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LC-Polymers with Axial Chirality

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LC-Polymers with Axial Chirality

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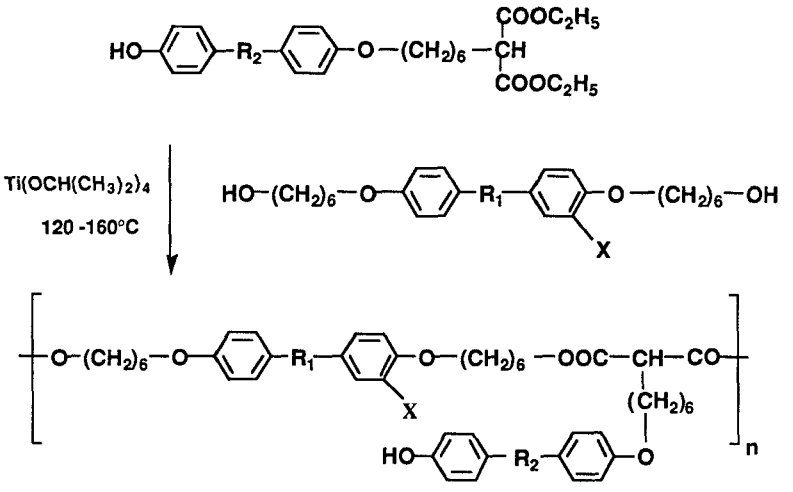
Liquid crystalline polymers with axial chirality are prepared. These polymers are chiral, not due to a single asymmetric carbon atom, but due to a larger molecular fragment, which is chiral as a whole. They exhibit cholesteric and chiral smectic C* phases. Dielectric spectroscopy proves strong ferroelectric properties in the chiral smectic C* phases of these polymers.

Keywords: LC-polymers, chiral smectic C phases, dielectric relaxation, axial chirality

INTRODUCTION

The interest in liquid crystalline (lc) polymers with ferroelectric properties (chiral smectic C* phases) is mainly due to three reasons: Because of their fast switching times in electric fields[1] these polymers are interesting for applications in electro-optics. Especially chiral side group polymers are investigated for this application.[1] Chiral lc elastomers can show piezo-electric properties[2,3] and are therefore interesting as piezo sensors. With respect to this property combined main chain/side group polymers (combined polymers) are studied.[2] The spontaneous polarization in chiral smectic C* phases offers the possibility to orient molecules with a high hyperpolarizibility in such a way that they can be used for frequency doubling of laser light in Non-Linear-Optics.[4] The use of copolymers excludes in this case the possibility of demixing.

A synthetic route to polymers, which are functionalized with hydroxy groups (see Schemes I and II), has been opened quite recently.[5] These polymers allow a



1 - 4

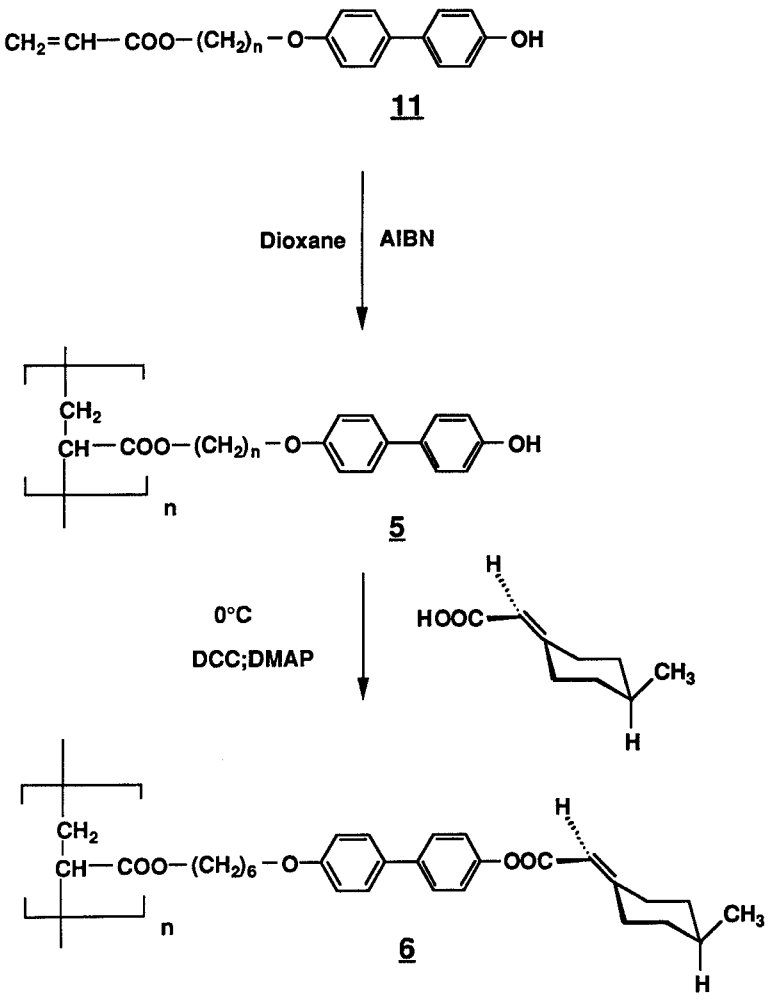
SCHEME I

simple formation of many chiral lc polymers, which can be prepared via a polymeranalogous reaction with different chiral carboxylic acids starting from one polymer.[5]

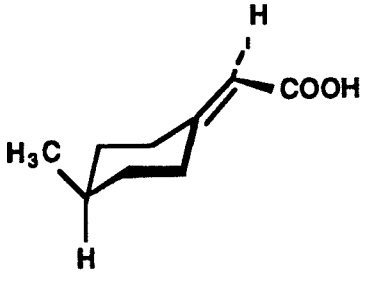
Knowing about the easy accessibility of these polymers, a new principle of chirality was tested for lc polymers. The lc polymers prepared so far (and also nearly all of the low molar mass liquid crystals) are chiral due to the presence of one or two asymmetric carbon atoms, which are incorporated into the flexible part of the molecule (the end group or the spacer group).[1,2] Because of the high mobility of these segments and the nearly free rotation of the mesogens around their long axes, the spontaneous polarization in the chiral smectic C* phase is much lower than the sum of the lateral dipole moments.[6] The incorporation of the chiral group into the rigid mesogenic core might therefore lead to an improved ratio between molecular dipole moments and macroscopic spontaneous polarization.[7] One possibility to achieve this goal is to use molecular structures, which are chiral not due to a asymmetric atom, but due to a larger, rigid structure, which is chiral as a whole. Structures with axial chirality fulfill these requirements. This has been investigated in detail by measurements of the helical twisting power in cholesteric phases.[8] The chiral compounds used in these investigations e.g., chiral atropisomeric esters of 1,1′-bi-2-naphthol are however not mesogenic by themselves. We have used a molecule with a more rod-like shape (4-methylcyclohexylidene acetic acid A,[9] to prepare chiral lc homopolymers, which are chiral due to a chiral molecular fragment, and not because of a single asymmetric carbon atom.

PREPARATION OF THE LC POLYMERS

The functionalized combined polymers in Table I are prepared by a melt polycondensation (see Scheme I). Due to the much higher reactivity of the alcoholic



SCHEME II



A

TABLE I

Phase transitions of the functionalized combined main chain/side group polymers 1–4 (see Scheme I)

No	R_1	R_2	X	$\bar{M}_{GPC}$	Phase transitions[a] in °C
1	—	—	Br	49000	g 29 Ic_1 97 Ic_2 105 i
2	- N (O) =N -	—	—	48000	g 24 s 139 i
3	- N = N -	- N (O) =N -	—	28000	c 85 Ic 137 i
4	- N (O) =N -	- N (O) =N -	—	30000	g 31 Ic_1 130 Ic_2 145 i

[a] c: Crystalline; g: glassy frozen phase; Ic, Ic_1, Ic_2: liquid crystalline phase, not further specified; s: smectic A or C; i: isotropic.

TABLE II

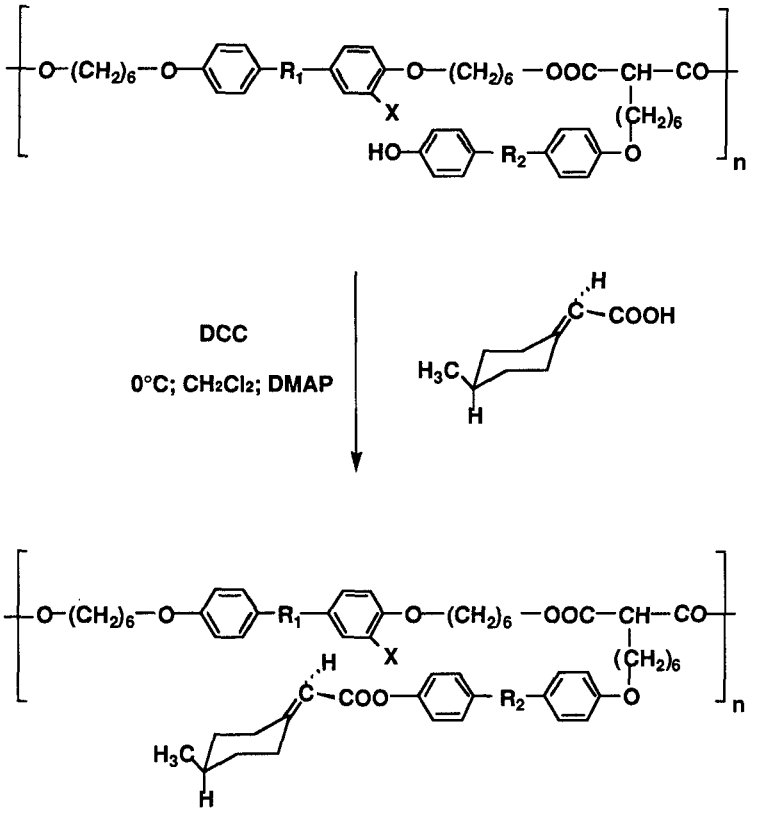
Phase transitions of side group polymers 5–6 (see Scheme II)

No	[c] $[\alpha]_D^{20}$	$\bar{M}_{GPC}$	Phase transitions[a] in °C
5	—	—	g 73 s 135 i
6	- 50.4	21.000	g[b] s_c^* 126 i

[a] See footnote to Table I, s_c^*: chiral smectic C* phase.
[b] Glass transition temp. between 80° and 110°C, not further specified.
[c] See footnote to Table III.

hydroxyl groups compared to the phenolic groups the synthesis of uncrosslinked polymers is possible in this way. The functionalized side group polymer in Table II is prepared by a free radical polymerization (see Scheme II). It is noteworthy that many of these functional polymers display liquid crystalline phases. Combined polymers with lateral substituents in the main chain (azoxybenzene or brominated biphenyl) show a glass transition (see Tables I and II).

The esterification of these polymers with the axial-chiral acid A can be done very easily with the help of N,N'-dicyclohexylcarbodiimid (DCC) (see Scheme II and III). NMR-measurements prove the reaction to be quantitatively within the limits of accuracy (see Figure 1), that means that nearly 100% of the hydroxy groups of the functionalized polymers are esterificated.[15] The chiral polymers prepared in this way are listed in Tables II and III. All polymers show broad liquid crystalline phases.



7 - 10

SCHEME III

PHASE ASSIGNMENT

The cholesteric phases were identified by their typical grandjean-textures. They showed no small angle X-ray scattering (see Figure 2). The selective reflection of visible light proved the ability of 4-methyl cyclohexylidene acetic acid to induce a cholesteric helix with a small pitch. The smectic phases were investigated by X-ray measurements of oriented and unoriented samples (see Figures 2 and 3). Tilted smectic phases-including chiral smectic C* phases-were observed in all cases (see Tables II and III). The ferroelectric properties of these smectic phases was studied by dielectric spectroscopy.[10] Very intensive Goldstone modes were observed in the chiral smectic C* phase (see Figure 4). The shift of the Goldstone mode towards lower frequencies is presumably due to the vicinity of the glass transition. The dielectric strength of the Goldstone mode, which is in the same order of magnitude as the one observed for low molar mass liquid crystals with α-chloro-carboxylic acids,[11] proves the ability of 4-methylcyclohexylidene acetic acid to induce a high

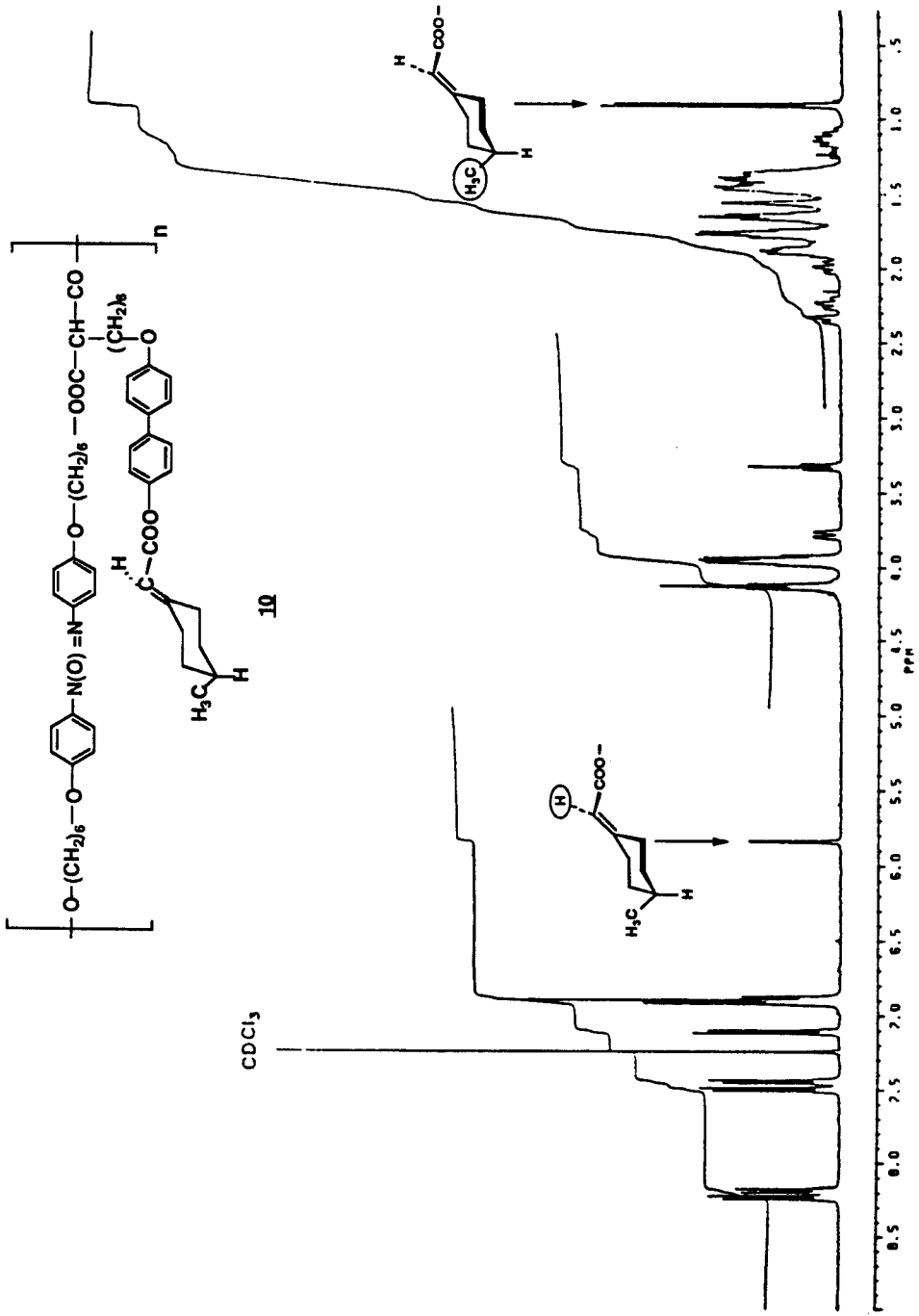


FIGURE 1 Proton NMR-measurement of polymer **10**.

TABLE III

Phase transitions of the polyesters 7–10, which are chiral due to axial chirality (see Scheme III)

No	R_1	R_2	X	Phase transitions[a] in °C	[b] $[\alpha]_D^{20}$
7	-N(O)=N-	-N(O)=N-	—	g 26 s_c* 82 n* 153 i	-37.1
8	—	—	Br	g s_1 62 s_2 105 i	-26.6
9	-N=N-	-N(O)=N-	—	g 28 s_1 90 n* 143 i	-28.0
10	-N(O)=N-	—	—	g 54 s_c* 110 n* 141 i	-26.1

[a] See footnote to Tables I and II, III; s_1: presumably smectic J*, s_2: presumably smectic F* or I*, n*: cholesteric.
[b] [· cm^3/g dm] c = 0.25 g/100 ml in Chloroform.

spontaneous polarization in the chiral smectic C* phase. The ferroelectric and optical properties are under further investigation.

EXPERIMENTAL PART

4-Methylcyclohexylidene acetic acid A. The synthesis and resolution of A is described elsewhere.[9] Following this procedure, starting with 10 g of the racemic acid, 1.1 g of each enantiomer (yield: 22%) could be obtained after resolution. The optical purity of the enantiomers were in both cases higher than 90% (R: ee = 97%; S = 93%).[12]

Synthesis of functionalized polymers 1–5. Synthesis of combined functionalized polymers 1–4 is described in Scheme I. The melt polycondensation was carried out according to Reference 5, keeping the reaction temperature between 150° and 170°C. Afterwards the polymers were purified by dissolving in THF, precipitating twice from methanol/acetone (Vol. ratio 1:1), and drying in a vacuum oven.

Synthesis of functionalized side group polymer 5. Synthesis of monomeric acrylate 11 was done according to Reference 13. Free radical polymerization of 11 was done in the following procedure: 400 mg monomer 11 and 2 mol-% 2,2′-azoisobutyronitrile were dissolved in dry dioxane and degased with an argon steam for 20 minutes. The mixture was polymerized in a sealed ampoules for 24 h at 65°. The polymer was precipitated in 100 ml methanol, redissolved in dioxane and reprecipitated twice in methanol. Drying in a vacuum oven gave the pure polymer 5; yield 75%.

^{1}H—NMR (DMSO-d_6; 200 MHz): δ 1.30–1.55 [m, 10H, —(C$\underline{H}_2$—CH)—, —COO—CH_2—(C$\underline{H}_2$)$_4$—], 2.21 [s, 1H, —(CH_2—C$\underline{H}$)—], 3.79 [m, 2H,

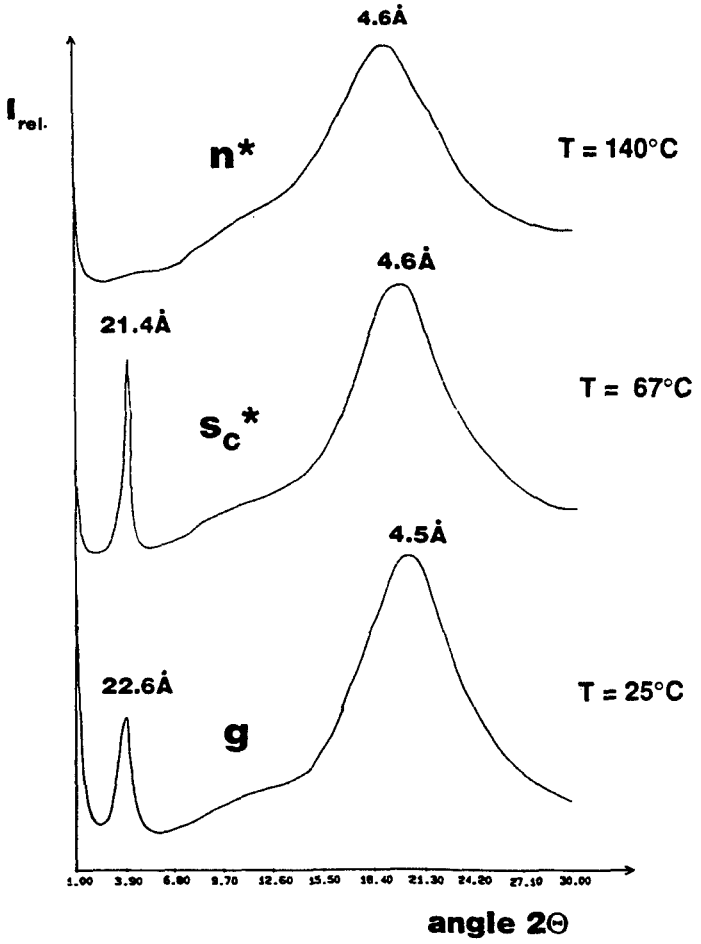


FIGURE 2 Temperature dependent X-ray measurement of polymer 7 (see Table III and Figure 3).

—COO—$(CH_2)_5$—C<u>H</u>$_2$—O—], 3.92 [m, 2H, —COO—C<u>H</u>$_2$—$(CH_2)_5$—], 6.76 [m, 4$H_{arom.}$, $H_{3,3',5,5'}$], 7.31 [m, 4$H_{arom.}$, $H_{2,2',6,6'}$], 9.43 [s, 1H, —C_6H_4—O<u>H</u>]

$C_{21}H_{24}O_4$(340.42):	Calc.	C 74.10	H 7.11
	Found	C 73.67	H 7.07

Preparation of homopolymers with axial-chiral group <u>6</u>–<u>10</u>. Synthesis of the chiral homopolymers followed the procedure of Reference 5. An example of the procedure is as follows: To a suspension of 0.12 mmol <u>7</u>–<u>10</u>[14] in 5 ml dry CH_2Cl_2, 0.36 mol 4-methylcyclohexylidene acetic acid <u>A</u> and 3–4 mg 4-dimethylaminopyridine (DMAP) were added. The reaction mixture was cooled to 0°C and 36 mmol N,N′-dicyclohexylcarbodiimid (DCC) were added. After stirring for 4 h at 0°C the precipitation of urea could be observed. Stirring over night at room temperature was done for the completeness of polymeranalogous reaction. The urea was filtered off and the filtrate was precipitated in a cooled methanol/acetone mixture (vol.

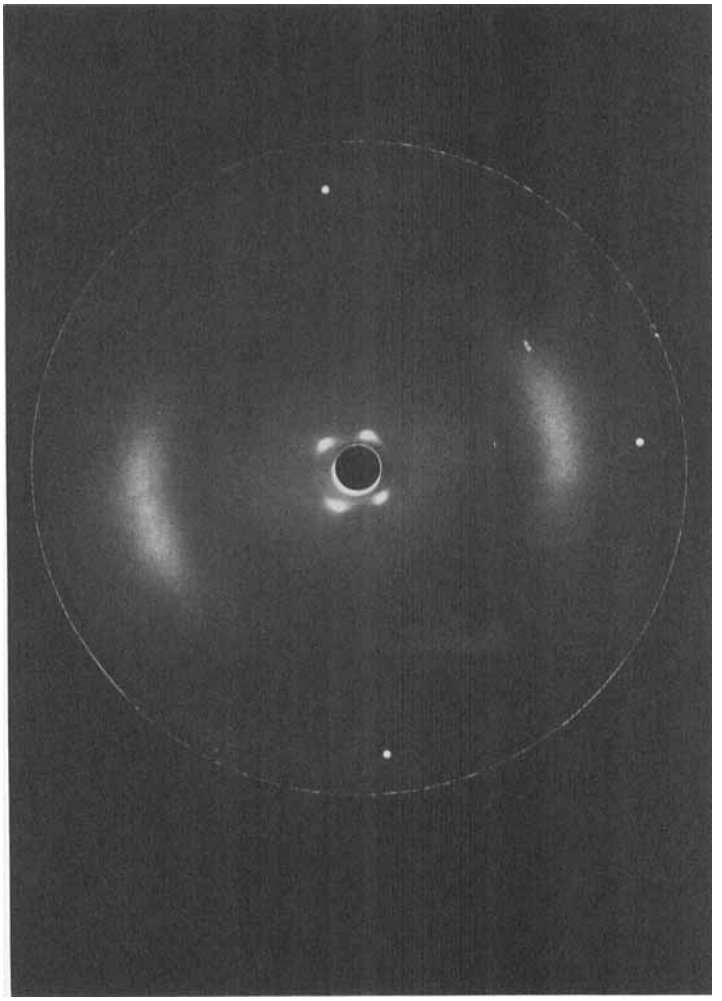


FIGURE 3 X-ray fiber pattern of polymer **7** (see Table III); the small angle reflection corresponds to a bragg-spacing of 22 Å, the wide angle to 4.5 Å.

ratio 1:1). Twice redissolving in $CHCl_3$ and precipitation gave the pure chiral polymers **6**–**10**. All polymers were checked by analytical GPC, ^{1}H-NMR, polarimetry and elemental analysis. As one example the characterization of polymer **10** (yield: 43%) is given:

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.90–0.92 [d, 3H, —C$\underline{H}_3$, J = 7 Hz], 1.09–2.36 [m, 35H, cyclohexylidene ring, 2 (—O—CH_2—(C$\underline{H}_2$)$_4$—CH_2—O—), CH—(C$\underline{H}_2$)$_5$—CH_2—O—], 3.30–3.34 [t, 1H, C$\underline{H}$—$(CH_2)_5$—CH_2—O—], 3.76–3.79 [m, 1H, cyclohexylidene ring], 3.91–3.98 [m, 6H, 2(—COO—$(CH_2)_5$—C$\underline{H}_2$—O—), CH—$(CH_2)_5$—C$\underline{H}_2$—O—], 4.10–4.15 [t, 4H, 2 (—COO—C$\underline{H}_2$—$(CH_2)_5$—CH_2—O—)], 5.8 [s, 1H$_{olefin}$, —C=C$\underline{H}$—], 6.87–6.91 [m, 6H$_{arom.}$, $H_{3,5}$-biphenylmoiety, $H_{3,3',5,5'}$-azoxybenzenemoiety], 7.09–7.11 [d, 2H$_{arom.}$, $H_{3',5'}$-biphenyl-

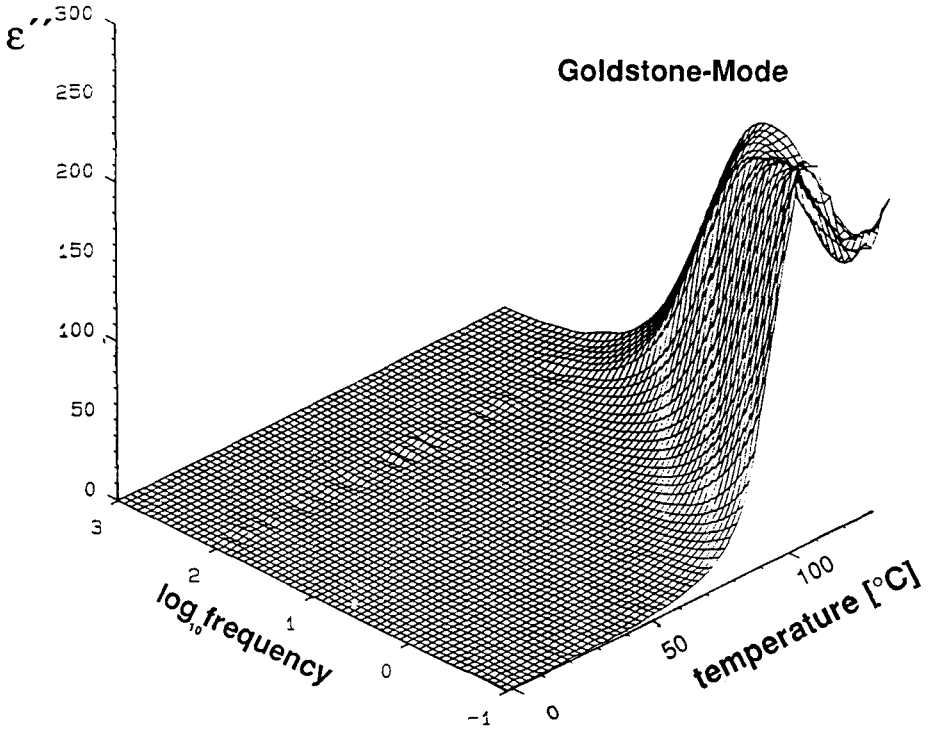


FIGURE 4 Plot of ε'' versus $\log_{10}$ frequency and temperature for polymer **6**.

moiety, J = 9 Hz] 7.43–7.51 [m, $4H_{arom.}$, $H_{2,2',6,6'}$-biphenylmoiety], 8.19–8.23 [m, $4H_{arom.}$, $H_{2,2',6,6'}$-azoxybenzenemoiety]

$C_{54}H_{66}N_2O_{10}$(903,14)	Calc.	C 71.82	H 7.37	N 3.11
	Found	C 71.21	H 7.44	N 2.93

$[a]_D$ = −26.1, c = 0.25 in $CHCl_3$

Measurements: DSC-measurements and polarizing microscopy were done according to Reference 16. X-ray measurements were performed as described in Reference 16. Optical activity was determined with a Perkin-Elmer polarimeter 241, where the specific rotations were extrapolated towards the Na-D-line. Dielectric measurements were performed according to Reference 11.

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