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Molecular Zip-fasteners

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Swallow-tailed mesogens of liquid crystalline side group polysiloxanes show a very strong tendency to form an antiparallel order in the short range and to connect in this way different oligomer strands – like a molecular zip-fastener. To check the strength of such a molecular cooperation swallow-tailed side groups of oligomers were exchanged stepwise by laterally aryl substituted mesogenes. The gradual destruction of the zip-like gearing caused by this variation can be observed by dielectric measurements. Comparing investigations show that the tendency to form antiparallel package is greater for the oligomers under discussion than in mixtures of the corresponding monomers.

Keywords: Swallow-tailed siloxanes, co-oligomers, dielectric measurements, antiparallel orientation.

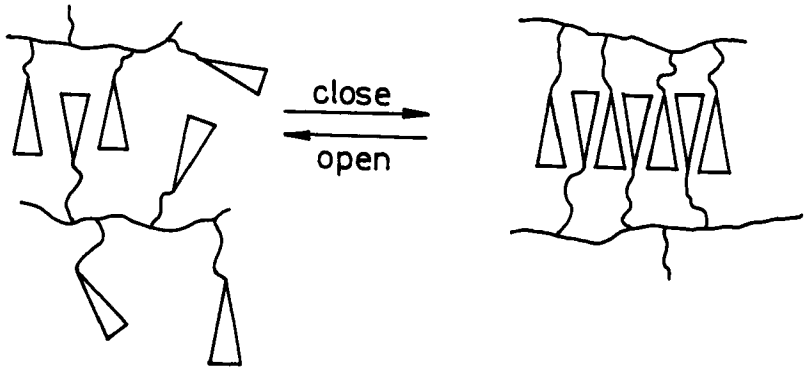
INTRODUCTION

Previous investigations have shown that the so-called swallow-tailed liquid crystals exhibit a strong tendency to assume an antiparallel orientation in the short range. This effect could be proven experimentally in the isotropic phase (I), in the nematic state and specially in the transition range from the nematic (N) to the smetic A (S_A) modification.[1] It was also demonstrated by dielectric measurements that the antiparallel order is the result of repulsive forces.

Therefore, it can be strongly reduced by addition of molecules with a suitable molecular shape[2]. It should be pointed out that the repulsive forces are much stronger than the dipolar one. Therefore, the tendency to form an antiparallel order in the short range is much stronger developed in this case as previously observed in azobenzenes[3] and cyanobiphenyls.[4] On the other hand, we are not dealing with singular associates as for example discussed in hydrogen bonded dimers.[5,6]

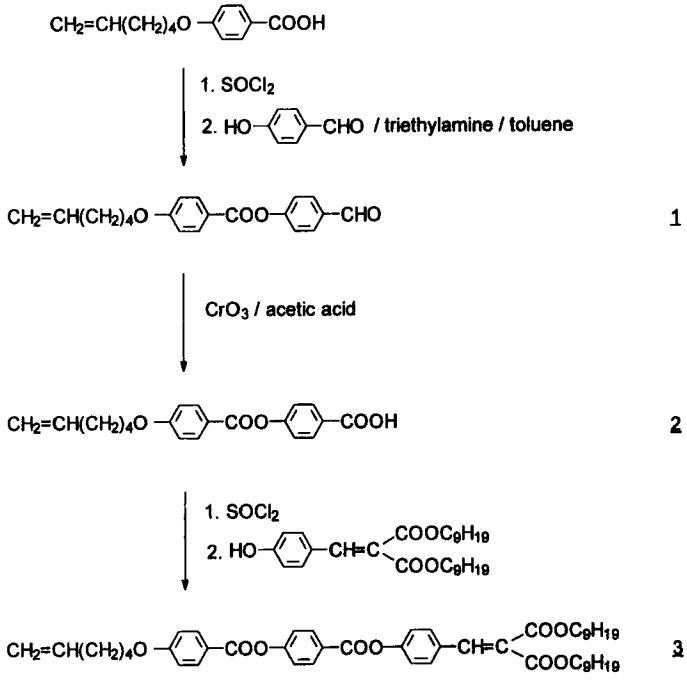
If now swallow-tailed molecules are fixed via a spacer on a main chain the resulting side group polymer acts as molecular zip-fastener as we will demonstrate[7] and as it is shown in the sketch below. Thereby the imagination of a zip-fastener is only an approximation of a three-dimensional effect by a one-dimensional description.

The aim of this article is to investigate the efficiency of such a zip-fastener. Therefore, the swallow-tailed side groups were systematically replaced by mesogens with a bulky lateral branch.

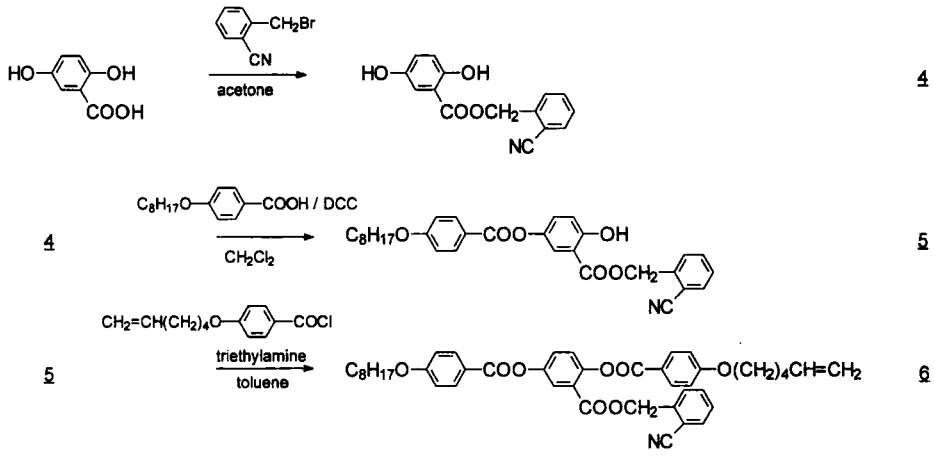


SYNTHESIS AND CHARACTERIZATION OF THE SUBSTANCES

Scheme 1 shows the reaction path to prepare the swallow-tailed compound 3. The 4-*n*-hexenyloxybenzoic acid is esterified with 4-hydroxybenzaldehyde. Oxidation of the aldehyde 1 by chromium(VI) oxide produces the two-ring benzoic acid 2. Aroylation of di-*n*-nonyl 4-hydroxybenzylidenemalonate by the acid chloride of the benzoic acid 2 yields the alkenyl substituted swallow-tailed compound 3. The laterally cyanophenyl-



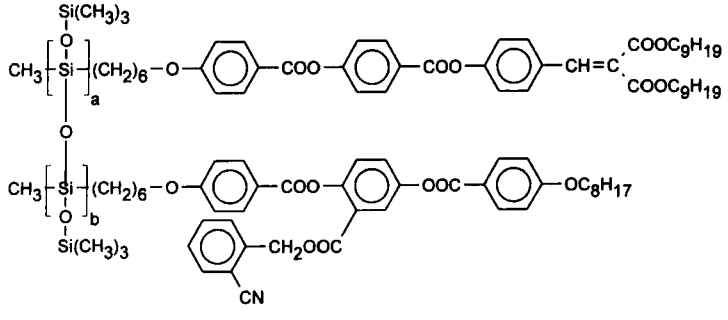
SCHEME 1



SCHEME 2

substituted mesogen 6 was prepared as shown in scheme 2 according to a method described by Stützer et al.[8]. Selective esterification of 2-cyanobenzyl 2,5-dihydroxybenzoate step by step performed firstly with 4-*n*-octyloxybenzoic acid/DCC and thereafter that with 4-*n*-hexenyloxybenzoyl chloride yields the monomer 6.

The obtained monomers 3 and 6 were recrystallized and purified by column chromatography on silica gel using chloroform as solvent. By hydrosilylation reaction[9] of the unsaturated monomers with the linear hepta(methylhydrogensiloxane) the corresponding liquid crystalline homo-oligomers and statistical co-oligomers were obtained. The respective chemical formula is:



a+b=7

To differentiate between monomers and linear oligomers with seven -$SiCH_3X$-units (L7) as well as the swallow-tailed compound 3 and the laterally branched 6 (see schemes 1 and 2) the designations 3 and 6 for the monomers and 3L7 and 6L7 for the respective homo-oligomers are used. The statistical co-oligomers are designated only with the relative molar content of 6 ($b/(a+b)$). The phase transitions were investigated by polarizing microscopy and DSC. Table 1 includes the data of the pure monomers 3 and 6, of the accompanying co-oligomers 3L7 and 6L7 as well as of the statistical co-oligomers.

TABLE I

Phase transition temperature (in K) of the monomers and homo-oligomers

Sample	cr/g	S_C	S_A	N	I
3	344 (cr)	(● 314)	● 352	● 359	●
6	372 (cr)	– –	– –	(● 358)	●
3L7	369 (g)	– –	● 316	● 340	●
6L7	350 (cr)	– –	– –	● 374	●
0.3[1]	(g)	– –	● 328	● 345	●
0.4[1]	(g)	– –	● 332	● 347	●
0.7[1]	(g)	– –	● 330	● 357	●

[1]relation $b/(a+b)$ as given in formula 1, the glass temperature could not be obtained by DSC-measurements.

DIELECTRIC MEASUREMENTS

Dielectric measurements have been performed in the frequency range from 1 Hz to 10 MHz with a Hewlett-Packard 4192 A self-balancing bridge. At low frequencies the impedance analyzer SI 1260 (Solartron Schlumberger) together with a Chelsea interface was used. The measuring cell ($A = 1\,\mathrm{cm}^2, d = 0.02\,\mathrm{cm}$) was calibrated with cyclohexane. The samples were oriented in a magnetic field of about 0.6 T that was sufficient for the given compounds. From the measured capacities and resistances the dielectric constants ε' and losses ε'' at different frequencies f were calculated. The dielectric absorption curves (ε'' versus $\lg f$) were fitted to the Cole-Cole equation[10]

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (\mathrm{if}/f_R)^{1-h}} \tag{1}$$

after subtraction of the conductivity in form of Af^{-n}. In this way the dielectric increment, $\Delta = \varepsilon_0 - \varepsilon_\infty$, the relaxation frequency f_R, the distribution parameter h and the static dielectric constant ε_0 could be obtained.

RESULTS OF THE MIXTURES OF MONOMERS

The phase diagram of the swallow-tailed (3) and the laterally branched liquid crystal (6) in Figure 1 shows a systematic decrease of the N/S_A transition temperatures and a complete miscibility of the nematic phases. Experimental data of the static dielectric constant are presented in figure 2. The static dielectric constant $\varepsilon_{\|0}$, measured parallel to the director, decreases with falling temperature specially in the N/S_A phase transition range. This is an effect of the increasing antiparallel correlation of the molecules in direction of the molecular long axes[2]. The gradual destruction of the antiparallel order of 3 is manifested by the systematic change of the static dielectric constants of the mixtures. At $x_6 > 0.6$ the antiparallel correlation can be neglected. Furthermore, it should be pointed out that the ε_0-values in the isotropic phase at $x_6 = 0.7$ even are higher than those of the pure compound 6. This again indicates the decreasing tendency to an antiparallel correlation that is connected with an increase of the mean dipole moment per unit volume.

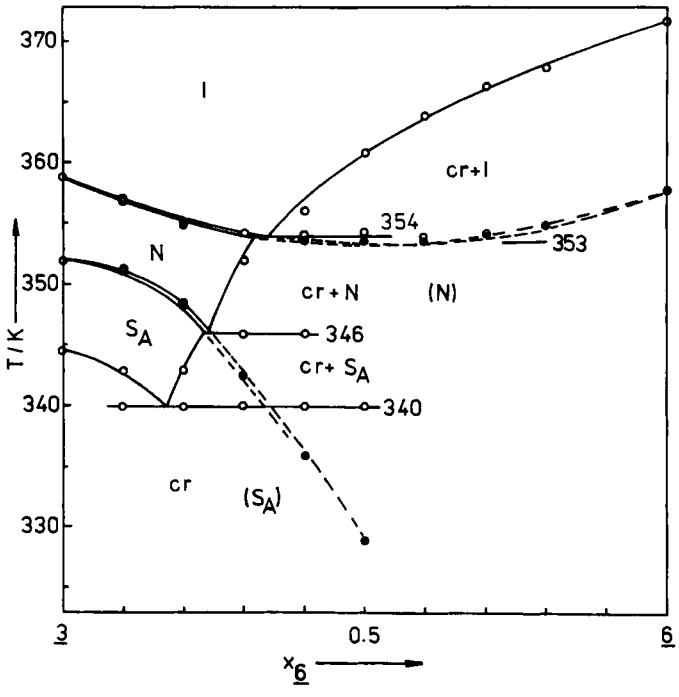


FIGURE 1 Phase diagram of the monomers. Phase transitions between metastable phases, detected by cooling of the sample, are indicated by ⊙ and connected by broken lines.

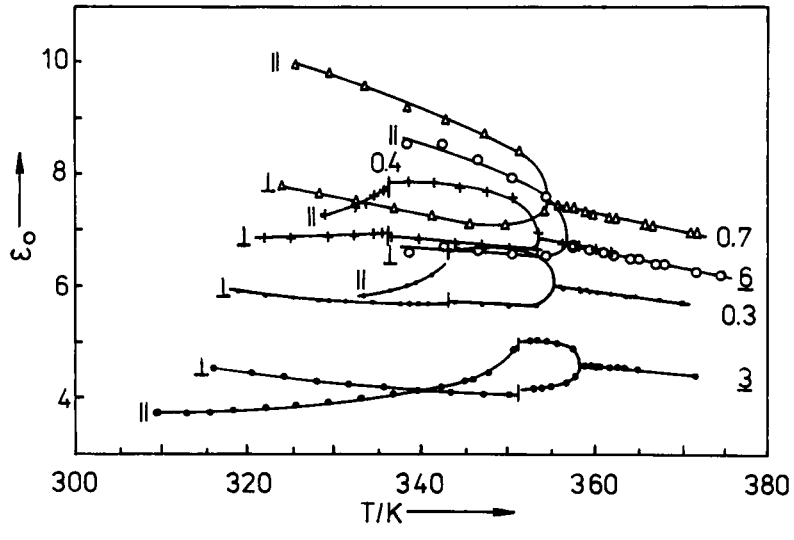


FIGURE 2 Static dielectric constants of the monomers and the mixtures at the given molar fraction of x_6.

At first sight it is surprising that the lateraly branched liquid crystal 6 with a strong dipole apparently situated perpendicular to the long axis has a positive dielectric anisotropy. This can easily be explained by the internal rotations of the lateral segment around the single bonds of the spacer group to give conformations like that shown in Figure 3. The relaxation frequencies for the reorientation of the longitudinal dipole $f_{R\parallel}$ and the perpendicular one $f_{R\perp}$ are shown in Figure 4. Generally, the relaxation frequencies decrease by addition of 6. For the pure compound 6 only a very small dielectric absorption with $\Delta_\parallel = 0.05 \pm 0.03$ at about $f = 5$ kHz could be detected at $T = 335$ K. This one could be connected with the reorientation of the hydroquinone diester part. Probably the polar side chain is strongly decoupled from the hydroquinone system and reorients so fast that it gives only contributions at high frequencies. All the other samples show a stepwise decrease of $f_{R\parallel}$ at the I/N transition. For the $f_{R\perp}$ relaxation WLF behaviour (dynamical glass process[11]) was found. Surprisingly, the difference between $f_{R\perp}$ of 3 and at $x_6 = 0.3$ is relatively big indicating stronger structural changes in the mixture. All the results well agree with previous measurements on mixtures of swallow-tailed compounds with laterally branched liquid crystals[12].

RESULTS OF STATISTICAL CO-OLIGOMERS

In contradiction to the phase diagram of the monomers presented in Figure 1 the statistical co-oligomers show a tendency for stabilization of the S_A phase in the middle concentration range (Figure 5). The respective static dielectric constants of three co-oligomers are plotted in Figure 6. Thereby the numbers are related to the ratio of $b/(a+b)$ as given in formula 1. It should be pointed out that the samples could be well oriented. This effect was proven by the low frequency δ-relaxation that could not be detected when the electrical measuring field and magnetic field are perpendicular to each other. At lower temperatures we have had problems to separate the very weak δ-relaxation from the conductivity. Therefore, no points for $\varepsilon_{\parallel 0}$ are given in Figure 6 at these temperatures.

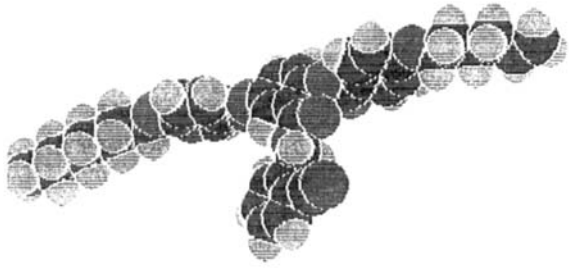


FIGURE 3 CPK-model of 6. As starting conformation a structure with a strong dipole moment in direction of the para-axis of the central core of 6 was taken. Therefore, the given model shows one of the possible conformations.

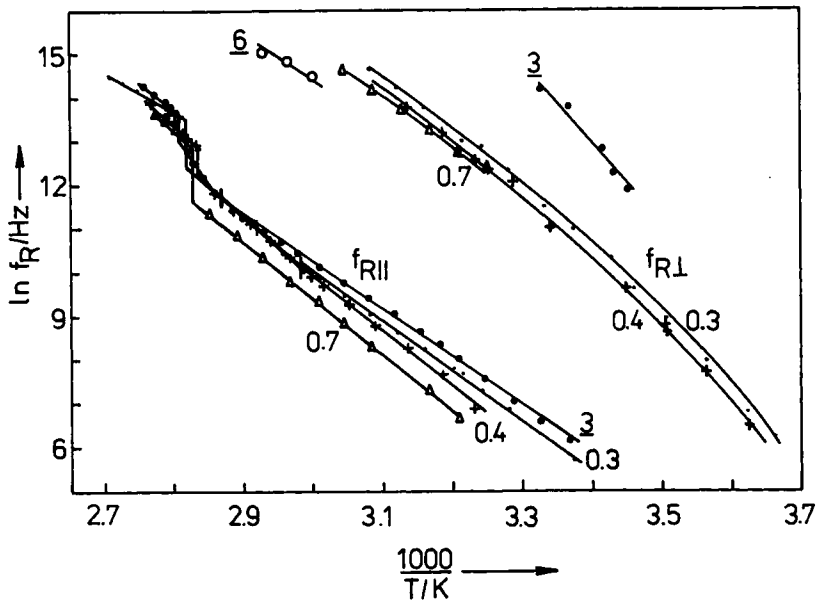


FIGURE 4 Arrhenius-plot of the relaxation frequencies f_R. The numbers are related to the molar fraction of 6.

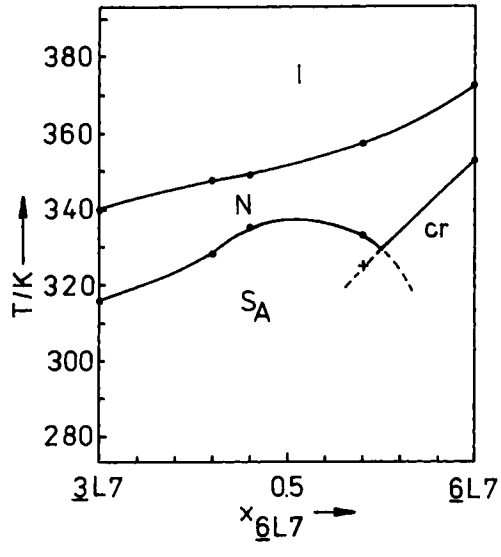


FIGURE 5 Sketch of the phase diagram of the statistical co-oligomers. The monotropic transition is indicated by a cross.

Comparing 3L7 with the monomer one can conclude that a strong antiparallel correlation parallel to the director can be detected in the nematic phase too. In this case, however, it is formed suddenly. The structure of the oligomer reminds on one half of a zip-fastener and maybe this is the reason for the observed tendency of the links to be

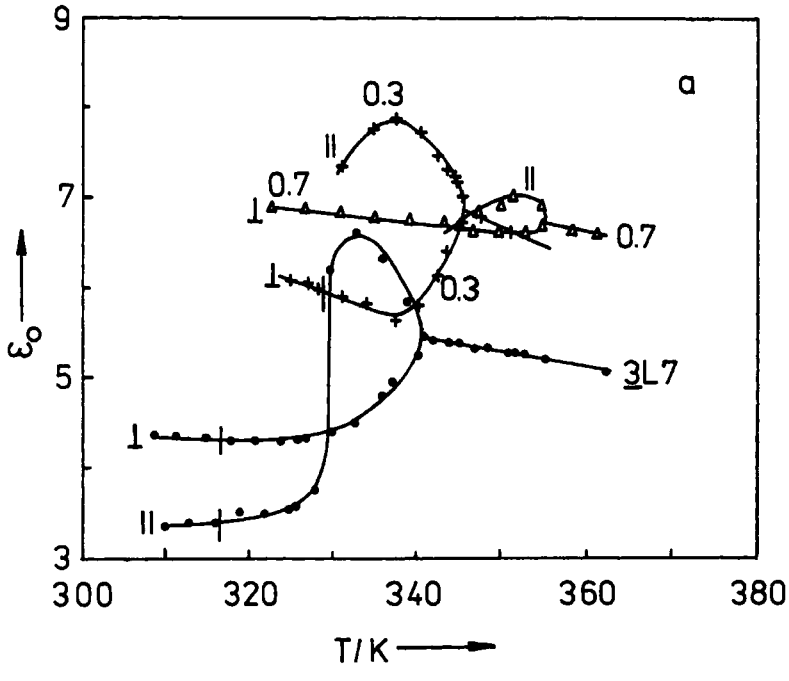


FIGURE 6a

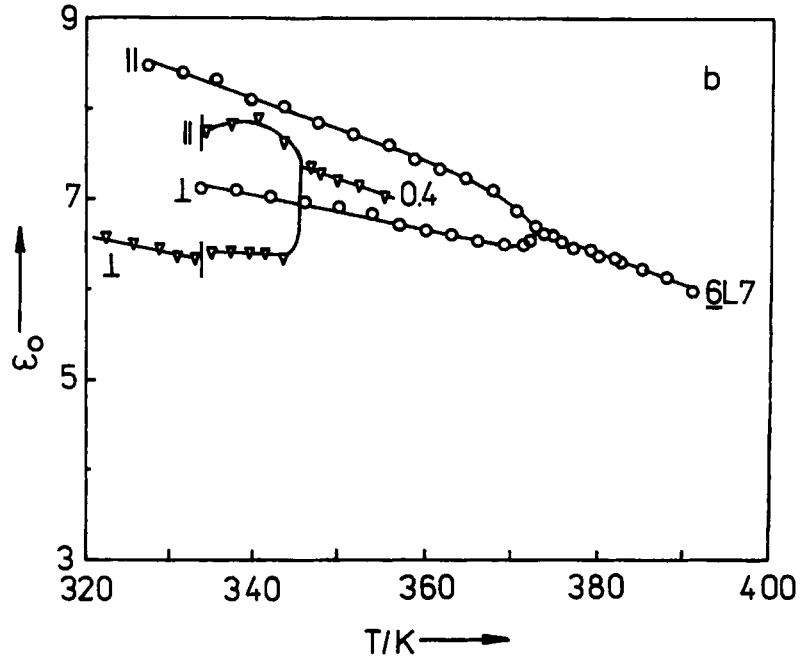


FIGURE 6 Dielectric constants of the statistical co-oligomers 0.3, 0.7 and the homo-oligomer 3L7 (6a) as well as of 0.4 and 6L7 (6b) at different temperatures. For comparison the same ε_o-scale was used.

more collectively antiparallel oriented (closing mechanism). The effect of opening was studied by heating of 3L7 starting from 320 K, were an increase of $\varepsilon_{\parallel 0}$ was measured. The obtained $\varepsilon'_{\parallel}$-data practically are the same as measured by cooling shown in Figure 6a.

If now one link of the zip-fastener is replaced by a quite different part, a normal zip-fastener will be blocked. But our molecular one still works as it can be seen in the strong step of $\varepsilon_{\parallel 0}$ for the statistical co-oligomer 0.3. By replacing more than 70% of the swallow-tailed monomer 3 (0.7) by laterally branched links 6 one can still see the strong tendency to form an antiparallel order at the N/S_A transition. In this sense the investigated oligomer 0.7 can be regarded as an example making ideal recognition process as known from biological systems.

The dielectric relaxation frequencies of the investigated oligomer siloxanes are summarized in Figure 7. Additionally to the low frequency $f_{R\parallel}$-absorption (δ-relaxation) an α-process is observed which shows WLF behaviour. The relaxation frequency decreases continously with increasing content of 6 in the co-oligomer. This indicates systematically decreases of the glass temperature from the homo-oligomers 3L7 to 6L7.

Only for the pure swallow-tailed homo-oligomer 3L7 a β-relaxation could be separated. This one corresponds to the $f_{R\perp}$-relaxation shown in Figure 4.

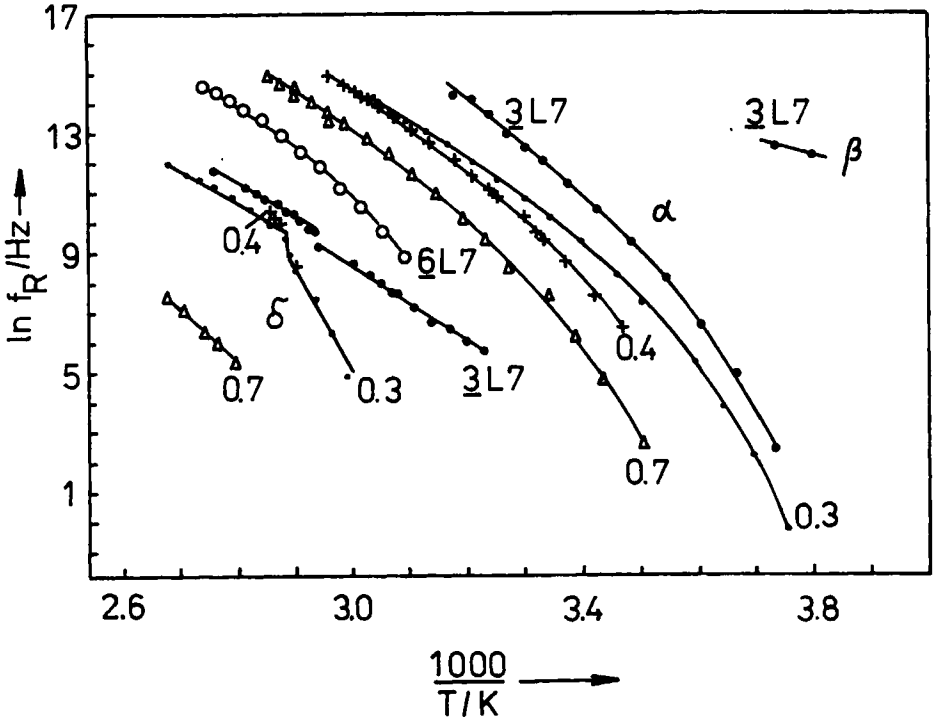


FIGURE 7 Arrhenius-plot of the homo-oligomers and the statistical co-oligomers indicated by the molar fractions of 6.

CONCLUSION

Summarizing all experimental data we can conclude that the closing and opening process of the molecular "zip-fastener" consisting only of a swallow-tailed molecule as side group is very efficient. A statistical substitution of some links in the zip-fastener by parts with different molecular shape results in a decreasing efficiency of the zip-fastener, but no blocking. Probably, the molecular mechanism is able to eliminate some incorrect links, perhaps by the formation of loops in the main chain.

The authors thank the Deutsche Forschungsgemeinschaft for financial support.

EXPERIMENTAL PART

4-[4-(5-Hexenyloxy)benzoyloxy]benzaldehyde (1): To 20 g (0.09 mol) 4-(5-hexenyloxy)benzoic acid 21.2 g (0.18 mol) thionyl chloride is added and this mixture has to stay one day at room temperature and one hour at 323 K. After removing the excess thionyl chloride the acid chloride is dissolved in 10 ml dry toluene. This mixture is given drop by drop to a solution of 11.0 g (0.09 mol) 4-hydroxybenzaldehyde, 10.1 g (0.1 mol) triethylamine and catalytic amounts of 4-N,N-dimethylaminopyridine (DMAP) in 250 ml dry toluene. After 10 h stirring at room temperature and 1 h at 323 K, the precipitated triethylamine hydrochloride is filtered of. The solvent is evaporated under vacuum and the raw product is recrystallized twice from ethanol.

Yield: 21.6g (74%) cr 315 N 3181
^{1}H-NMR(80 MHz, $CDCl_3$): δ = 1.6–2.3(several m, 6H, CH_2=CH—(CH_2)$_3$—CH_2—O—), 4.1 (*t*,2H, CH_2=CH—(CH_2)$_3$—CH_2—O—), 5.0(*t*, 2H,CH_2=CH—(CH_2)$_3$—CH_2—O—), 5.6-6.1(*m*, 1H, CH_2=CH—(CH_2)$_3$—CH_2—O—), 7.0(*d*, 2H,—CH_2—O—Ar—COO), 7.4(*d*, 2H,—COO—Ar—CHO), 7.9(*d*, 2H,—COO—Ar—CHO), 8.1(*d*,2H,-CH_2—O—Ar—COO), 10.0(*s*, 1H,—CHO).
Elemental analysis: $C_{20}H_{20}O$ (324.38 g mol^{-1}): calculated C, 74.02; H, 6.21; found C, 73.74; H, 6.19

4-[4-(5-Hexenyloxy)benzoyloxy]benzoic acid (2): 20 g (0.06 mol) of 1 is solved in 100 ml acetic acid in a water bath at 313 K. To this solution a solution of 11 g (0.11 mol) CrO_3 in 3 ml hot water and 12 ml acetic acid is given dropwise during stirring and cooling. After 12 hours stirring at 323 K the precipitated acid 2 is separated, washed with water and recrystallized from ethanol.

Yield: 11.2 g (55%) cr 409 N 503 I
^{1}H-NMR(80 MHz, $CDCl_3$): δ = 1.6–2.3(several m, 6H, CH_2=CH—(CH_2)$_3$-CH_2—O—), 4.1 (*t*,2H, CH_2=CH—(CH_2)$_3$—CH_2—O—), 5.0(*t*, 2H,CH_2=CH—(CH_2)$_3$—CH_2—O—), 5.6-6.1(*m*, 1H, CH_2=CH—(CH_2)$_3$—CH_2—O—), 7.0(*d*, 2H,—CH_2—O—Ar—COO), 7.4(*d*, 2H,—COO—Ar—CHO), 7.9(*d*, 2H,—COO—Ar—CHO), 8.1(*d*,2H,—CH_2—O—Ar—COO).
Elemental analysis: $C_{20}H_{20}O_5$ (340.38 g mol^{-1}): calculated C, 70.57; H, 5.92; found C, 70.25; H, 5.89

di-n-Nonyl 4-4-[4-[5-hexenyloxy)benzoyloxy)benzoyloxy)benzylidenemalonate (3):

A solution of 3,58 g (0.01 mole) 4-[4-(5-hexenyloxy)benzoyloxy]benzoylchloride in 40 ml dry toluene is added slowly during stirring at 313 K to a mixture of 4.6 g (0.01 mole) di-*n*-nonyl 4-hydroxybenzylidenemalonate (prepared according to[13]) and 1.5 g (0.015 mole) triethylamine in 20 ml dry toluene. The mixture is stirred for 10 hours at room temperature and for 1 hour at 323 K. After filtration of the hydrochloride the product is washed with water, 300 ml 5% sodium hydrogencarbonate and water again. After that the solution is dried on sodium sulphate and the toluene is evaporated under vaccum. The residue is recrystallized from ethanol.

Yield: 5.0 g (64%)
^{1}H-NMR(80 MHz, $CDCl_3$): δ=0.8 – 1.4 (m, 34H, 2 × $C_8\underline{H}_{17}$—CH_2—), 1.6–2.3 (several m, 6H, CH_2=CH—($C\underline{H}_2$)$_3$—CH_2—O—), 4.1 (t, 2H, CH_2=CH—(CH_2)$_3$—$C\underline{H}_2$—O—), 5.0 (t, 2H, $C\underline{H}_2$=CH—(CH_2)$_3$—CH_2—O—), 5.6–6.1 (m, 1H, CH_2=C$\underline{H}$—(CH_2)$_3$—CH_2—O—), 7.0–8.2 (several m, 12 H, Ar) 7.7 (s, 1H, —C$\underline{H}$=C)
Elemental analysis: $C_{48}H_{62}O_9$ (719.02g mol^{-1}): calculated c, 73.63; H, 7.98; found c, 73.48; H, 6.98

2-Cyanobenzyl 2,5-dihydroxybenzoate (4): A solution of 19.6 g (0.1 mol) 2-(brommethyl) benzonitrile in 100 ml dry acetone is added slowly to 15.4 g (0.1 mol) 2,5-dihydroxybenzoic acid, 10.1 g (0.1 mol)triethylamine and catalytic amounts of NaI in 100 ml dry acetone during stirring. After refluxing for 4 hours the mixture is put into 400 ml water, the precipitated product is filtered of and recrystallized from ethanol.

Yield: 21.5 g (80%) m.p. 452K
^{1}H–NMR (80 MHz, $CDCl_3$): δ=4.75 (s, 1H,—O$\underline{H}$), 5.6 (s, 2H, COO—C$\underline{H}_2$—Ar), 6.9–7.7 (several m, 7H, $\underline{Ar}$), 10.1 (s, 1H, $\underline{H}$O—)
Elemental analysis: $C_{15}H_{11}O_4N$ (269.26 g mol^{-1}): calculated C, 66.91; H, 4.12; N, 5.20; found C, 66.79; H, 4.06; N, 5.17

2-Cyanobenzyl 2-hydroxy-5-(4-octyloxybenzoyloxy)benzoate (5): A mixture of 13.45 g (0.05 mol) 4, 12.5 g (0.05 mol) 4-octyloxybenzoic acid, 11.3 g (0.055 mol) N, N-dicyclohexylcarbodiimide (DCC) and catalytic amounts of 4-N, N-dimethylaminopyridine (DMAP) in 300 ml dry methylene chloride is stirred for 48 hours. After filtration of the precipitated urea the solution is washed with water, sodium hydrogencarbonate (5% solution) and again with water. Then, it is dried on sodium sulphate and the solvent is evaporated. Recrystallization from ethanol yields the pure product.

Yield: 21.5 g (86%) m.p. 375 K
^{1}H-NMR (80 MHz, $CDCl_3$): δ=0.9 (m, 3H, $C\underline{H}_3$—) 1.2–1.4 (m, 12H, CH_3—($C\underline{H}_2$)$_6$—CH_2—O), 4.0 (t, 2H, O—$C\underline{H}_2$—(CH_2)$_6$—), 5.6 (s, 2H, COO—$C\underline{H}_2$—Ar), 6.8–8.2 (several m, 11H, $\underline{Ar}$), 10.4 (s, 1H,—O$\underline{H}$)
Elemental analysis: $C_{30}H_{31}O_6N$ (501.58 g mol^{-1}): calculated C, 71.84; H, 6.23; N, 2.76; found C, 71.68; H, 6.15; N, 2.76

2-Cyanobenzyl 2-[4-(5-hexenyloxy) benzoyloxy]-5-(4-octyloxybenzoyloxy)-benzoate (6): 4.8 g (0.02 mol) 4-(5-hexenyloxy) benzoyl chloride in 50 ml dry toluene is added

drop by drop to a mixture of 10 g (0.02 mol) of 5, 2.5 g (0.025 mol) triethylamine and catalytic amounts of DMAP in 300 ml dry toluene under stirring. After that, stirring is continued for 10 hours at room temperature and 1 hour at 323 K. The hydrochloride is filtered, the solution is washed with water, 300 ml 5% sodium hydrogencarbonate and water again. Then the solution is dried on sodium sulphate and the toluene is evaporated under vacuum. The substance is recrystallized from ethanol.

Yield: 10.5 g (0.016 mol)
^{1}H-NMR (200 MHz, $CDCl_3$): δ=0.8–0.9 (m, 3H, CH_3—), 1.2–2.2 (m, 18H, $(CH_2)_9$), 4.0 (t, 4H, —CH_2—O), 5.0 (t, 2H, CH_2=CH—), 5.4 (s, 2H, COO—CH_2—), 5.8 (m, 1H, CH_2=CH—), 6.8–8.2 (several m, 15 H, Ar)
Elemental analysis: $C_{43}H_{45}O_8N$ (703.83 g mol^{-1}): calculated C, 73.38; H, 6.44; N, 1.99; found C, 73.18; H, 6.44; N, 1.94

Hydrosilylation reaction

A mixture of 0.075 g (0.128 mmol) siloxane and 0.001 mol of the appropriate alkene or mixtures of alkenes is solved in 5 ml dry toluene. 40µl of the catalyst (0.05 M solution of $H_2PtCl_66H_2O$ in dry isopropanol) is added to the reaction mixture und mixture is heated at 373 K (normally for 24 h) until the Si–H absorption in the infrared spectrum (2160 cm^{-1}) is reduced to a residual level. The oligomer is purified by repeated precipitations with methanol until free from any detectable (TLC) concentration of side chain precursor. The pure oligomer is given over a short column of AI_2O_3, eluent is chloroform, to filter of residue of the catalyst. The pure oligomer is dried vacuo in the isotropic state.

^{1}H-NMR:
3L7 (200 MHz, $CDCl_3$): δ(ppm) = 0.08 (s, 6H, CH_3—Si—) 0.53–0.56 (m, 2H, Si—CH_2—), 0.80–0.86 (t, 6H, 2 × CH_3—), 1.14–1.32 (m, 30H, Si—CH_2—$(CH_2)_3$—CH_2—CH_2—O, 2 × CH_3— $(CH_2)_6$—CH_2—CH_2—O), 1.58–1.70 (m, 4H, 2 × COO—CH_2CH_2—), 1.76–1.83 (t, 2H, CH_2—CH_2—CH_2—O—), 3.97–4.04 (t, 2H, CH_2—CH_2—O—), 4.19–4.28 (t, 4H, COO–CH_2—CH_2—), 6.92–8.27 (several m, 12H, Ar), 7.70 (s, 1H, —CH=C)

6L7 (200 MHz, $CDCl_3$): δ (ppm) = 0.09 (s, 6H, CH_3—Si—) o.52–0.58 (m, 2H, Si—CH_2—), 0.84–0.90 (t, 3H, CH_3—), 1.22–1.52 (m, 16H, Si—CH_2—$(CH_2)_3$—CH_2—CH_2—O, CH_3—$(CH_2)_5$—CH_2—CH_2—O), 1.76–1.83 (t, 4H, 2 × CH_2—CH_2—CH_2—O—), 3.96–4.05 (t, 4H, 2 × CH_2—CH—O—), 5.35 (s, 2H, COO—CH_2—Ar), 6.84–8.12 (several m, 15H, Ar)

0.3: (500 MHz, $CDCl_3$): δ (ppm) = 0.09 (s, 8H, CH_3—Si—) 0.56 (m, 2H, Si—CH_2—), signals from 3: 0.84–0.88 (t, 6H, 2 × CH_3—), 1.24–1.46 (m, 30H, Si—CH_2—$(CH_2)_3$—CH_2—CH_2—O, 2 × CH_3—(—$(CH_2)_6$—CH_2—CH_2—O), 1.57–1.69 (m, 4H, 2 × COO—CH_2—CH_2—), 1.80–1.89 (t, 2H, CH_2—CH_2—CH_2—O—), 4.01–4.09 (m, 2H, CH_2—CH_2—O—), 4.23–4.24 (t, 4H, COO—CH_2—CH_2—), 6.92–8.27 (several m, 12H, Ar), 7.70 (s, 1H, —CH=C) signals from 6: 0.84–0.88 (t, 3H, CH_3—), 1.24–1.46 (m, 16H, Si—CH_2—$(CH_2)_3$—CH_2—CH_2—O, CH_3—$(CH_2)_5$—CH_2—CH_2—O), 1.80–1.89 (t, 4H, 2 × CH_2—CH_2—CH_2—O—), 4.01–4.09 (t, 4H, 2 × CH_2—CH_2—O—), 5.36 (s, 2H, COO—CH_2—Ar), 6.92–8.27 (several m, 15H, Ar)

signals from 3 and 6 are in mole ratio 7:3
0.4: (500 MHz, $CDCl_3$): δ (ppm) = 0.09 (s, 8H, CH_3—Si—) 0.56 (m, 2H, Si—CH_2—), signals from 3: 0.84–0.88 (t, 6H, 2 × CH_3—), 1.24–1.46 (m, 30H, Si—CH_2—$(CH_2)_3$—CH_2—CH_2—O, 2 × CH_3—$(CH_2)_6$—CH_2—CH_2—O), 1.57–1.68 (m, 4H, 2 × COO—CH_2—CH_2—), 1.80–1.89 (t, 2H, CH_2—$CH_2{}^{CH}{}_2$—O), 4.02–4.09 (m, 2H, CH_2—CH_2—O—), 4.23–4.24 (t, 4H, COO—CH_2—CH_2—), 6.87–8.25 (several m, 12H, Ar), 7.71 (s, 1H, —CH=C) signals from 6: 0.84–0.88 (t, 3H, CH_3—), 1.24–1.46 (m, 16H, Si—CH_2—$(CH_2)_3$—CH_2—CH_2—O, CH_3—$(CH_2)_5$—CH_2—CH_2–O), 1.80–1.89 (t, 4H, 2 × CH_2—CH_2—CH_2—O—), 4.02–4.09 (t, 4H, 2 × CH_2—CH_2—O—), 5.39 (s, 2H, COO—CH_2—Ar), 6.87–8.25 (several m, 15H, Ar)

signals from 3 and 6 are in mole ratio 3:2

0.3: (500 MHz, $CDCl_3$): δ (ppm) = 0.10 (s, 8H, CH_3—Si—) 0.57 (m, 2H, Si—CH_2—), signals from 3: 0.84–0.88 (t, 6H, 2 ×, CH_3—), 1.19–1.46 (m, 30H, Si—CH_2—$(CH_2)_3$—CH_2—CH_2—O, 2 × CH_3—$(CH_2)_6$—CH_2—CH_2—O), 1.66 (m, 4H, 2 × COO—CH_2—CH_2—), 1.80 (t, 2H, CH_2—CH_2—CH_2—O—), 4.02–4.09 (m, 2H, CH_2—CH_2—O—), 4.24 (t, 4H, COO—CH_2—CH_2—), 6.86–8.20 (several m, 12H, Ar), 7.70 (s, 1H, —CH=C)
signals from 6: 0.84–0.88 (t, 3H, CH_3—), 1.19–1.46 (m, 16H, Si—CH_2—$(CH_2)_3$—CH_2—CH_2—O, CH_3—$(CH_2)_5$—CH_2—CH_2—O), 1.80 (t, 4H, 2 × CH_2—CH_2—CH_2—O—), 4.02–4.09 (t, 4H, 2 × CH_2—CH_2—O—), 5.36 (s, 2H, COO—CH_2Ar), 6.86–8.20 (several m, 15H, Ar) signals from 3 and 6 are in mole ratio 3:7

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