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Synthesis and characterization of glycidyl ethers modified by mesogenic units

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Summary

New types of epoxy compounds containing biphenyl and azophenyl groups were synthesized. Model glycidyl ethers with one epoxy group were prepared to study the first reaction steps during the curing process. Diglycidyl ethers with or without a hexamethylene spacer were made to obtain epoxy networks. The structures of some intermediates and of the epoxy compounds synthesized were confirmed by Proton and Carbon-13 NMR spectroscopy.

Introduction

Liquid crystalline thermosets (LCT) have been developed in recent years in order to introduce LC properties in crosslinked thermoset systems (1). The idea is to create an organized network with ordered anisotropic structures. It is not surprising that after the investigation of LC thermoplastics and LC elastomers (2) highly crosslinked materials are now a main field of interest. Recently, a comprehensive review was published (3) and new types of LCT are in progress (4).

One of the most interesting types of LCT base on epoxy LC networks (5). This is due to the important role of epoxies in material research. In our group epoxy networks have been investigated for some years, mainly regarding the crosslinking mechanism influenced by different accelerators (6). Using model compounds we found different types of oligomerization products (7), and we tried to find these segments again in crosslinked and more applied systems. The investigation of chemical and physical properties of epoxy networks modified by these accelerators permits the explanation of structure property relationships. Using this concept it should be possible to extend our research work to LC epoxy compounds. Therefore, we synthesized mono- and bifunctional glycidyl ethers with mesogenic units and investigated their oligomerization and crosslinking behaviour.

This paper deals only with the synthesis and the characterization by Proton and Carbon-13 NMR spectroscopy of these biphenyl and azophenyl groups containing epoxides. Crosslinking and investigation of network properties (LCT) will be published later.

Results and Discussion

Synthesis of Monofunctional Model Compounds

According to our previous results with monofunctional glycidyl ethers as a model for crosslinking procedures of epoxies, we are also interested in analogous compounds containing mesogenic units. Furthermore, we should be able to solve problems connected with the high insolubility in common solvents and the higher melting point of these materials, which is still more significant for bifunctional epoxies with mesogens.

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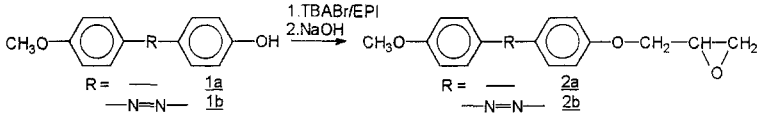
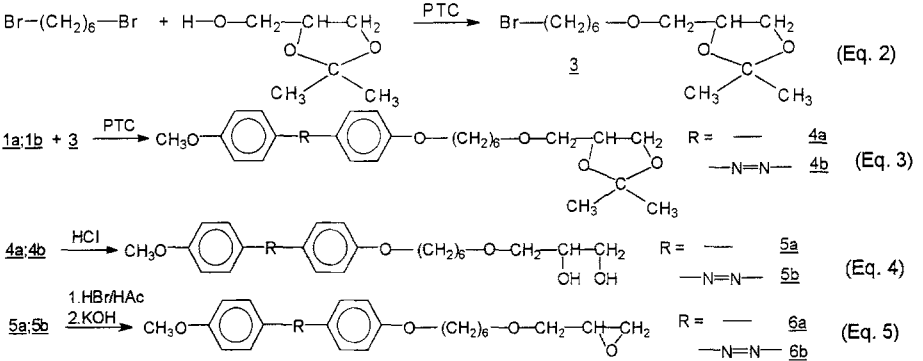


(Eq. 1)

We prepared monofunctional starting materials of the biphenyl and azophenyl type by using the methoxy derivative of the corresponding biphenols 1a and 1b. The glycidyl ethers 2a and 2b are easily synthesized following the classical route with epichlorohydrin and NaOH according to (Eq. 1). Both compounds are not yet described in the literature. Only a copolymer with LC properties formed by polymeranalogous reaction of polyepichlorohydrin with the sodium salt of p-methoxy-p'-hydroxy biphenyl is mentioned (8). Compound 2b shows LC properties.

The synthesis of analogous model compounds with a spacer between the mesogen and the glycidyl group proved to be more difficult. It is advantageous to use a "capped " epoxide as 1,3-dioxolane. The reaction proceeds via phase transfer catalysis (PTC) (9) with an excess of dibromohexane according to (Eq. 2). The synthesis of the intermediates 4a and 4b was also accomplished by PTC (Eq. 3). Compound 4a is already known as an optically pure product (10). Our racemic intermediates 4a and 4b are not LC. Contrary to the synthesis published by SCHLEIER et al. (10), we avoided CH_2Cl_2 as solvent in PTC in order to prevent the formation of byproducts.

The hydrolysis of 4a and 4b to the corresponding glycols 5a and 5b proceeds with hydrochloric acid (Eq. 4). Instead of acetone as solvent (preferred by SCHLEIER et al. (10)), which is a reaction product, we propose ethanol or acetonitrile as suitable solvents. The glycol with the azophenyl mesogen 5b shows LC properties. Finally the glycidyl ethers 6a and 6b are prepared via bromoacetate intermediates followed by epoxide formation with KOH (Eq. 5). The compound 6a, which is not LC, was already prepared by SCHLEIER et al. (10). The product 6b could not be found in the literature and shows monotropic mesomorphism.



(Eq. 2)

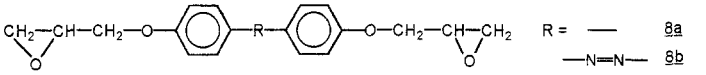
(Eq. 3)

(Eq. 4)

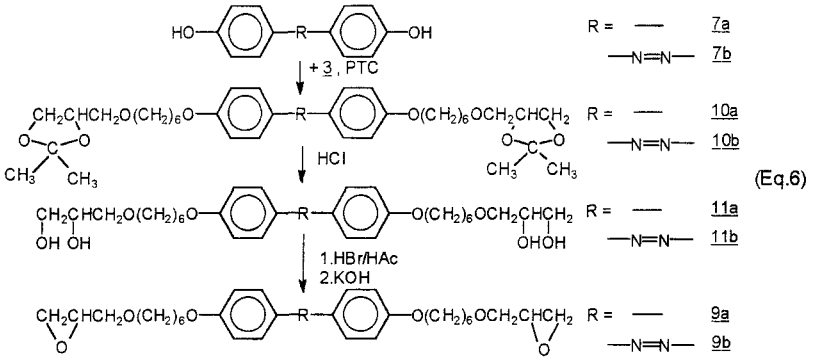
(Eq. 5)

Synthesis of bifunctional glycidyl ethers with mesogenic units

Diglycidyl ethers 8a and 8b of the biphenols 7a and 7b are described in the literature (11,12). The synthesis follows the above mentioned route for the analogous compounds 2a and 2b. The phase behaviour of 8a is discussed differently in the literature. On the one hand 8a does not show LC properties, on the other hand the resulting network is a LCT (11). GUTHRIE, MORTON and NIELD report both for the starting compound and the network LC properties (13), and also CARFAGNA et al. (14) found a smectic phase for the bisepoxide.



New aspects for suitable starting compounds for LCT's are expected with spacer containing epoxies. Therefore, the diglycidyl ethers 9a and 9b are synthesized. The preparation is similar to the monofunctional model glycidyl ethers 6a and 6b (Eq. 6). Both the diglycidyl ethers 9a and 9b, the intermediates 10a and 10b as well as the glycols 11a and 11b are not yet known. The glycols 11a and 11b as well as the epoxy compound 9b show LC behaviour.



(Eq.6)

Characterization

All the products prepared were investigated using elemental analysis, ^{1}H- and Carbon-13 NMR spectroscopy. Synthesizing these series of epoxy compounds, the preparation of intermediate products was necessary. Furthermore, the glycols are one type of the expected oligomerization products during the curing reaction (6,7). A detailed NMR study was carried out in order to verify and to confirm the structures wanted. The assignment could be more easily done by comparing the complete data measured for the different product types. The data obtained confirms the structure and the purity of the compounds in every case.

The results of the ^{1}H-NMR spectroscopy are summarized in Table 1. The localization of the protons inside the molecule parts is shown in Fig. 1. Problems in giving exact values (marked with "nr") are concerned with the resolution of the peaks caused by the solution behaviour of some products. In Table 2 the values known for the phenyl glycidyl ether are listed showing the expected ranges of spin-spin coupling constants of glycidyl compounds. Our results demonstrate an outstanding agreement with the published values (15). This is unambiguous evidence for the correct peak assignment in these complex ^{1}H-NMR spectra.

The data of the Carbon-13 NMR spectroscopy is shown in the experimental part. Some values were marked with "*". In these cases, the exact assignment is complicated because of very small differences in the chemical shifts or identical values (e.g. inside the hexamethylene spacer, similar substituted aromatic rings). Furthermore, we are not able to distinguish between the methyl groups of the 1,3-dioxolanes, where sterical effects cause a difference in the chemical shifts of about 1.4 ppm (product Nº 4a and 4b as well as 10a and 10b). However, the products possess the shown structures in every case.

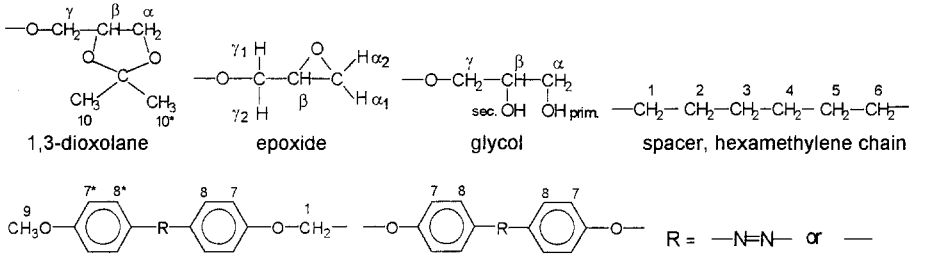


Fig. 1: Localization of the protons within the different molecule parts (see Table 1 and 2)

Table 1: Assignment (see Fig. 1) and chemical shifts in ppm (HMDS) for the ^{1}H-NMR in $CDCl_3$; 5a, 5b, 11a and 11b in DMSO-d_6; The columns "α" and "γ" contain two values for ABX spin systems ($\alpha_1\alpha'_1 + \alpha_2\alpha'_2$ and $\gamma_1\gamma'_1 + \gamma_2\gamma'_2$)

№	1	2	3/4	5	6	7	8	7*	8*	9	α	β	γ	10/10* or OH
2a	-	-	-	-	-	6.93	7.45	6.95	nr	3.82	2.89+2.75	3.35	3.98+4.23	-
2b	-	-	-	-	-	6.97	7.85	6.99	7.85	3.86	2.91+2.76	3.36	4.00+4.28	-
4a	3.96	1.61	1.41	1.79	3.48	6.92	7.44	6.93	7.45	3.82	3.53-3.38	4.25	3.71+4.04	1.41/1.35
4b	3.97	1.59	1.39	1.78	3.46	7.07	7.81	7.09	7.83	3.83	3.51-3.36	4.23	3.69+4.02	1.39/1.33
5a	3.95	1.50	1.37	1.70	3.35	6.95	7.50	6.97	7.51	3.76	3.2-3.3	3.56	3.2-3.3	pr. 4.47/sec. 4.60
5b	4.04	1.51	1.39	1.73	3.37	7.08	7.81	7.09	7.83	3.84	3.2-3.4	3.55	3.2-3.4	pr. 4.42/sec. 4.54
6a	3.96	1.62	1.46	1.79	3.49	6.92	7.45	6.93	7.46	3.81	2.77+2.58	3.13	3.35+3.70	-
6b	3.97	1.60	1.43	1.78	3.46	6.94	7.83	6.96	7.84	3.82	2.75+2.56	3.10	3.33+3.68	-
8a	-	-	-	-	-	6.95	7.44	-	-	-	2.90+2.75	3.35	3.97+4.23	-
8b	-	-	-	-	-	7.00	7.85	-	-	-	2.91+2.77	3.37	4.00+4.29	-
9a	3.93	1.59	1.43	1.76	3.46	6.89	7.42	-	-	-	2.74+2.56	3.10	3.33+3.67	-
9b	3.98	1.60	1.43	1.78	3.46	6.94	7.83	-	-	-	2.75+2.56	3.11	3.33+3.68	-
10a	3.95	1.60	1.40	1.78	3.47	6.91	7.43	-	-	-	3.51-3.37	4.24	3.70+4.03	1.40/1.34
10b	4.00	1.60	1.40	1.80	3.47	6.95	7.83	-	-	-	3.52-3.38	4.24	3.70+4.03	1.40/1.34
11a	3.96	1.48	1.38	1.71	3.37	6.95	7.50	-	-	-	3.2-3.4	3.55	3.2-3.4	no sharp signal
11b	4.04	1.51	1.39	1.73	3.37	7.08	7.81	-	-	-	3.2-3.4	3.54	3.2-3.4	pr. 4.41/sec. 4.54

Table 2: Spin-spin coupling constants in Hz for epoxy compounds
PGE ... phenyl glycidyl ether reported by (15)

product	$^3J\alpha_1,\beta_{cis}$	$^3J\alpha_2,\beta_{trans}$	$^3J\gamma_1,\beta_{trans}$	$^3J\gamma_2,\beta_{cis}$	^2Jgem $\alpha_1\alpha_2$	^2Jgem $\gamma_1\gamma_2$
PGE	4.54	2.65	5.69	3.13	-4.97	-11.04
2a	4.48	2.61	5.56	3.16	-4 77	-11.07
2b	4.48	2.62	5.68	3.04	-4.84	-11.02
6a	4.53	2.58	5.82	2.94	-4.77	-11.52
6b	4.56	2.64	5.88	2.76	-4.86	-11.55
8a	4.48	2.61	5.61	3.09	-4.71	-11.06
8b	4.41	2.64	5.68	2.94	-4.65	-10.98
9b	4.95	2.70	5.85	2.94	-4.74	-11.49

Conclusion

The success of our efforts to obtain model and curable glycidyl ethers with mesogenic units is summarized in Table 3. More details concerning the LC phases of these compounds and the crosslinking experiments will be reported soon.

Table 3: DSC and polarization microscopy results representing the transition temperatures, the heat of transition and the phase behaviour of LC compounds

Nº	Heating		Cooling		Polarization microscopy	
	T (°C)	ΔH (J/g)	T (°C)	ΔH (J/g)	T course	LC texture
2b	125.4	97.9	100.4 118.9	78.6 3.1	cooling	monotropic nematic
5b	117.6	96.6	108.7 114.5	86.8 3.7	cooling	monotropic nematic
6b	82.5	99.5	63.8 81.6	86.8 3.7	cooling	monotropic nematic
9b	84.8	83.9	71.4 84.2	71.3 4.0	cooling	monotropic nematic
11a	89.5 159.0	29.5 68.8	89.0 158.9	25.9 63.5	-	not determined
11b	102.4 131.5 150.3.	25.1 25.1 26.7	103.8 132.5 152.8	18.0 24.8 26.9	-	not determined smectic c

Measurements

Proton and Carbon-13 NMR spectra were obtained on a VARIAN Gemini 300 spectrometer (frequency: 300.075 and 75.43 MHz, respectively).

DSC was run on a Perkin Elmer DSC 7 using a heating or cooling rate of 10 K/min under nitrogen. The calibration was carried out with indium (temperature/area) and tin (temperature).

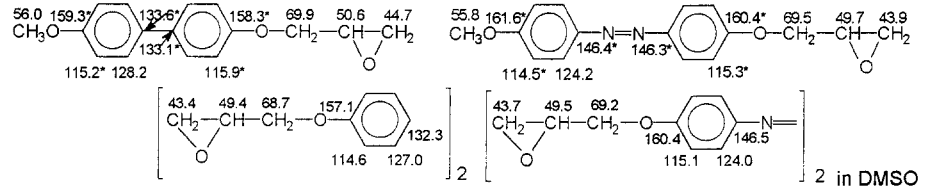
LC behaviour was determined using a polarization microscope JENAPOL (Carl Zeiss Jena) equipped with a heating table unit LINKAM (TMS 91, THMS 600) from RACZEK, Analysentechnik GmbH. Heating or cooling rate 10 K/min; lower at the transition; inert gas: N_2

Materials

Synthesis of 2a, 2b, 8a and 8b

4-Hydroxy-4'-methoxybiphenyl (1a (16)), 4-hydroxy-4'-methoxyazobenzene (1b (17)) and 4,4'-dihydroxyazobenzene (7b (18)) were synthesized according to literature procedures. A tetrabutylammonium bromide (TBABr) catalysed etherification was used for the alkylation of phenolic hydroxyl groups of the mesogenic moieties with epichlorohydrin (EPI). E.g. 0.5 mol 1a, 10 mol EPI and 1.25 mmol TBABr were stirred for 10 hrs at 60 °C. Ring closure proceeds after dropwise addition of 48 g 50 % w/w aqueous NaOH with continuous removing of water at 60 °C and 130 mbar during 2 hrs. After cooling the mixture to room temperature the crude product was filtered off, washed with water and dried in vacuo. Recrystallization from acetonitrile gave 111.9 g 2a (87.4% yield). Analogous reaction gave 2b (yield 68.3%, twice from toluene), 8a (yield 73.8 %, from toluene) and 8b (yield 63.5 %, from toluene).

2a $C_{16}H_{16}O_3$	(256.1)	Calc./ Found	C: 75.0%/ 74.8%	H: 6.3%/ 6.3%
2b $C_{16}H_{16}N_2O_3$	(284.3)		C: 67.6%/ 66.4%	H: 5.7%/ 5.6% N: 9.8%/ 9.8%
8a $C_{18}H_{18}O_4$	(298.3)		C: 72.4%/ 71.4%	H: 6.1%/ 6.0%
8b $C_{18}H_{18}N_2O_4$	(326.4)		C: 66.2%/ 65.1%	H: 5.6%/ 5.4% N: 8.6%/ 8.6%



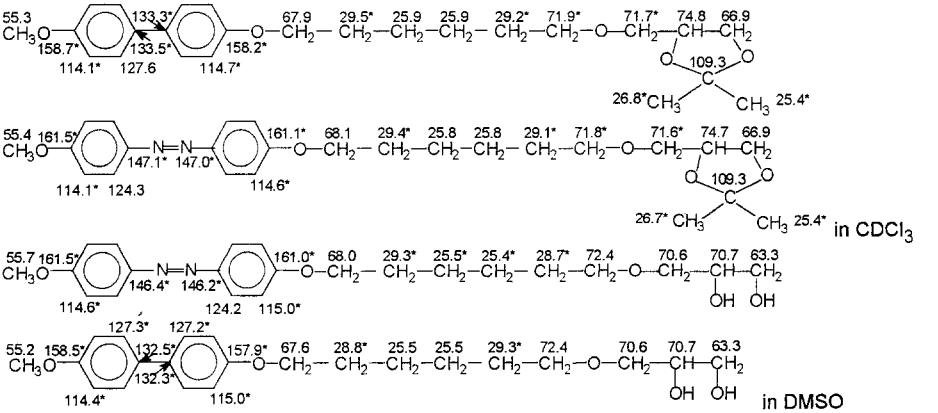
Synthesis of 3

A mixture of 5 mol 1,6-dibromohexane, 0.05 mol TBABr, 400 g 50 % w/w aqueous NaOH and 100 ml DMSO was vigorously stirred at 75 °C. 1 mol 1,2-O-isopropylidene glycerol was gradually added during 3 hrs. After 30 hrs the reaction was complete. Then the mixture was cooled to room temperature, and 300 ml $CHCl_3$ was added. The organic phase was washed with water to neutrality, dried over $NaSO_4$, and then the solvent was evaporated in vacuo. Fractional distillation gave 147.9 g (50% yield) desired compound 3 (b.p. 150-155 °C/ 2 mm). $C_{12}H_{23}BrO_3$ (295.2) Calc./Found C: 48.8%/ 48.8% H: 7.8%/ 8.3% Br: 27.1%/ 27.0%

Synthesis of 4a, 4b, 5a and 5b

0.15 mol 1a or 1b, 7.5 mmol TBABr, 120 ml Skellysolve B, 30 ml DMSO and 60 g 50 % w/w aqueous NaOH was heated to reflux temperature. Then 0.165 mol 3 was added. After about 5 hrs of reaction the mixture was cooled, and a white precipitate formed. A CH_2Cl_2 solution of the precipitate was washed several times with water. Then the solvent was removed, and the remaining residue was recrystallized from methanol to obtain 4a or 4b. Then 4a and 4b were dissolved in ethanol and treated with 50 ml 2 N HCl for 2 hrs at reflux temperature. The precipitate was filtered off, dried under reduced pressure and recrystallized from acetonitrile. Yield: 5a: 46.6 g (0.124 mol, 82.9 %) 5b: 48.3 g (0.120 mol, 80 %)

4a $C_{25}H_{34}O_5$	(414.5)	Calc./Found	C: 72.4%/ 72.1%	H: 8.3%/ 7.8%
4b $C_{25}H_{34}N_2O_5$	(442.6)		C: 67.8%/ 67.2%	H: 7.7%/ 8.5% N: 6.3%/ 6.2%
5a $C_{22}H_{30}O_5$	(374.2)		C: 70.5%/ 70.0%	H: 8.1%/ 8.4%
5b $C_{22}H_{30}N_2O_5$	(402.5)		C: 65.6%/ 65.5%	H: 7.5%/ 8.2% N: 7.0%/ 6.7%

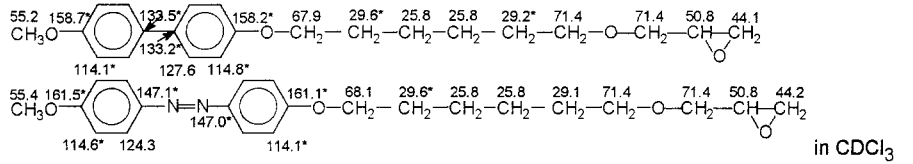


Synthesis of 6a and 6b

100 ml 33 % solution of HBr in acetic acid was added dropwise to 0.1 mol 5a or 5b suspended in 100 ml CH_2Cl_2 under stirring and ice-cooling during half an hour. After 2 hrs of stirring at room temperature the mixture was poured into 200 ml iced water and extracted with CH_2Cl_2. Then the organic phase was washed with 5 % Na_2CO_3, water, dried over Na_2SO_4 and the solvent removed in vacuo. The remaining residue was dissolved in 130 ml THF and treated with methanolic KOH (0.1 mol in 80 ml) for 2 hrs. Finally 130 ml water was added, the precipitate filtered off and washed with 50 % v/v water/methanol and dried in vacuo. After recrystallizing from toluene the epoxies were obtained in a good yield (56.1 % 6a, 54.7 % 6b).

6a $C_{22}H_{28}O_4$ (356.5) Calc./ Found C: 74.1% / 71.6 % H: 7.9% / 8.6%

6b $C_{22}H_{28}N_2O_4$ (384.5) C: 68.7% / 68.5 % H: 7.3% / 7.9% N: 7.3% / 7.2%



Synthesis of 10a, 10b, 11a and 11b

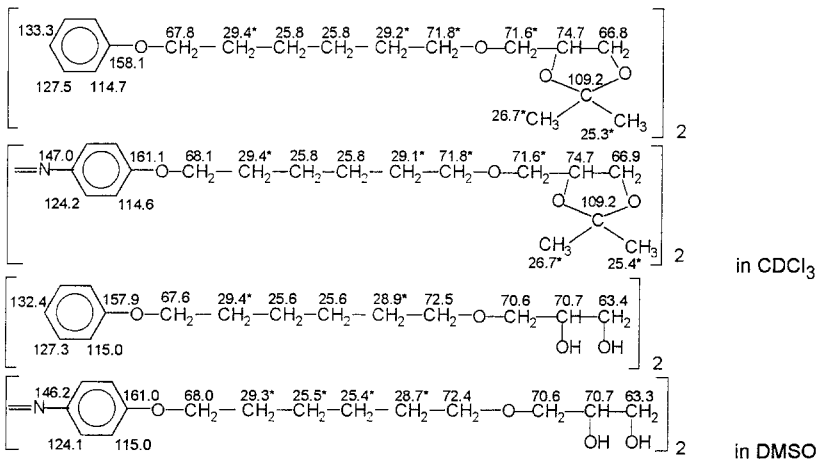
0.22 mol 3, 0.01 mol TBABr, 80 g 50 % w/w aqueous NaOH, 20 ml DMSO and 80 ml Skellysolve B was stirred vigorously and heated to 60 °C. During a period of 60 min 0.1 mol difunctional phenol 7a or 7b dissolved in 200 ml 15 % aqueous NaOH was added dropwise. After 2 hrs of reaction the mixture was cooled to room temperature, the precipitate filtered off and dissolved in CH_2Cl_2. The solution was washed several times with water to neutrality and dried over Na_2SO_4. After evaporation of the CH_2Cl_2 and crystallization from methanol 10a and 10b were obtained. Treating their ethanolic solution with 2N HCl for 2 hrs at reflux temperature a precipitate was produced, which was filtered off, washed with water, dried and recrystallized from acetonitrile to give 11a (35.1g, yield: 65.6 %) or 11b (28.5 g, yield: 50.7 %).

10a $C_{36}H_{54}O_8$ (614.8) Calc./ Found C: 70.3%/ 70.1% H: 8.8%/ 8.9%

10b $C_{36}H_{54}N_2O_8$ (642.8) C: 67.3%/ 66.8% H: 8.5%/ 8.7% N: 4.4%/4.5%

11a $C_{30}H_{46}O_8$ (534.7) C: 67.4%/ 67.5% H: 8.7%/ 8.9%

11b $C_{30}H_{46}N_2O_8$ (562.7) C: 64.0%/ 63.6% H: 8.2%/ 8.7% N: 5.0%/5.0%

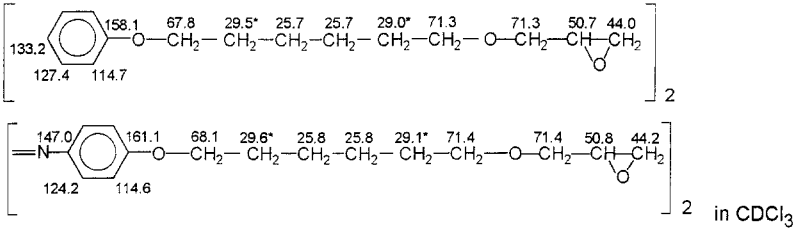


Synthesis of 9a and 9b

These compounds were prepared in a manner analogous to 6a and 6b, but using half the amount of the starting phenols to yield the corresponding epoxides (80.2 % 9a, 85.3 % 9b).

9a $C_{30}H_{42}O_6$ (498,7) Calc./ Found C: 72.3%/ 70.5% H: 8.5%/ 9.0%

9b $C_{30}H_{42}N_2O_6$ (526.8) C: 68.4%/ 67.7% H: 8.0%/ 8.3% N: 5.3% / 5.3%



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References

(1) L. STRZELECKI, L. LIEBERT: Bull. Soc. Chem. (France) 597 (1973)
(2) H. FINKELMANN: Adv. Polym. Sci. 60/61, 99 (1984)
(3) G. G. BARCLAY, C. K. OBER: Prog. Polym. Sci. 18, 899 (1993)
(4) J. J. MALLON, P. M. ADAMS: J. Polym. Sci., Polym. Chem. Ed. 31, 2249 (1993)
(5) G. G. BARCLAY, C. K. OBER, K. I. PAPATHOMAS, D. W. WANG: J. Polym. Sci., Polym. Chem. Ed. 30, 1831 (1992)
(6) M. FEDTKE: Makromol. Chem., Makromol. Symp. 7, 153 (1987)
(7) M. FEDTKE: Frontiers of Macromol. Sci., Ed. T. SAEGUSA, Blackwell (1989) p. 149
(8) C. PUGH, V. PERCEC: Polym. Bull. 16, 521 (1986)
(9) H. H. FREEDMAN, R. A. DUBOIS: Tetrahedron Letters 38, 3251 (1975)
(10) G. SCHLEIER, G. GALLI, E. CHIELLINI: Polym. Bull. 6, 529 (1982)
(11) S. KIRCHMEYER, H. MÜLLER, A. KARBACH: EP 445 401 A2 , 11.9.91; CA 115 257592d
(12) S. A. HARRISON: US Patent 3 383 360, 14.05.68; CA 69 19997b
(13) J. T. GUTHRIE, A. MORTON, E. NIELD: Surf. Coat. Int. 75, 212 (1993)
(14) C. CARFAGNA, E. AMENDOLA, M. GIAMBERINI, A. G. FILIPPOV, R. S. BAUER: Liq. Cryst. 13, 571 (1993)
(15) M.- P. BENTE: Thesis, Université Pau/ France (1992)
(16) J. v. ALPHEN: Recl. Trav. Chim. Pays-Bas 50, 657 (1931)
(17) M. KRAUSE: Ber. Dtsch. Chem. Ges. 32, 124 (1899)
(18) R. WILLSTÄDTER, M. BENZ: Ber. Dtsch. Chem. Ges. 39, 3492 (1906)

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