Polymer Bulletin 27, 473–479 (1992)

Polymer Bulletin

Dithioles – constituents for telechelic prepolymers with glycidyl or thiol endgroups

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SUMMARY

Telechelic prepolymers **2-5** containing thiol- or glycidyl endgroups, respectively are obtained by addition polymerization of dithiols **1a-1f** and diglycidylether of bisphenol-A (DGEBA). They have molecular weights of 800 to 2000 g/mol. The structure of the prepolymers is determined by combination of elemental analysis, M_n(VPO)-values, IR-, ^{1}H-NMR- and ^{13}C-NMR spectroscopy. By means of TLC and HPLC these prepolymers were shown to be a mixture of a series of homologous compounds. Furthermore, their oligomer distribution is analysed.

INTRODUCTION

For decades amine- and anhydrid hardened epoxides have been used for the preparation of linear polymers, networks, laminates, casting resins, coatings etc. They found a technical introduction in electrotechnics/microelectronics, in optical industry and in other fields[1,2].

More recently, we have shown that the copolymerization of DGEBA and primary monoamines or disecondary diamines, respectively results in high molecular weight, soluble epoxide-amine addition polymers[3-5]. Using an excess of one of the components telechelic prepolymers were obtained which contain amino- or glycidyl endgroups[6,7]. Their structure and oligomer distribution is intensively investigated using M_n(VPO)-values, IR-, ^{1}H-NMR, ^{13}C-NMR and ^{15}N-NMR spectroscopy, TLC and HPLC analysis.

However, the addition polymerization of dithiols and diepoxides is not so intensively investigated. Recently, E.Klemm have shown that 1,8-dimercapto-3,6-dioxaoctane **1a** react with DGEBA to a high molecular weight and soluble addition polymer [8,9].

Excessive diepoxide or dithiol lead to a telechelic prepolymer **2a** containing epoxide endgroups[10] or thiol endgroups **5a** [11], respectively.

For investigating the structure and the oligomer distribution of prepolymers **2a** and **5a** we have repeated their synthesis.

Further, we prepared five dithioles **1b-1f** including the corresponding prepolymers and studied their structure and properties.

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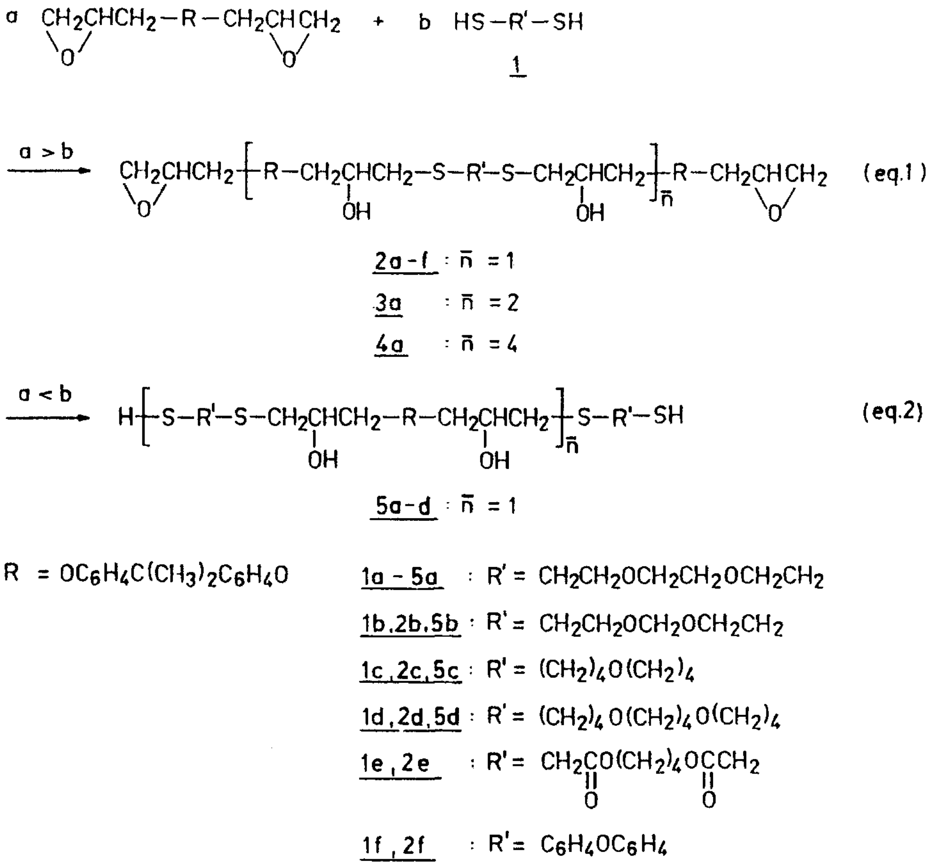

EXPERIMENTAL

1. Monomers

The diglycidylether of bisphenol-A was purified by recrystallization from aceton/methanol.Fp.42-43^{o}C.

1,8-Dimercapto-3,6-dioxaoctane **1a**:
195,7 g (2,6 mol) thiourea, 100ml ethanol and 218,3 g (1,01 mol) triethyleneglycol dichloride were taken in a 2l flask with condenser and refluxed for 6 hours. After cooling 1,175 l 5N NaOH was added dropwise in under a slow stream of argon and refluxed for a further period of 2 hours. The neutralised reaction mixture was extracted with chloroform, and the extracts were dried over $MgSO_4$. Then the solvent is redistilled and the dithiol is distilled in vacuum using a slow argon stream. 125 g (59 % of th.), Kp. 90,5 ^{o}C/0,08 Torr,
n_D^{20}= 1,5082, IR: ν_{SH}= 2560 cm^{-1}

1,7-Dimercapto-3,5-dioxaheptane **1b** was prepared analogous to **1a** from 87,4 g (0,56 mol) 1,7-dichloro-3,5-dioxaheptane (Chemiewerk Greiz-Dölau) and 97,8 g (1,3 mol) thiourea. 35 g (37,6 % of th.), Kp. 73,5 °/0,7 Torr, IR: ϑ_{SH} = 2560 cm^{-1}
$C_5H_{12}O_2S_2$ (166,3) calc. S 38,11 found S 37,55

1,9-Dimercapto-5-oxanonane **1c** was prepared analogous to **1a** from 100,5 g (0,505 mol) 1,9-Dichloro-5-oxanonane [12] and 97,9 g (1,3 mol) thiourea. 46,1 g (47 % of th.), Kp.95 °C/0,55 Torr, IR: ϑ_{SH}= 2560cm^{-1}
$C_8H_{18}OS_2$ (194,3) calc. C 49,44 H 9,34 S 32,99
found C 50,78 H 9,63 S 34,85

1,14-Dimercapto-5,10-dioxatetradecane **1d** was prepared analogous to **1a** from 70 g (0,258 mol) 1,14-dichloro-5,10-dioxatetradecane[12] and 50,6 g (0,664 mol) thiourea. 29 g (56,5 % of th.), Kp.145 °C/0,55 Torr, IR: ϑ_{SH}=2560 cm^{-1}
$C_{12}H_{26}O_2S_2$ (266,4) calc. C 54,09 H 9,83 S 24,06
found C 55,41 H 10,14 S 24,21

Mercaptoacid-1,4-butanediolester **1e** was prepared[12] from 45,1 g (0,5 mol) butandiole-1,4 and 115,2 g (1 mol) thioglycolacid. 67,3 g (56,5 % of th.), Kp.135 °C/0,1 Torr, IR: ϑ_{SH} = 2570 cm^{-1}, ϑ_{CO}= 1730 cm^{-1}
$C_8H_{14}O_4S_2$ (238,2) calc. C 40,32 H 5,92
found C 40,44 H 5,96

4,4'-Oxy-dithiophenole **1f** was prepared[13] from 9,0 g (26,8 mmol) diphenylether-disulfonylchloride by reduction with zinc-amalgam. 4,2 g (73,9 % of th.), Fp.97 °C, IR: ϑ_{SH}=2555 cm^{-1}

2. Prepolymers **2a-2f**, **3a**, **4a** and **5a-5d**

Prepolymer **2a**: 6,808 g (20,0 mmol) DGEBA and 1,823 g (10,0 mmol) **1a** were homogeniously mixed under argon at 60 °C and polymerized 40 h at 100 °C. M_n(VPO)=830 g/mol.
Further seven prepolymers **2b-2f**, **3a** und **4a** were prepared analogous. Amounts of monomers used, M_n-values and glass transition temperatures T_g are shown in Tab.1.
Prepolymer **6a**: 1,702 g (5,0 mmol) DGEBA and 1,823 g (10,0 mmol) **1a** were homogeniously mixed at 60 °C and polymerized 50 h at 100 °C. M_n(VPO)=950 g/mol.
Further 3 prepolymers **5b-5d** were prepared analogous. The monomers used and M_n-values are summarised in Tab. 1.

3. Spectroscopy, M_n(VPO)-values and HPLC-analysis

The IR-Spectra were measured by SPECORD M 80 (Carl Zeiss Jena) and the ^{1}H-NMR- und ^{13}C-NMR-Spectra with a KRH 100 R (ZWG AdW). The M_n(VPO)-values were estimated by a KNAUER-vapour pressure osmometer at 37 °C in $CHCl_3/CH_3OH$(4:1). The HPLC-analysis were carried out with a HPLC instrument (KNAUER, on LiChrosorb RP-18, 5 µm, elution gradient H_2O/CH_3CN).

RESULTS and DISCUSSION

According eq.1 and eq.2 the addition polymerization of DGEBA and dithiols **1a-1f** results in prepolymers with glycidyl endgroups **2a-2f,3a, 4a** and thiolterminated telechelics **5a-5d**, respectively, if one of the monomers is used in excess. The prepolymers contain β-hydroxythioether units in the backbone. These are mixtures of oligomers having n = 1,2,3,4,5... and contain in every case a regular content of unreacted excessive monomer (n = 0).
Using HPLC analysis a separation of telechelics **2-5** is achieved. Fig.1 show a separation of **2a** and **5a** into molecules with n=1,2, 3,4,5...and the excessive monomers (n=0).

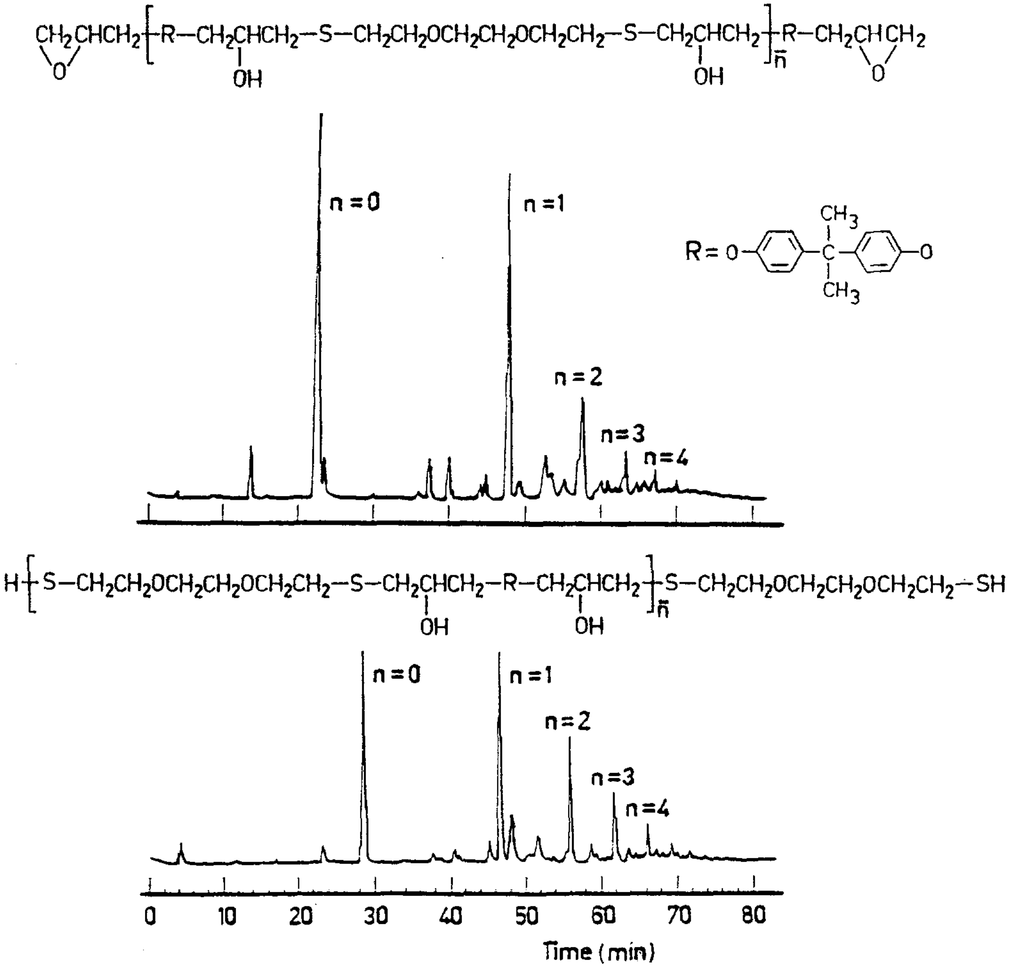

Fig.1 HPLC analysis of prepolymers **2a** and **5a**

The mol portion n_x and the weight portion w_x of the single molecules in the prepolymer mixture were calculated according to

$$n_x = P_n \cdot r^x \cdot (1-r)^2/(1+r) \quad \text{and}$$

$$w_x = 0{,}5 \left[P_n(1+m)+(m-1)\right] \cdot r^x \cdot (1-r)^2/(m+r),$$

using $m = M_a/M_b$, $r = b/a$ for **2-4** and $m = M_b/M_a$, $r = a/b$ for **5**.

For the prepolymer **2a** the following mol and weight portions were calculated: $n_0=0{,}167$, $n_1=0{,}250$, $n_2=0{,}208$, $n_3=0{,}146$, $n_4=0{,}094$ etc. and $w_0=0{,}197$, $w_1=0{,}250$, $w_2=0{,}201$, $w_3=0{,}138$, $w_4=0{,}088$ etc. As qualitatively shown in fig.1, the portion of oligomers degreases as theoreticaly calculated with incrasing degree of polymerization.
The degree of polymerization P_n is calculated according:

$$P_n = (1+r)/\left[2r(1-p)+1-r\right] .$$

On supposing a complete reaction of the excessive monomer (p=1), P_n depends only from the mole ratio of the monomers:

$$P_n = (1+r)/(1-r).$$

For prepolymers **2-4** M_n(VPO)-values 800 to 2000 g/mol were obtained in complete accordance with the calculated molecular weights (tab.1).

Tabele 1: Amount of monomers used and properties of prepolymers **2-5**

	monomers				properties of prepolymers		
	DGEBA g	mmol	dithiol g	mmol	M_n(calc.) g/mol	M_n(VPO) g/mol	T_g °C
2a	6,808	20	1,8229	10	863	830	17,5
2b	6,808	20	1,6827	10	849	820	29,0
2c	1,5639	4,594	0,4464	2,297	875	780	17,0
2d	3,404	10	1,3322	5	950	990	5,0
2e	6,808	20	2,3819	10	919	900	29,0
2f	1,0375	3,048	0,3571	1,524	915	950	23,0
3a	6,808	20	2,4305	13,33	1386	1260	17,5
4a	6,808	20	2,9166	16	2431	2200	17,5
5a	1,702	5	1,8229	10	705	950	-42,0
5b	3,404	10	3,3654	20	677	750	-+)
5c	1,8378	5,4	2,0985	10,8	729	1700	-35,0
5d	1,702	5	2,6645	10	873	860	-+)

+) no T_g observed in the range of -70 °C to +50 °C

Consequently, no side reaction of the type of epoxide polymerization or ether formation takes place. Only in the case of thiol-terminated telechelics **5** higher M_n(VPO)-values than calculated were found.
Obviously, it is due to an oxidation of the dithiols **1** and **5**, respectively to disulfanes. ^{1}H-signals of the SH-groups at 1,50 ppm (**5a**) were not observed. The IR-absorption of the thiol groups was found at 2560 cm^{-1} (**5a**). In the IR-spectra of **2-4** the absorption of glycidyl endgroups is registered at 915 and 3050 cm^{-1}. The absorptions of OH...X-hydrogen bond were obtained at 3150 to 3650 cm^{-1} with a maximum at 3450 cm^{-1} (**2a**), 3430 cm^{-1} (**2f**), 3455 cm^{-1} (**5a**).
Furthermore, in the ^{13}C-NMR spectrum of **2a** the signals of the glycidyl endgroup (δ=44,6, 49,9, 68,5 ppm) were found as same as in the spectrums of **2-4**. Thiol endgroups of **5a** appeared at δ=24.4 ppm (HS-CH_2-).

The prepolymers **2-5** were characterized by relative low glass transition temperatures between -42 and 30°C (tab.1) due to the flexible oligoether-dithiol units.

CONCLUSION

With an excess of DGEBA, the addition polymerization of DGEBA and dithioles form regular prepolymers having epoxide endgroups. Only when applying an excess of dithioles, higher molecular weights than calculated were observed. This is caused by partial oxidation reaction of the thiol to the corresponding disulfane.
The epoxide-dithiole prepolymers can be very well used for the preparation of linear polymers, networks, composites and laminates. The introduction of flexible chain segments in polymers as reported here results in materials with lower glass transition temperatures. Due to the ß-hydroxythioether unit, they have further a good adhesion to glass and metal surfaces.

LITERATURE

/1/ Lee, H., Neville, K.: Handbook of Epoxy Resins, McGraw-Hill, New York 1967.
/2/ Jahn, H.: Epoxidharze, VEB Deutscher Verlag für Grundstoff industrie, Leipzig 1969.
/3/ Hörhold, H.-H., Klee, J., Flammersheim, H.J.: Makromol. Chem., Rapid Commun. **2**, 113 (1981).
/4/ Klee, J., Hörhold, H.-H., Schütz, H.: Acta Polymerica **38**, 293 (1987).
/5/ Klee, J., Hörhold, H.- H., Flammersheim, H.-J.: Angew. Makromol. Chem. **178**, 63 (1990).
/6/ Klee, J., Hörhold, H.-H., Tänzer, W.: Crosslinked Epoxies (Ed.B.Sedlacek, J.Kahovec), W.de Gruyter, Berlin, New York 1987, S.47.
/7/ Klee, J., Hörhold, H.-H., Tänzer, W., Fedtke, M., Acta Polym. **37**, 272 (1986).
/8/ Klemm, E., Hörhold, H.-H., Neubauer, K.: DD 232058 (1986), C.A. **106**, 19453d (1987).

/9/ Klemm, E., Flammersheim, H.-J., Hörhold, H.-H.: Crosslinked Epoxies (Ed. B. Sedlacek, J. Kahovec), W. de Gruyter, Berlin, New York 1987, S. 55.
/10/Hörhold, H.-H., Klemm, E.: DD 232057 (1986), C.A. **106**, 19452c (1987).
/11/Klemm, E., Hörhold, H.-H.: DD 232504 (1986), C.A. **106**, 5629d (1987).
/12/Reppe, A.: Liebigs Ann. Chem. **596**, 119 (1955).
/13/Zochniak, P., Galka, S.: J. Macromol. Sci. Chem. **A18**, 1021 (1982).
/14/Marvel, C.S., Caesar, P.D.: J. Amer. Chem. Soc. **73**, 1098 (1951).

Accepted October 29, 1991 C