The peculiarity of side-chain liquid crystalline polymers with mesogenic units attached directly in a side-on mode

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The peculiarity of a series of side-chain liquid crystalline polymers with mesogenic units attached directly in a side-on mode was studied by using nuclear magnetic resonance, wide-angle X-ray diffraction, polarizing microscopy and molecular simulation techniques. It was found that in special cases molecules of side-chain liquid crystalline polymers may become rather rigid as a whole and take the more extended conformation, like a rod with the main chain approximately parallel to the rod axis. The side-chain mesogens are packed around the main chain with their axes almost perpendicular to the main chain. These side-chain polymers may exhibit behaviour similar to that of main-chain polymers. The effect of interaction between main-chain and side-chain mesogens on the mesophase formation of side-chain polymers and the influence of mesogen location in molecules on the behaviour of liquid crystalline polymers are discussed.

(Keywords: side-chain mesogens; liquid crystalline polymer; molecular simulation)

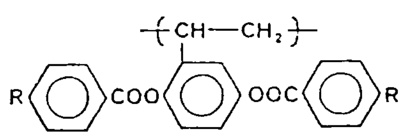
INTRODUCTION

Liquid crystalline polymers are usually divided into two types, main-chain and side-chain polymers, according to the structural characteristics of their molecules, i.e. whether the mesogenic units are located in the backbone or in the side chains of the molecules. A lot of work has been done in recent years to study the structure and properties of these polymers. Results indicate that the behaviour of main-chain liquid crystalline polymers is quite different from that of side-chain polymers. Molecules of main-chain polymers are usually rather rigid and take extended conformations, while the side-chain molecules are flexible coils. Main-chain liquid crystalline polymers may exhibit thermotropic or lyotropic behaviour, or both, but usually only thermotropic liquid crystals are reported for side-chain polymers. Banded texture is common for main-chain polymers in oriented specimens, but is not observed for side-chain polymers. The main-chain polymers are considered to be possible structural materials, while the side-chain polymers find applications in the field of functional materials.

Molecules of side-chain polymers usually have a flexible main chain with mesogenic units longitudinally attached to it. In order to reduce the interaction between the main chain and the mesogenic units, flexible spacers are usually introduced between them. It was evidenced in many cases that the decoupling effect of the flexible spacers is very important for liquid crystal formation of side-chain polymers. Recently, a new class of mesogenic side-chain polymers has been synthesized. The molecules of these polymers have mesogenic units laterally attached to the backbone through or without a flexible spacer[1-6]. It is thought that the two types of connection between the rigid mesogens and the flexible main chains may have very different influences on the molecular conformation and also on their properties. In this work the peculiarity of some side-chain liquid crystalline polymers with mesogenic units attached directly to the backbone in a side-on mode was investigated.

EXPERIMENTAL

The side-chain liquid crystalline polymers used in this work have the following general structure, where the end groups of the mesogens, R, are H, C_2H_5 or OCH_3.



The apparent average molecular weight of the samples, determined by gel permeation chromatography with tetrahydrofuran as the solvent, is given in *Table 1*. The synthesis of the samples has been described elsewhere[5]. Oriented specimens were prepared by shearing the polymer samples in their mesomorphic state between two glass slides at about 280°C and subsequent quenching on metal blocks to room temperature.

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Table 1 The apparent molecular weight of S samples

Sample	R	$M_n \times 10^{-4}$	M_w/M_n
S(H)	H	5.4	1.9
S(E)	C_2H_5	6.8	2.5
S(OM)	OCH_3	2.5	2.1

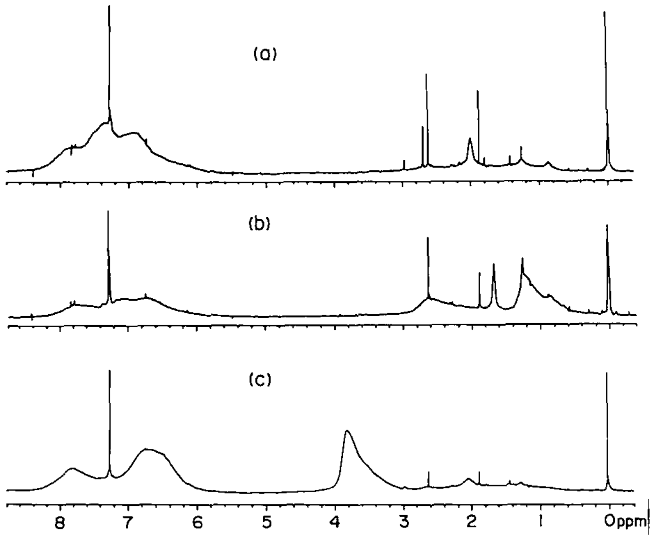


Figure 1 ^1H n.m.r. spectra of side-chain polymers: (a) S(H); (b) S(E); (c) S(OM)

^1H nuclear magnetic resonance (n.m.r.) spectra were recorded on a Varian XL200 FT spectrometer with proton frequency of 200 MHz, acquisition time 3-7 s and pulse width 13 μs. ^{13}C n.m.r. spectra were recorded on the same spectrometer operating at 50.3 MHz; broad band noise decoupling was used. Delay time was 5 s between pulses and 10 000 scans were required. Attached proton test (APT) spectra were obtained with the same instrument. Both the acquisition time and delay time were 1 s. Measurements were performed at room temperature for polymer samples in $CDCl_3$ solutions of concentration 10% (w/v).

The Ni-filtered CuKα radiation (40 kV, 150 mA) was used for wide angle X-ray diffraction (WAXD) measurements, and the angular dependence of diffraction was recorded on a Rigaku automatic X-ray diffractometer of type D/max-γA. Diffraction patterns were also recorded on flat films with pinhole collimation. In order to get high diffraction intensity, about 10 pieces of oriented film specimens were stacked together with their shearing directions parallel to each other.

RESULTS AND DISCUSSION

It is of great interest to investigate the rigidity of these side-chain polymers having very bulky and rigid mesogens attached directly to the backbone. N.m.r. is a useful technique in examining molecular dynamics in solids and fluids. Studies of isolated macromolecules in solution are better able to elucidate the pecularities of individual molecules free from intermolecular interactions. The 200 MHz ^1H n.m.r. spectra of the S-series polymers are given in *Figure 1*, and the relative intensity and assignment of peaks are listed in *Table 2*. The relative intensity data are determined by assuming that the value for peaks of aromatic protons equals the number of these atoms in the repeating unit of the polymer chain.

Table 2 Relative intensity and assignment of peaks in ^1H n.m.r. spectra of S samples

Chemical shift (ppm)	Relative intensity			Assignment
	S(OM)	S(H)	S(E)	
6.0–8.4	11	13	11	Benzene ring
3.0–4.0	6.8	–	–	$-OCH_3$
2.0–2.8	–	–	4.0	$-CH_2$
1.6–2.1	1.8	1.2	1.5	–
0.6–1.4	–	–	6.2	$-CH_3$

From comparison of the spectra given in this figure and also from the general experience of n.m.r. spectrum assignment, it is clear that the region of the spectra downfield from $\delta = 5.6$ to $\delta = 8.4$ ppm corresponds to the aromatic protons of the pendent mesogens having 13 aromatic protons for S(H) and 11 for the others, respectively. The peak at 3.81 ppm with a shoulder at the upfield side for sample S(OM) could be attributed to the end methyl groups of the mesogens. In the case of sample S(E), the methyl and methylene protons at the ends of the mesogens give their n.m.r. response in the region of 0.6–1.4 ppm and 2.0–3.2 ppm, respectively. The values of their relative intensity are consistent with the composition of molecules in each case. In these spectra there also appear some narrow lines including the peak at 7.3 ppm due to the $CDCl_3$ solvent. However, these lines cannot be ascribed to the S(R) polymers; they probably originate from some impurities remaining during or after polymerization and purification processes.

One of the general characteristics of these ^1H n.m.r. spectra is the obvious peak broadening phenomenon. The peaks are very broad, about 100–120 Hz in half-height width, as compared to those of the conventional main-chain[7] and side-chain[8] liquid crystalline polymers in solution, which usually have an average linewidth around 10 Hz, as can be understood by comparing *Figures 1* and *2*. The n.m.r. line-broadening phenomenon has also been reported for some polymers in their solution system, such as poly(γ-benzyl-L-glutamate)[9], nuclear acid, polyisocyanates[10] and poly(*N*-vinylcarbazole)[11,12], and these broadenings were explained in relation to the limited mobility and rigidity of polymer chains or segments within them. Besides, we were not able to find out the n.m.r. response of the main-chain protons in the present spectra. All the three samples have a small peak in a region around $\delta = 2.0$ ppm, where the methine or methylene proton peaks might be in usual cases. However, they could hardly be assigned to the main-chain protons. The position of these peaks changes from sample to sample, although it is expected that the influence of substitutions at the ends of the mesogens on the main-chain protons is very small or negligible due to the large distance between them. Besides, the relative intensity of these peaks is not consistent with the number of main-chain protons. The relative intensity of these peaks is too low. This means that the response of main-chain protons is very depressed or even disappears in the n.m.r. spectra.

Figure 3a shows the proton-decoupled ^{13}C n.m.r. spectrum of the sample S(OM). The assignment of the

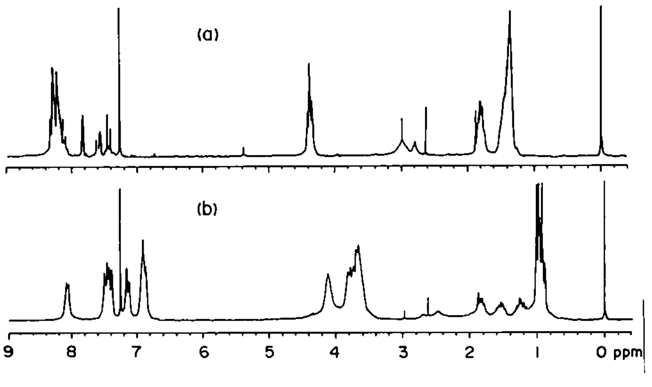


Figure 2 ^{1}H n.m.r. spectra of conventional main-chain (a) and side-chain (b) polymers

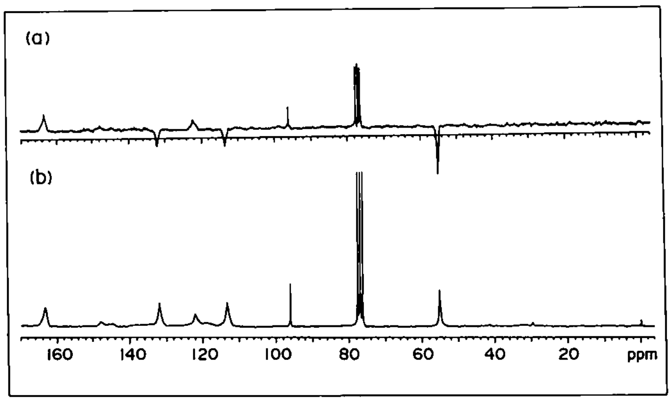


Figure 3 ^{13}C n.m.r. (a) proton decoupled and (b) APT spectra of S(OM)

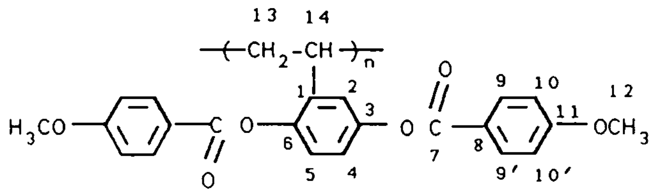
spectrum is based on the study of a similar mesogenic moiety, 1,4-bis(4-heptyloxybenzoylozy)-benzene (HBB)[13]. By combining the useful information from the APT spectrum (*Figure 3b*) of S(OM), the ^{13}C resonance of this sample could be interpreted unambiguously as presented in *Table 3*. Also given in the table are the calculated values of peak positions of different carbons determined by the addition rule. The chemical shift of 128.5 ppm was used as a standard value of benzene carbons. The additional shift for each carbon due to intramolecular interaction was obtained from the results of molecules $RO–C_6H_4COOC_6H_5$, given in Sadtler ^{13}C Standard Spectra Data. As in the spectra, the carbon resonance lines for the side chains of S(OM) are much broader than the ^{13}C lines of the model compound HBB. It should be noted that these broad peaks are only the response of carbons of the two side benzene rings and the end groups of the mesogens. N.m.r. peaks for carbons of the central benzene ring are even broader or weakened, and only a very slight trace could be detected at their likely positions. As for the main-chain carbons, they are supposed to have their response at about 40–47 ppm, but in the present case no detectable signal could be observed.

The n.m.r. peak broadening and weakening effects may result from the very limited mobility of molecules or segments or groups of molecules. These effects are extremely important for solids where the nuclei are almost fixed in position. For polymers dissolved in a mobile solvent, the line broadening is controlled by the rigidity of the molecules. In the case of conventional flexible macromolecules in solutions, these effects could be minimized or effectively erased. So the line broadening of polymers in solution may reflect the rigidity of molecules.

Table 3 The assignment of the ^{13}C n.m.r. spectrum of S(OM)

Carbon atom number[a]	Chemical shift (ppm)	
	Measured	Calculated
1	138	142
2	119.5	119.5
3	145	145.5
4	121	121.5
5	119	119
6	148	147.4
7	163.3	163
8	122	130
9,9′	132	129.1
10,10′	113.4	113.8
11	163.2	169.2
12	55.3	55.3
13,14	–	40–47[b]

[a]



[b] Data for main-chain carbons of polystyrene

Typical experimental data exhibiting the influence of molecular rigidity on n.m.r. spectra can be found in studies of polypeptides. It was reported that during the transition from coil to α-helix, the n.m.r. peaks of poly-γ-benzyl-L-glutamate[9] became very broad and in extreme cases no spectrum was evident at all. Our results, from both ^{1}H and ^{13}C n.m.r. spectra, may indicate that the mobility of the molecules should be extremely limited and the rotation around the main-chain bonds, and also the bond connecting the main chain and the central benzene ring of the side-chain mesogens, is severely hindered. This implies that the side-chain polymer molecules may become rather rigid as a whole, even in the solution state, owing to the laterally attached bulky and rigid mesogens without flexible spacers.

Evidence of molecular rigidity of these side-chain polymers has also been obtained in morphological studies of these samples in the oriented state[14]. *Figure 4* shows the polarizing micrograph of an oriented S(OM) film specimen obtained by shearing in the mesomorphic state. The shear direction here is vertical. Typical banded texture with width around 1 μm was observed. Banded texture has been found to be a common phenomenon for main-chain liquid crystalline polymers, but never for side-chain polymers with mesogens fixed end-on. It is considered that the molecules of main-chain polymers are rather rigid and take extended conformation. They are packed in parallel in the form of fibrils under shear. The formation of banded texture after shear cessation is the result of a zigzag rearrangement of the fibrils as a whole under crushing along the orientation direction. This means that the high stability of ordering of parallel

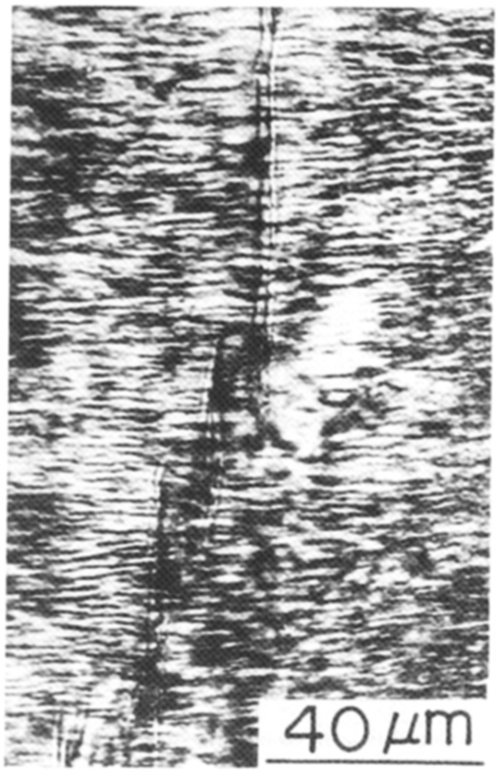


Figure 4 Polarizing micrograph of an oriented specimen of S(OM)

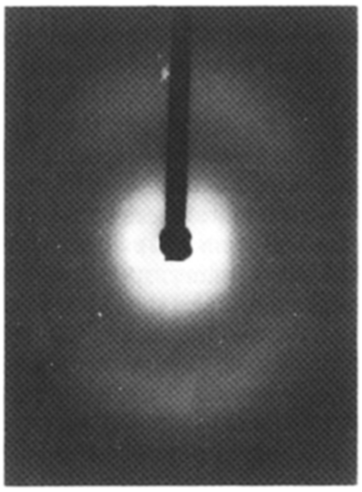


Figure 5 WAXD pattern of oriented S(OM) film specimens. The orientation direction is vertical

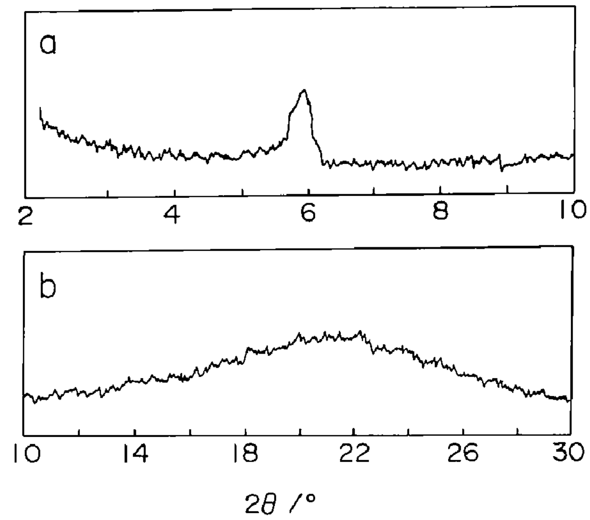


Figure 6 2θ Dependence of X-ray diffraction intensity along (a) the equator and (b) the meridian

alignment of neighbouring molecules in a fibril, due to the very limited molecular motion of polymer chains, is a necessary condition for band formation. Therefore the formation of banded texture in the oriented state of our samples indicates that the molecules of side-chain liquid crystalline polymers may become rather rigid as a whole and take the more extended conformation like their main-chain counterparts, when mesogenic units with three benzene rings are attached laterally to the backbone without a flexible spacer. It also implies that in special cases a side-chain polymer may exhibit behaviour like that of main-chain polymers. This is also evidenced by the lyotropic behaviour of these samples: their solution-cast specimens show clear birefringence and typical mesomorphic texture.

Of course, it is of great interest to know the internal structure of these rigid side-chain polymers. Preliminary results have been obtained in a previous study on oriented S(OM) specimens by means of polarizing microscopy and infra-red dichroism[15]. It was found that the main-chain axes of the molecules tend to orient in directions close to the direction of shearing under which the oriented specimens are prepared, while the mesogens fixed side-on are packed around the backbone with their axes approximately perpendicular to the latter.

In order to obtain more detailed information about the molecular conformation of these rigid side-chain polymers, oriented specimens of S(OM) were also analysed by WAXD, and the X-ray diffraction patterns are given in *Figure 5*. There are two characteristic diffractions in the patterns, and both are split into two arcs. The inner one is concentrated around the equatorial direction, and the outer one around the meridional direction. *Figures 6a* and *b* give the 2θ dependence of diffraction intensity along the equator and meridian, respectively. The inner diffraction peak is fairly sharp, at around $2\theta = 5.89°$, while the outer diffraction is rather diffuse with a maximum at about 21°. These diffractions can be assigned on the basis of our polarizing microscopy and infra-red dichroism studies. The inner diffraction, which is grouped around the equator, can be attributed to the interference of radiation from neighbouring molecules. They tend to pack in parallel with each other along the shear direction. The average distance between these parallel molecules can then be determined based on the deVries modification of the Bragg equation[16] and was 16.7 Å in this case. For main-chain liquid crystalline polymers the lateral distance between molecules, determined by WAXD, for their oriented specimens is usually in the range of about 4.8–5.1 Å. However, the relatively large value of average lateral distance, 16.7 Å, between the parallel molecules obtained for this polymer, with mesogens fixed side-on, seems reasonable if the extended length of the mesogen (23 Å) is considered. The sharpness of the diffraction peak implies that the lateral distance between the parallel molecules is rather uniform. The

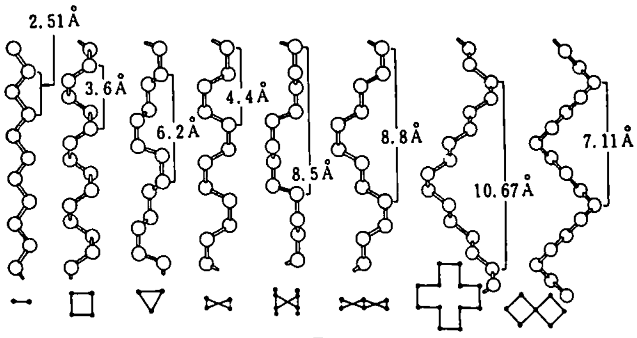


Figure 7 Some extended forms of polymethylene main chain

intensity of the inner diffraction is distributed around the equator at an azimuthal angle of about ±20°, which is supposed to be related to the deviation of the molecular axes from the shear direction.

The outer diffraction indicates the existence of a periodic spacing of about 4.7 Å in these specimens, which can be assigned to the average lateral distance between the mesogenic units. As reported above, the axes of the mesogens fixed side-on tend to orient perpendicularly to the axis of the backbone and a concentration of diffraction intensity around the meridian is anticipated. The outer diffraction peak is quite broad, as shown in *Figure 6b*. It is related to the very complicated distribution of distance between the mesogens including intramolecular and intermolecular distances. The relative packing of mesogens of different molecules should be quite random. The distance between intramolecular mesogens is determined by the configurational sequence of the main chain. *Figure 7* shows some common configurational sequences that may result in a more extended form of molecules. The approximate distance between mesogens in the direction of the molecular axis is also depicted. The distance of 4.4 Å between the next neighbouring mesogens along the $TGT\bar{G}$ sequence is closer to the experimental value of 4.7 Å. This may imply that $TGT\bar{G}$ is the preferred configurational sequence of these polymers with mesogenic units directly attached to the main chain in a side-on mode.

The molecular structure of polymer S(OM) has also been analysed by the molecular simulation technique. *Figures 8* and *9* give the side view and top view of the molecule S(OM), respectively. They were obtained for a chain of 15 repeat units with a given stereo-sequence minimized under DREIDING II force field. It is clear that the molecule is really in an extended conformation and is rod-like in shape as a whole, with the main chain approximately parallel to the rod axis. The side-chain mesogens are packed around the main chain with their axes almost perpendicular to the latter. The diameter of the molecule and the distance between the mesogens are consistent with the experimental data from WAXD measurements.

Two points should be noted from the experimental results shown above. First, we might get some new idea about the effect of interaction between the main chain and side mesogens on the mesophase formation of side-chain polymers. It is usually accepted that the mesogenic units are the ordering moiety of the molecules giving the driving force for liquid crystal formation. Although the main chain connects the side mesogens together, its flexible nature may result in a random coil conformation and hence destroy the ordered packing of mesogens. This means that the flexible main chain is a negative factor for liquid crystal formation. It is then reasonable to consider that the side mesogens will form mesophase more easily, if the influence of main chain on the mesogenic units can be reduced. This was realized about 15 years ago, and flexible spacers were introduced between the main chain and side mesogens to decouple their interactions[17]. A lot of side-chain polymers exhibiting enantiotropic liquid crystalline behaviour have been synthesized since then, in accordance with this idea. The results given in this work may imply that there is another

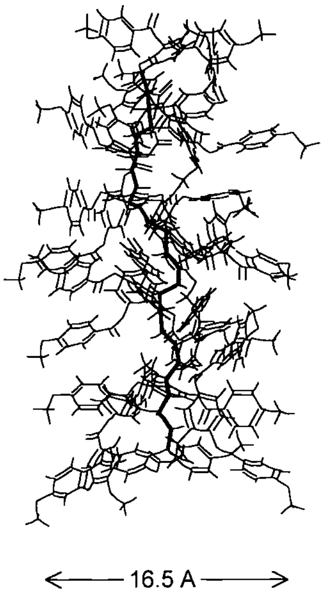


Figure 8 Side view of S(OM) molecule obtained by molecular simulation technique. The main chain is indicated by heavy lines

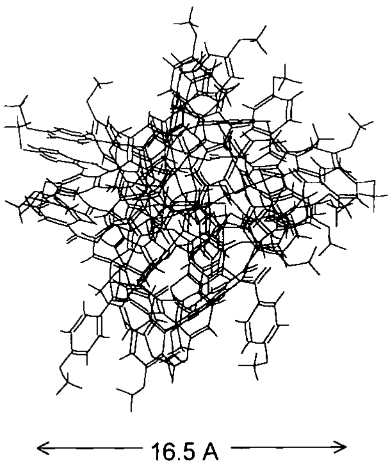


Figure 9 Top view of S(OM) molecule obtained by molecular simulation technique

possibility in the competition between the ordering and disordering effects of the molecules. In extreme cases of strong interaction between main chain and side mesogens, the flexibility or the disordering nature of main chain can be minimized or even completely inhibited under the influence of powerful mesogenic side chains. The main chain may be tightly coupled with the mesogens and becomes a part of the liquid crystal forming entities.

The second point is that the position of mesogens in the molecules is not the only decisive factor for elucidating the properties of liquid crystalline polymers. In some special cases a side-chain polymer may exhibit behaviour similar to that observed for main-chain polymers. As main-chain and side-chain polymers are often prepared by different synthesis methods, so the results shown above may indicate the possibility of developing new methods to obtain high performance liquid crystalline polymers.

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