Chapter 1. Polymeric Liquid crystals.

1.1. Polymeric Liquid crystals: general overview.

1.1.1 Liquid crystal (LC) a thermodynamic stable phase characterized by anisotropy of properties without the existence of a three-dimensional crystal lattice. Generally, LC is placed in the temperature range between the solid and isotropic liquid phase. Therefore, the term mesophase is often used as a synonym of liquid crystalline phase [I.1].

The basic characteristic of mesophase is the tendency of the molecules (mesogens) to orient themselves along a common axis, called the director (see Fig 1.1). The LC phase creation is more prominent for the substances where the molecules have a strong asymmetry either prolate or oblate. It this case the anisotropy of the properties can originate from the spatial restriction as a consequence of the impossibility to arrange the anisotropic molecules in isotropic manner to fulfill the requirements of the free energy minimization [I.2]. Most of the liquid crystals demonstrate a polymorphism, i.e. condition where several "subphases" are observed in the liquid crystalline state. These subphases are formed by changing of the orientational order degree in the sample either by imposing order in one or two dimensions, or by allowing the molecules to have a degree of translational motion. More detailed information about different mesophases and phase transitions can be found in Appendix I (A.I).

1.1.2 Order parameter

To describe the measure of the orientation order of the liquid crystal, in general case, the molecular anisotropy tensor, or order tensor is to be used. [A.I]. However, in the case of threefold or higher symmetry of the molecules shape, a single number is usually enough for the quantification of the orientation degree, which is called order parameter. It is traditionally defined as:

![Fig. 1.1 Liquid crystalline state of the substance: no long range order presents (opposite to the solid-state). The molecules axes have preferable orientation given by the local director N (opposite to the random orientation in isotropic liquid). In some subphases the LC exhibits an ordering of the molecules gravity centers (smectic LC).](image-url)
where $\theta$ is the angle between long molecular axis and local director, (see Fig 1.2) $P_2$ is the second order Legendre polynomial and brackets means the averaging in time, which occurs because of the thermal motion [AI, I.3]. In some cases, however, the ensemble averaging over all the molecules of the sample can be suggested when speaking about the order parameter or orientation degree. For most of mesophases both definitions, in principle, are equivalent.

\[
S = \left\langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right\rangle = \left\langle P_2(\theta) \right\rangle
\]  

(1.1)

1.1.3. Polymeric Liquid Crystal

Polymer liquid crystals (PLC) are a kind of macromolecular compounds, which combine the properties of polymers with those of liquid crystals. These systems show the anisotropic characteristic of the liquid crystals, and, in the same time, demonstrate a many of useful and versatile properties of polymers. The properties of the PLC mesophases can differ sufficiently from their analogs of the «classical» low molecular LC. In contrast to Low Molecular Liquid Crystals (LMLC) a number of PLC have no similarity to the classical liquids even in low ordered subphases and look like a solid glassy samples with melting temperature more than 100$^\circ$C. However, traditionally, the same terms are used to denote the similar states of the molecular ordering in both LMLC and PLC. In order to polymer molecules demonstrate the ordering properties, the anisotropically shaped rod-like or disk-like elements (called mesogenic unit) must present inside. In the same time, for creating the liquid crystalline state of the sample

\[
\text{Liquid Crystalline Main-Chain Polymer (LCMP)}
\]

\[
\text{Liquid Crystalline Side-Chain Polymer (LCSP)}
\]

Fig 1.3 Schematic representation of the polymeric liquid crystals with mesogenic units in main (left) and side-chain (right).
these units must be decoupled from each other by the flexible segment of certain length called \textit{spacer}. Additional factors providing the mesomorphic behavior of polymers include the certain polymerization degree, and regular alternation of rigid and flexible units along the main chain.

Depending on the location of the mesogenic moieties the PLC can be separated into \textit{main-chain} and \textit{side-chain}. The first ones have the mesogenic unit as a part of the main-chain of the polymer molecule and for the second the mesophase is formed by the anisotropic molecular segments of the side-chain (see \textbf{Fig 1.3}). The origins of the main-chain PLC theory and synthesizing can be found in the classical works of de Gennes [I.4] and Roviello at al.[I.5]. Because the subject of this work concerns the problems of orientation order of the side-chain polymer liquid crystals they will be considered in more details below.

\textbf{1.2 Liquid-Crystalline Side-chain polymers. (LCSP)}

The attempts of synthesizing of the LC polymers with the mesogenic units in side-chain were stimulated by the fast progress of low molecular LC investigations. It seemed to be very attractive to create the polymer systems, which combine in one material the unique properties of the low molecular LC and macromolecular compounds with their ability to create films, tissues and covers. However, the first try to solve this problem by the creation of the polymers with side-chain units directly connected to the main-chain was not quit successful [I.7, I.8]. Finally, it was found that the most convenient matrices for the synthesizing of the PLC with mesogenic moieties in side-chain are so called \textit{comb-like polymers}. The main feature of the structure of such a kind of macromolecules is the relatively long (usually aliphatic) side units connected directly to the \textit{backbone} chain (see \textbf{Fig 1.4a}). The general approach to creating of the macromolecular systems based on this kind of polymers shown on \textbf{Fig 1.4b,c}. Being developed by the different groups [I.8-I.10] it provides the possibility to synthesize the thermotropic LC polymers with the mesogenic units in side-chain.
The most important point of the method is the decoupling of the backbone and mesogenic unit in the side-chain from each other by the flexible spacer of methylene chain. This provides the necessary isolation of the backbone and mesogenic groups making possible their cooperation in the creation of the mesophase. The example of the spacer length importance for the mesogenic properties of the side-chain PLC will be discussed later on the particular examples. There are several possibilities of how the side-chain unit can be connected to the spacer. Fig 1.5 demonstrates the basic type of the rod-like mesogenic fragments, particularly are «end-on», «side-on» and «twin».

1.3. Phase transitions and orientational order in LCSP. The role of the macromolecular properties.

Independently on the particular structure of the LCSP, their macromolecules generally have the similar design, which includes the rigid side-chain units connected in some way to the main-chain backbone. It is assumed that the side-chain units define the mesogenic properties when the backbone is responsible for the polymeric qualities of the compound. If to take into account the interconnecting flexible spacers both in side- and main chain it is clear that the nature of this kind of objects is quite complicated. The influence of each component on the mesophase state of side-chain PLC will be considered shortly in following.

1.3.1 Backbone

Despite of the fact that mesogenic properties of the LCSP originate from the side-chain mesogenic unit, the polymer «skeleton» of main chain defines the important features of
mesophase forming. Especially important factor is the degree of the polymerization (DP) i.e. the average number of the monomer blocks in the main chain. For instance, it was established in a number of experiments for the side-chain polysiloxanes that the temperatures of the subphases transitions are strongly affected by the DP in the regime of oligomers (i.e DP<10) independently on the spacer length. In the same time for 10<DP<100 the transitions temperature changes much slowly achieving a plateau for DP>100 value (see Fig 1.6).

![Phase transition temperature for polysiloxane M6](image)

**Fig 1.6.** Phase transition temperature of the polysiloxanes samples as a function of the polymerization degree.

![Polysiloxane with cyanobiphenil unit (PSCB) and low molecular cyanobiphenil LC (LMCB) phase transitions temperatures](image)

**Fig 1.7** Dependence of the phase transition temperatures for the polysiloxane LCSP with cyanobiphenil mesogenic units and its low-molecular analog. The temperature range of the mesophase existence for LCSP is sufficiently broader than for low-molecular CB LC.
Generally, the presence of the main-chain backbone leads to much higher thermostability of the mesophase in comparison to the low-molecular LC. This can be seen when comparing the transition temperatures of the LC of alkocyanbiphenyl type with LCSP having the same mesogenic groups (Fig 1.7) in side chain.

1.3.2. Spacer

Spacer or flexible bridge, which connects the side-chain with the backbone, has several functions important for the LC properties. The first one is providing of the independent behavior for mesogenic units that often define the mesophase forming. As it is seen from Table 1, the decrease of the spacer length leads to the narrowing of the temperature range of mesophase existence. Another important function is the plastification influence of the spacer. The increasing of the spacer length leads to decrease of the glassy state transition temperature for the LCSP (Table 1.1). In addition, the number of the methylene units in spacer quite often can define the ability of a polymer to form more than one subphase. Usually, for the other equal parameters, by the increasing the spacer length it is possible to turn from the nematic to smectic state.

1.3.3. Mesogenic unit.

Obviously, the side-chain mesogenic unit has the strongest influence on the character of mesophase formed by the particular polymer. For instance, the nematic type of LC structure is characteristic for the homopolymers, which have the short end-groups (CH3, OCH3 and CN) with 2..6 methylene groups in spacer.
Additionally, the forming of the nematic phase can be promoted by the including of a side substitutes into the mesogenic unit. This can be clearly seen by comparison two different series of the polysiloxanes:

All the polymers of type I starting from the n=3 form only the smectic phase, while in the LCSP of series II the nematic phase can be observed at n=5,6 at clearance temperature $T_N=40-60^\circ$C. The further increase of the spacer length (n=7-11) again leads to the smectic ordering $T_S=90^\circ$ for n=7 and $T_S=130$ for n=11. More examples of the phase transition temperature variation depending on the structure of the mesogenic unit can be found in [I.11].

1.3.4. Mutual orientation of the backbone and the mesogenic units

The statistical conformation of the isotropic chain polymers is not consistent with the mesogenic structure [I.2]. This can be confirmed on the example of the mixture of low-molecular LC with linear chain polymers where even if the isotropic phases are completely miscible, the phase separation occurs when the low-molecular system turns to the nematic state. In the case of LCSP no phase separation is possible. That way, the trend of the main chain to form the random coils will conflict with the liquid crystalline ordering of the side-groups. This will makes the side chain to adopt the anisotropic conformation according to the LC phase structure. Generally, it leads to the different orientation character of the mesogenic groups and the backbone that was confirmed in the experiments. This difference seems to be determined by the number of structural features, including the length of the spacer and the flexibility of the main chain. The relation between these two parameters defines the correlation of the side- and main chain behavior under influence of the orientation factors. It is necessary to notice, however, that the effect of the mechanical field (deformation) on the orientation of LCSP is quit different from the
magnetic or electric field. In the later case the orientation more selectively affecting the side-chain, rather than main chain and, that way, a higher orientation degree with monodomain structure chain be achieved. In more details the problem of the orientational order in main and side-chain as well will be considered in the next section.


The conformation and ordering of the backbone is the question of great importance for characterization of the structural and dynamical properties of LCSP. The structure of main chain influences both on mechanical and thermodynamic properties, such as viscosity, strength, elastic modules, transition temperatures. During a long time the question of the conformation of the main chain was not discussed in literature. A priori, it was suggested that in the case of the smectic LCSP the main chain is located between the layers of mesogenic units. For nematic state a one-dimensional order of mesogenic groups with disordered conformation of main-chain coils was expected. In the first time the preposition about the anisotropic ordering of the main chain was discussed in [I.12] when studying the orientation of the polysiloxane LCSP by the external magnetic field. Using the neutron scattering for investigation of selectively deuterated side-chain polysiloxanes oriented in the magnetic field, the first information about the conformation of the macromolecules of the side-chain polymers in blocks was obtained.[I.13,14] There are some theoretical approaches to the problem of main-chain conformation. Vasilenko at al [I.15] have used the lattice model. It is based, however, on athermal parameters and can not give the comprehensive explanation of the experimental data, which include a number of temperature dependent results. Another theory developed by Wang and Warner uses the model of cross-coupling between rod-like side-chain and flexible main chain to explain the different structures of the nematic phase in LCSP. The structures are classified by the order parameter of the mesogenic units \( S_A \) and backbone \( S_B \). When \( S_A > 0, S_B < 0 \) the shape of the backbone supposed to be the oblate spheroid and the phase is called \( N_I \). The phases with prolate conformation of main-chain with \( S_A < 0, S_B > 0 \), and \( S_A, S_B > 0 \) are called \( N_{II} \) and \( N_{III} \) respectively. The segment-segment, segment-mesogen, and mesogen-mesogen interactions in this case are described using the Maier-Saupe theory potentials. Considering the conventional LCSP (with poly(meth)acrylate or polysiloxane main-chain) where in the sense of Maier-Saupe theory the anisotropy of polarizability of the backbone segments is negligible as compared to the mesogens it might be concluded that all mentioned kinds of LCSP have to have the same nematic phase \( N \), that is in contrast to the experimental data. On the other hand, the Warner’s theory gives no explanation
about the influence of the spacer length on the orientational properties of the polysiloxanes LCSP. It can be seen on the Fig 1.8 in the case of the polymer M4 (spacer length m=4) the mesogenic units are aligned parallel to the segments of main chain (phase \( N_{III} \)), and whole sample is optically uniaxial. The opposite picture is observed for the samples of M3 and M6 (m=3, and 6 respectively). The mesogenic units are oriented in the direction perpendicular to the main chain and the sample is biaxial (phase \( N_{I} \)). The cross-coupling model predicts only the perpendicular orientation of the main- and side-chain in both cases for the realistic values of the volume fraction of mesogens.

1.4.1. Evaluation of the backbone anisotropy parameters using SANS.

A number of experimental investigations of the backbone conformations were done using the small angle neutron scattering method (SANS) [I.16] on the samples of polysiloxane and polymethacrylate series (Fig 1.9). The samples were mixed from deuterated and hydrogenated molecules to provide the necessary SANS neutron scattering contrast of the molecules to the surroundings. The mesogen induced backbone anisotropy can be described in the terms of the inertia radii \( R_{\parallel} \) and \( R_{\perp} \) parallel and perpendicular to the local director. The results obtained for deuterated polymethacrylates and polysiloxanes samples exhibit the obvious anisotropy of the macromolecules in mesogenic phase. As it can be seen from the data in the Table 1.2 for the polymethacrylates sample in nematic phase the ratio \( R_{\parallel} > R_{\perp} \) is valid, but the anisotropy factor \( \eta = R_{\parallel}/R_{\perp} \) is quit low (\( \eta = 1.1 \)). Significantly larger anisotropy can be observed in smectic phase. This means the anisotropic conformation of the main chain in the direction perpendicular to the local
director. Based on the results of SANS studies the model of the macromolecular chain allocation within one smectic layer with multiple crossing was proposed [I.14](see Fig 1.10a).

\[
\begin{align*}
\sim\text{CD}_2 & \sim \text{C(CD)}_3 \sim \text{O} \sim \\
& | \\
\text{OCO} & \sim (\text{CH}_2)_6 \sim \text{O} \sim \text{CN} \\
\sim\text{O} & \sim \text{Si(CH)}_3 \sim \text{O} \sim \\
& | \\
\text{CD}_2 & \sim (\text{CDH}) \sim \text{CD}_2 \sim \text{O} \sim \text{CN}
\end{align*}
\]

Fig 1.9 Polymethacrylate (top)(PMA) and polysiloxane(bottom)(PS) samples studied by SANS in [I.13] to determine the gyration radii of the macromolecules. The partial deuteration of both main chain (in the case of PMA) and spacer were done to provide the contrast for the neutron scattering. The model of the smectic phase ordering was build basing on the data analysis (see text).

<table>
<thead>
<tr>
<th>PMA</th>
<th>Phase transition temperature</th>
<th>PS</th>
<th>Phase transition temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>C45→50S110→N116→I</td>
<td>Tg45→36S146→I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>680</td>
<td>63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R_g</td>
<td>106</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R_l</td>
<td>59±5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R_⊥</td>
<td>65±5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R_⊥/R_g</td>
<td>1.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R_g</td>
<td>22±3</td>
<td>9.9±0.2</td>
<td></td>
</tr>
<tr>
<td>R_⊥</td>
<td>65±5</td>
<td>15.8±0.2</td>
<td></td>
</tr>
<tr>
<td>R_⊥/R_g</td>
<td>4.0±1</td>
<td>1.6</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.2 Gyration radii obtained by SANS for the polymethacrylate (left) and polysiloxane (right) samples (Fig 1.9)

1.4.2. Bilayer model

Another model of the conformation of the backbone in LCSP was proposed in [I.25] with account of data from the work [I.14]. The basic idea of this model introduces the so-called anisotropy of local rigidity approach with consideration of the smectic phase like a state with microphase separation of the mesogenic groups and main chains. In this case the backbone is pushed out of the smectic layer and creates the intermediate layer (Fig 1.10b). Contrast to the layer crossing model, [I.14] according to this approach, the transition of the backbone through the smectic layers occurs very seldom. The part of the main chain, which tunnels through the mesogenic unit layers (called “tunneling segment”) is located perpendicular to the smectic layer creating a small defect in it. The details of this defect are not known, but the SANS allows one to estimate its density. That way, all the polymeric chain is divided into the separate two-
dimensional coils allocated into the smectic planes. However, despite of the sufficient progress, which gives the application of SANS for the studying of the molecular orientation of LCSP, still there are some problems arises from the necessity of the sample deuteration for the purpose of providing a better contrast. Particularly, this takes place in the polysiloxanes because they are deuterated in different positions in the side groups (see Fig 1.9).

That way, the shape of the molecule obtained by the neutron scattering is not necessarily to be a backbones one. The way for making corrections is shown in [I.17], where the apparent molecular shape was estimated for different label distance to the backbone and extrapolated to zero distance. Alternative possibility is given by Noirez et al. [I.18]. Here, another possible problem was also studied: segregation into deuterated and hydrogenated phases could occur in some cases. The sufficient difficulties of both synthesizing the deuterium-labeled substances and neutron scattering experiments, require looking for alternative methods of main-chain conformation studies. X-rays are effective for the smectic phase investigation [I.19]. Although in nematic, the information about main chain obtained from diffraction pattern is relatively poor. $^2$H NMR experiments show that in a particular polyacrelate the main chain and also spacer are parallel to the mesogenic unit side groups, while corresponding polymethacrylate demonstrates a perpendicular structure [I.20]. In the same time, SANS experiment demonstrates the oblate backbone conformation [I.18]. This contradiction can arise from the different length scale to which NMR and SANS are sensitive (will be discussed later) and also from the mentioned above problem concerned with molecules deuteration. However, the polysiloxanes give the additional possibilities for the backbone conformation investigation by using the $^{29}$Si NMR. This method promises to bring good results because the information about the molecular order is provided by

![Fig 1.10.a,b](image-url) The models of the backbone and mesogenic units arrangement for the smectic phase basing on the SANS experiments. (a) - the model proposed in [I.14], - the backbone is placed within one smectic layer with multiple crossing. (b) – microphase separation model [I.26]. The backbone is pushed out of the smectic layers of mesogenic units and creates the own intermediate layer. The tunneling of the backbone through the side-chain layers occurs rather seldom.
the silicon atoms, which position in main chain is unambiguous. No special preparation of the samples is required in this case and the problems concerned with the sample deuteration needed for SANS and $^2$H NMR can be avoided. That way, in our work the polysiloxanes and $^{29}$Si NMR were chosen to find a reliable method of the LCSP main chain conformation study.

1.5 Orientation of the side and main chain in side-chain liquid crystalline polysiloxanes

1.5.1 Chemical constitution of the polysiloxanes. Samples synthesizing.

Generally, the method of the polysiloxane-based LCSP synthesis bases on the reaction of the polysiloxanes with the mesogenic monomers of olefin series. The sufficient advantage of this method is that the samples with different polymerization degree can be obtained. Also, the samples with various mesogenic segment structure and desirable spacer length can be obtained. The main stages of the synthesis are shown on Fig 1.11. In our work the samples with spacer length $m=4$ and $m=6$ were used, which will be in the future denoted as $M_4$ and $M_6$ respectively.

1.5.2 Physical properties and phase transitions.

The basic thermodynamic properties of the polysiloxane samples chosen for the main-chain conformation investigation measured by DSC are shown in Table 1.3. It should be noticed that the M4 sample has narrower temperature region of the mesophase existence as compared to
M6, but the difference is not too significant (about 5%). However, the nematic to isotropic liquid (NI) transition enthalpy $\Delta H_{NI}$ differs on more than 20%. More important is the difference of the heat capacity for the glassy state transition. For the M6 sample it exceeds the $\Delta C_p$ of the M4 on more that 35%. This can be easily understood if to look at the DSC diagram, which shows the existence of two different mesophase for M6 sample (smectic-C and nematic $T_g$274±4→SC308±4→N377±2→I) when M4 sample demonstrates only nematic phase ($T_g$280±4→N368±4→I). The molar mass distribution parameter $U=M_w/M_n-1$ (where $M_n$ is number averaged and $M_w$ is weight averaged value of molar mass) obtained by the light scattering (LS) shows that the polymerization degree in M6 sample is sufficiently more homogeneous ($U_{M6}=1.16$) than in the M4 ($U_{M4}=1.57$). The average polymerization degree $<p_n>$ of the molecules estimated from the $M_n$ gives also the higher absolute value for M6 ($<p_n>=97±5$) than for M4($<p_n>=87±5$).

<table>
<thead>
<tr>
<th>PS</th>
<th>$T_g$ [K]</th>
<th>$\Delta C_p$ [J/gK]</th>
<th>$T_{NI}$ [K]</th>
<th>$\Delta H_{NI}$ [J/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>M3</td>
<td>287±4</td>
<td>0.4±0.1</td>
<td>347±4</td>
<td>1.2±0.4</td>
</tr>
<tr>
<td>M4</td>
<td>280±4</td>
<td>0.32±0.04</td>
<td>368±4</td>
<td>2.0±0.3</td>
</tr>
<tr>
<td>M6</td>
<td>274±4</td>
<td>0.5±0.2</td>
<td>377±2</td>
<td>2.5±0.5</td>
</tr>
</tbody>
</table>

**1.5.3 Liquid crystalline orientational properties of the polysiloxane samples.**

As it was mentioned, the liquid crystalline properties of the LCSP are mainly connected with the anisotropy of the side-chain segments ordering due to their rod-like shape. However, the macroscopic orientation and forming poly- or monodomain LC (see A.I) usually are defined by the external factors, such as electric or magnetic field. Opposite to the case of low-molecular liquid crystals, the homogeneous orientation of the polymers is not always possible even in nematic state. Therefore, the task of separation of the orientation effects on macro and micro level is important. One of the approaches to the macroscopic orientation studying is based on the estimation of the parameters of the local director orientation distribution obtained from analysis of the $^1$H NMR spectrum [I.21-22]. The orientation distribution of local directors can be characterized by the macroscopic order parameter $S_M=<P_{2M}>$ or so-called orientation degree defined in a manner similar to the microscopic order parameter $S$ (Eqn. 1.1, for more details see A1.5-8) Generally, for LCSP the procedure of the sample macroscopic orientation is the same as for low-molecular liquid crystals. The sample is to be heated to turn into the isotropic state, and then cooled down to the mesophase in presence of the external magnetic field, which provides
the preferable orientation direction for the molecules over the whole sample. However, the specific properties of the polymer samples lead to the strong dependence of the orientation degree $S_M$ from (i) the field strength and (ii) kinetics of the cooling down process. The order parameter in this case can be different for various atomic positions. The selective order parameter estimation for different atomic positions in side-chain polysiloxanes using the $^{13}$C NMR is described in [II.23]. Discussing the questions concerning with $^2$H NMR studying of the LCSP it is necessary to mention the results obtained in [I.24]. The partial deuteration of the methylene groups and mesogenic units allows estimating the order parameters of the rigid and flexible parts of the side-chains. Binding the mesogenic units with polymer backbone has insignificant influence on the order parameter of the mesogenic units. However, the order parameter of the aliphatic chain decreases by the factor of 2 demonstrating the strong mutual perturbation influence of the of the polymer chain and mesogenic segments. Obviously, the orientation of the LCSP in the magnetic field is caused by the anisotropy of the magnetic susceptibility $\Delta \chi$. For the polysiloxane samples M4 and M6 it was in the first time measured in [I.22]. The coincidence of the $\Delta \chi$ values for both samples ($\Delta \chi = (1.5 \pm 0.5) \cdot 10^7$ SGSE/g] with known susceptibility values of the analogous low-molecular LC shows some similarity of the structure of LCSP and low-molecular nematics. Therefore, when studying the orientational properties of the LCSP, the question of the mutual influence of the mesogenic units reorientation by the external fields and main chain adopting to the new molecular arrangement becomes quit interesting and important. The first data on elastic constants determination of the polysiloxanes LCSP were obtained in [I.22]. The authors estimated the «splay», «bend», «twist» and elastic deformation coefficient ($K_{11}$, $K_{22}$, and $K_{33}$) (Fig 1.12) and their temperature dependence for different samples including M4 and M6 and compared this data with one obtained for low-molecular analogous. The experimental results show that the reducing of spacer length from 6 to 4 units does not make a significant influence on the $K_{11}$ coefficient but changes strongly $K_{33}$ and therefore $K_{11}/K_{33}$ ratio. This can be treated like a confirmation of the backbone contribution to the elastic properties of the side-chain polymer LC phase. However, there was not found any significant influence of the main chain length (polymerization degree) on the «twist» elastic constant $K_{22}$. In general, basing on the experimental data obtained for the polysiloxane LCSP it

$\text{«Twist» div } \vec{N} = 0 \quad \text{«Splay» ro} \vec{t} \vec{N} \parallel \vec{N} \quad \text{«Bend» ro} \vec{t} \vec{N} \perp \vec{N}$

Fig. 1.12 Schematic representation of the viscoelastic deformations in the nematic LC.
should be noticed that there can not be done any unambiguous conclusion about the influence of the backbone conformation on the elastic and reorientation properties of the LC phase.

1.5.4. Relation between SANS and NMR results of the backbone conformation studies in polysiloxanes.

As it was mentioned above, the conclusions, which could be done concerning the mutual orientation of the main and side-chain in polysiloxanes using the data obtained by different methods are not unambiguous. The extensive investigation of the polysiloxane samples M4 and M6 with the SANS method was done by Siebert in [I.24]. The gyration radii $R_\parallel$ and $R_\perp$ were determined for different temperatures below the isotropic-to-nematic state transition. Fig 1.13 demonstrates the variation of the parameter $\eta=R_\parallel/R_\perp$ with the temperature for the M4 and M6 samples respectively. The obvious conclusion from these data is that for the M4 sample a prolate shape of the molecule is characteristic in the nematic phase for the temperatures below $T_{NI}$ approximately on 10K (where $\eta$ turns from the values $\eta>1$ to $\eta<1$). In the same time for the M6 sample $\eta$ goes down continuously with the temperature starting from the value $\eta=0.63$ in nematic state and decreasing by nearly the factor of 2 in smectic phase. However, the information about the shape of the polysiloxane LCSP molecules obtained by SANS does not allow one making an undisputable suggestion about the orientation of the main-chain there. Moreover, the length scales to which this method is sensitive does not allow to estimate the degree of the backbone orientation and to compare it with the orientation of the mesogenic units. As it was remarked in section 1.2 the information about the orientation properties of the backbone can be also obtained by the NMR. Because the NMR spectroscopy is sensitive to the interactions on the length scale of the chemical bonds, the orientation of the individual segments
of the polysiloxane LCSP main chain can be, in principle, determined using the NMR spectrum of $^{29}$Si nuclei. Using the angular dependence of the $^{29}$Si NMR spectra the orientation degree of the backbone molecular segments in different polysiloxane samples was estimated in the work of Dr. G. Hempel and colleagues [I.25]. In details the theoretical and practical aspects of the method will be described in the next chapter. Here, it should be mentioned that the main result of the work is the issue that for the M4 sample the orientation degree of the main chain segment with respect to local director has positive value, $<P_2>_S=0.18$ that means parallel orientation of the main-chain and mesogenic units. In contrast, the orientation degree for the M6 sample is negative $<P_2>_S= -0.23\pm0.02$ i.e. the segments of the backbone are oriented preferably orthogonal to the side-chain. That way, the NMR measurements in this case are in qualitative agreement with the SANS data. However, the situation when the prolate shape of the molecule (determined by SANS) corresponds to the perpendicular orientation of the backbone with respect to the mesogenic units preferable direction (found by the $^{29}$Si NMR,) can also take place for the polysiloxane LCSP [I.26]. As it was mentioned already, such a strong contradiction can occur because of the different sensitivity length scales belonging to these methods (NMR: at maximum size of the monomer unit, SANS: size of a macromolecule). **Fig 1.14** demonstrates one of the possible examples of such a backbone conformation. The largest part of the main chain can be compressed between mesogenic layers perpendicular to the local director even if the average shape of the molecule is prolate.

The NMR methods are able to monitor directly the tiny details of the molecular arrangements with possibility to quantify the distribution in the orientation of the backbone individual segments. However, the features of the polysiloxanes structure make difficulties for extraction of the information about molecular ordering of the main-chain directly from NMR spectra. The detailed description of these problems will be done in the next chapter. That way, the task of polysiloxane LCSP backbone conformation investigation requires the development of special $^{29}$Si NMR techniques and data interpretation methods. The solving of these problems was chosen to be the main subject of the present work.

**Fig 1.14** Sketch of the possible example of the backbone arrangement. The most part of the molecular segments of the main chain is oriented perpendicular to the mesogenic units, when the averaged shape of the molecule is prolate.