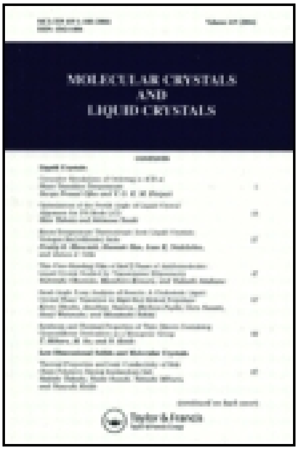

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Thermotropic Liquid Crystalline Polymers V Structure of Liquid Crystalline Polymeric Azomethynes

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Thermotropic Liquid Crystalline Polymers V
Structure of Liquid Crystalline Polymeric Azomethynes

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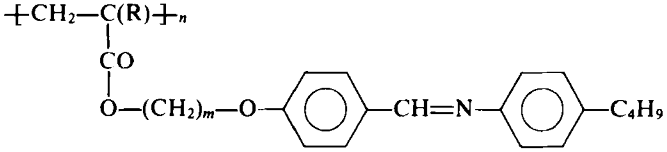
The study of the structure and properties of the comb-like polymers with long aliphatic side chains in each monomeric unit (Figure 1a) has helped start the new field of macromolecular chemistry and physics of polymeric liquid crystals.[1,2] Liquid crystalline (LC) properties of such polymers appear to be due to the incorporation of the mesogenic fragments into the side groups of macromolecules (Figure 1b).[3,4]

Structural and optical features are well known to play a big role in the properties of low molecular weight liquid crystals. Despite the fact that polymeric liquid crystals have been described in several publications, the structural polymorphism and optical textures in these polymers have not been studied yet. These questions are closely connected with two main problems. The first one is the correctness of the description of the LC polymers in the framework of the traditional classification of thermotropic low molecular weight liquid crystals. The second one is polymer structure regulation by means of external forces.

To study these problems a homologous series of polymeric liquid crystals having the general formula



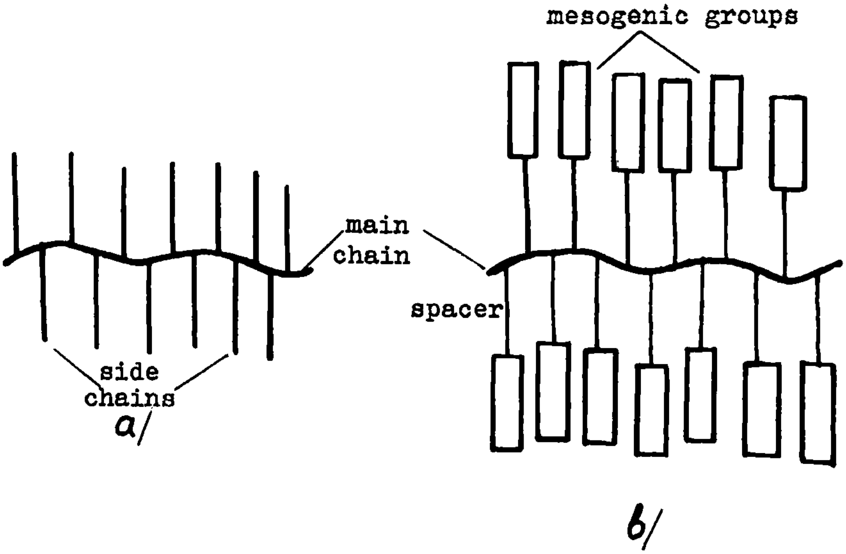


FIGURE 1 Schematic structure of comb-like macromolecule (a) and comb-like macromolecule with mesogenic groups (b).

has been synthesized. The chemical structure of the polymer chain and the length of the methylene sequences have been varied $m = 3,6,11$ and $R = H$ (polyacrylates, denoted as But-*m*-PA) and $R = CH_3$ (polymethacrylates, denoted as But-*m*-PM).

EXPERIMENTAL PART

Polymers were synthesized following the scheme described in Ref. 5. X-ray patterns were obtained by using a flat-plate URS-55 camera with a specimen-to-film distance of 60.6 mm at room temperature. A high temperature X-ray camera with variable distance also has been used. A nickel-filtered Cu radiation was employed.

Optical studies of the textures were conducted with a polarizing MIN-8 microscope equipped with a heating stage. Photos were taken with a Zenit-3M camera mounted on the microscope tube by a micro attachment.

Phase transitions were followed by using a scanning microcalorimeter, DSM-2, with a heating rate 1.5–25.0°C/min (DSC).

RESULTS AND DISCUSSION

As has been previously reported,[2] the majority of LC polymers do not display LC polymorphism and the same structure preserves within the whole range of

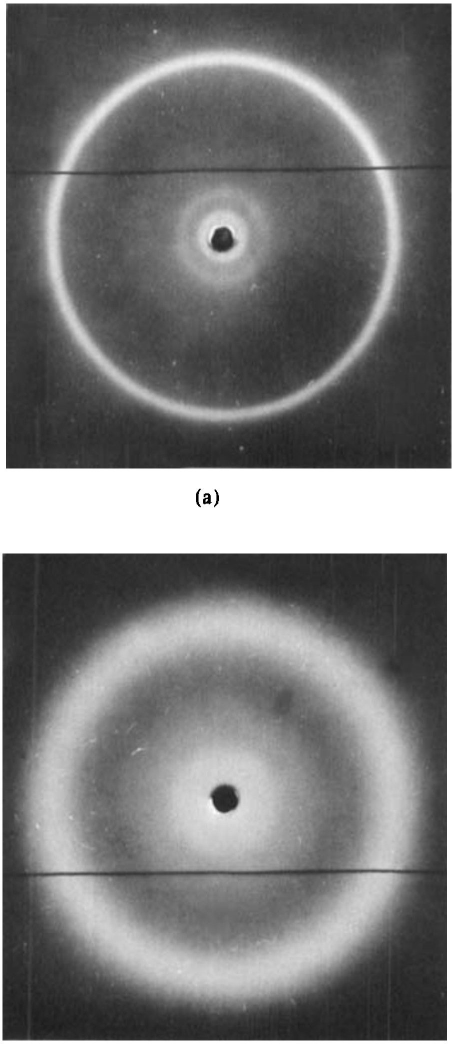
LC state in glassy, elastic and viscous-flow states of polymers. That is why there is only one peak on the DSC curves corresponding to the transition from the optically anisotropic state into the isotropic one (T_{cl}) In such a case the thermomechanical (TM) curves are typical for glassy polymers.

The polymer azomethynes But-*m*-PA and -PMA belong to another group of polymers which has two phase transitions within the LC state range. As has been shown by TM tests, the first peak at T_1 is related to solid-viscous flow state transition. One can see from the X-ray patterns (Figure 2, Table I) that at T_1 the sharp diffraction outer ring d_5 at wide angles is replaced by the diffuse maximum with $d_5 = 0.45$–0.46 nm. At the clearing point optically anisotropic polymers become isotropic and the value "d" of the diffuse reflection is increased up to $d = 0.48$–0.49 nm.

The question arises: what type of LC phase is thermodynamically stable between T_1 and T_{cl}? The optical textures usually observed in thin polymeric films do not allow one to identify the mesophase type by polarizing microscopy (Figure 3a).

The polymeric nature of these liquid crystals obviously causes the formation of a poorly defined texture. So far as the LC phase is formed by the packing of the side groups,[1] backbones are a kind of defects distorting the packing of the mesogenic groups and preventing the growth of the large LC aggregates. The substitution of the methacrylic main chain in But-*m*-PMA for a more flexible one could diminish the number of defects and increase the LC aggregates' size. And indeed the polyacrylic derivatives (But-*m*-PA) have another optical texture (Figure 3b) formed by the annealing of the polymer film in LC state near T_{cl}. Such a "fan" texture is similar to that of low molecular smectics A. The enthalpies of the mesophase-isotropic melt transition varied from 0.8 to 1.5 kkal/mol and are also of the same order as transition enthalpies of low molecular weight smectics. These results are in accordance with the X-ray data confirming the layered S_A structure of But-*m*-PA and But-*m*-PMA (Table I).

The transition of the "fan" texture to a pseudo-isotropic one has been observed when the glass cover is shifted at the temperature above T_1. On one hand this effect can be regarded as an additional evidence of the S_A structure, and on the other hand, it indicates that the polymer structure can be regulated within the mesomorphic state. Such pseudo-isotropic texture can be freezed in by cooling the samples below T_1. So it is possible to obtain stable, solid polymer films with a uniform molecular alignment. Figure 4a represents a conoscopic picture of the oriented film. One can conclude that such a polymer film is characterized by the anisotropic optical properties of a uniaxial positive single crystal when the optical axis is perpendicular to the film surface. The positive magnitude of the birefringence has been proved by using the "Rot. 1" plate.



(a)

(b)

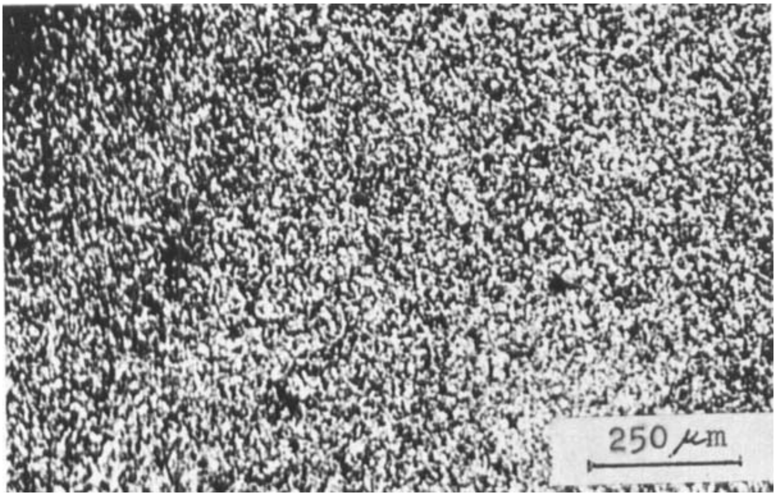
FIGURE 2 X-ray diagrams of But-11-PA at 20° (a) and 120° (b).

TABLE I

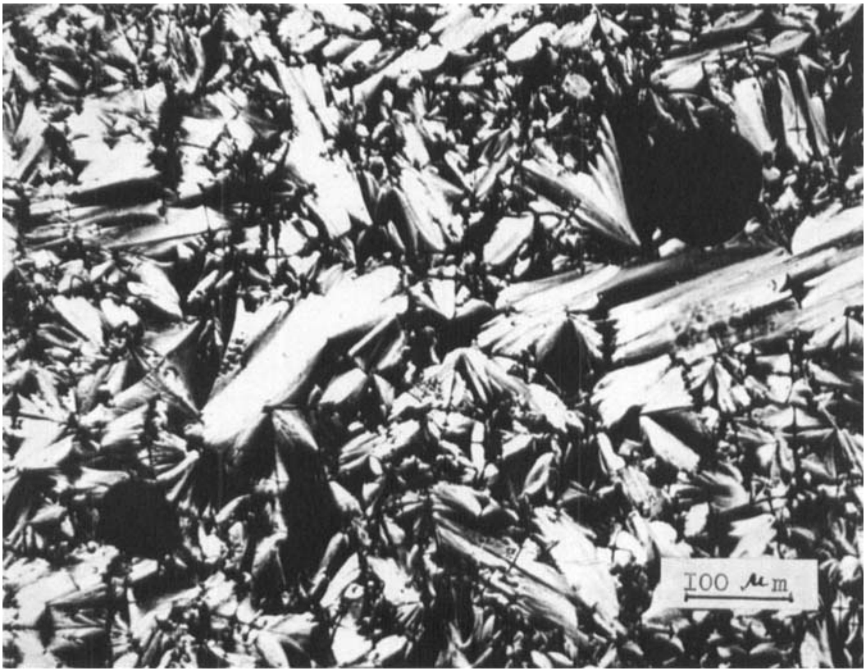
Interplanar spacings, temperatures and heats of transitions of polymeric azomethynes

		Interplanar spacings, nm						Calculated L, nm	Transitions			
									$S_B \leftrightarrow S_A$		$S_A \leftrightarrow S_A$	
Polymer	T_{exp}, °C	$d_1 \pm 0.11$	$d_2 \pm 0.05$	$d_3 \pm 0.05$	$d_4 \pm 0.005$	$d_5 \pm 0.001$	d_6 dif.	±0.1	T_1, °C	H, kj/mol	T_{cl}, °C	H, kj/mol
But-6-PM	20	2.7	—	0.9	—	0.436	—	2.7	75	1.42	115	3.34
	100	2.7	—	0.9	—	—	0.45					
	125	—	—	—	—	—	0.48					
But-11-PM	20	3.3	1.7	1.15	0.875	0.436	—	3.2	86	2.46	140	5.98
	120	3.3	1.7	1.15	0.875	—	0.46					
	165	—	—	—	—	—	0.49					
But-3-PA[a]	20	4.2	2.1	1.35	—	0.436	—	2.4	70	—	160	0.91
	120	4.2	2.1	1.35	—	—	0.46					
But-6-PA	20	2.7	1.3	0.95	—	0.436	—	2.7	77	1.7	115	3.40
	100	2.7	—	—	—	—	0.46					
But-11-PA	20	3.3	1.7	1.15	—	0.436	—	3.2	95	3.13	145	5.28
	120	3.3	1.7	1.15	—	—	0.46					
	165	—	—	—	—	—	0.48					

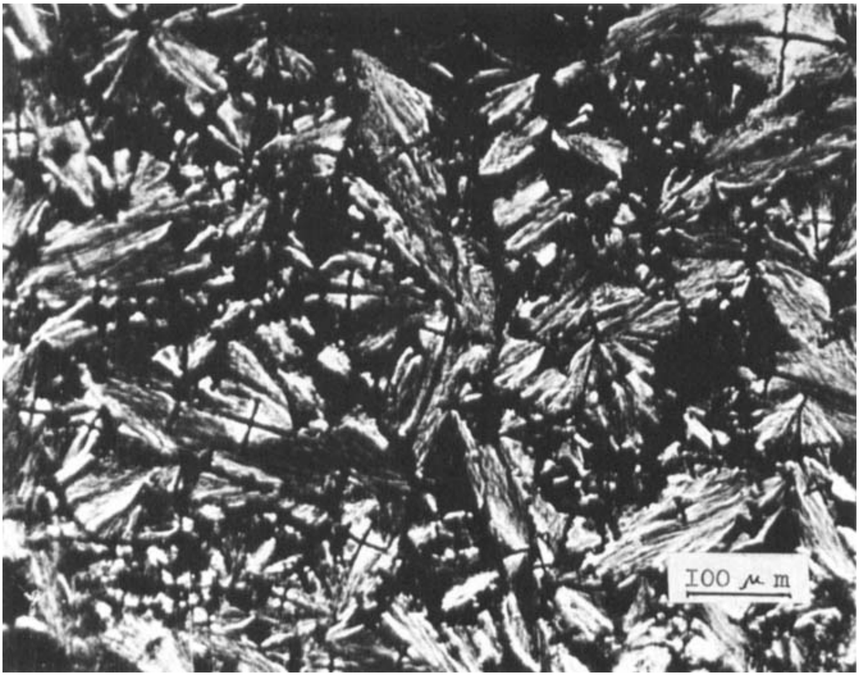
[a] In this case two more diffraction rings ($d = 7$ nm, $d = 3.1$ nm) appear on the X-ray pattern. This can be attributed to some other type of structure which may be present in a very small amount.



(a)



(b)

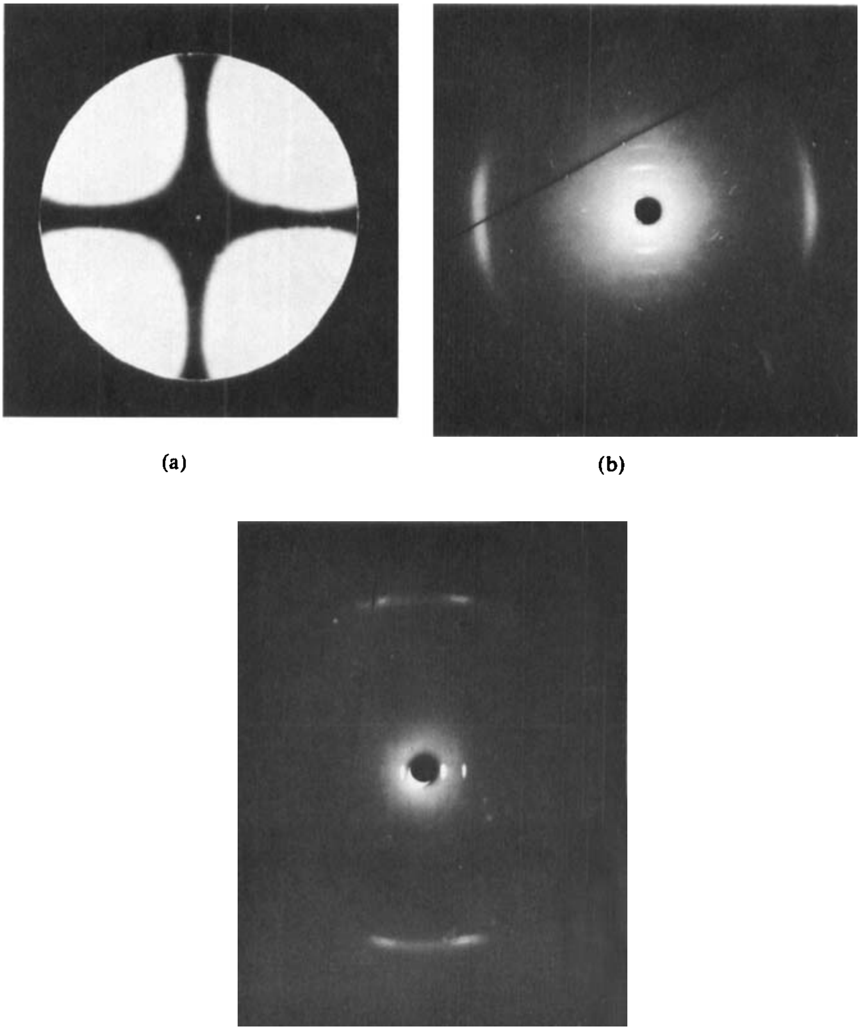


(c)

FIGURE 3 Optical textures of But-11-PMA (a) and But-11-PA in S_A (b) and solid smectic phase (c).

An idea about the molecular structure of these pseudo-isotropic oriented polymer films can be taken from their X-ray diagrams (Figures 4b, c). The scheme of the X-ray experiment is shown in Figure 5. The direction of the incident beam is parallel to the film surface. The outer ring is responsible for the interaction of the neighboring parallel side chains. In But-*m*-PMA ($m = 6.11$) this ring is split up into two crescents (Figure 4b). This means there is a normal arrangement of the side chains toward the film surface and a coincidence of the optical axis with the direction of the side groups. The inner ring determined by the length of the side chains appear to be split up into two equatorial maxima. Hence it follows that the long side groups form the layer structure with the chain axis normal to the plane of the layer.

The same picture of X-ray diffraction at small angles indicates also the layer structure formation in polyacrylic polymers (Figure 4c). But the side chain axis arrangement differs from the first one. The outer maximum of the X-ray diagram of But-11-PA is split up into four crescents. This means that the side chains are tilted about 14° to the layer plane normal. Their directions in



(a) (b)

(c)

FIGURE 4 Conoscopic figure of But-11-PMA oriented film (a), X-ray pattern of oriented films of But-11-PMA (b) and But-11-PA (c).

the sample as a whole form the surface of a cone with an angle of 28°. Such a structure also indicates the optical uniaxiality of the system.

Thus, by orienting the polymers in a smectic A phase and by cooling them below the first transition temperature T_1 it is possible to get an oriented optically transparent polymer film with the optical properties of a uniaxial single crystal. Fixation of the pseudo-isotropic texture by cooling of the sample

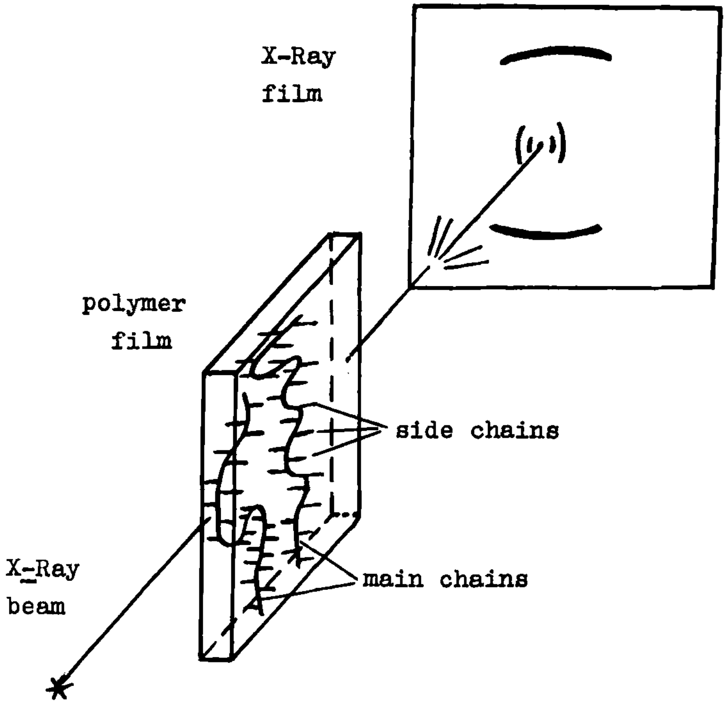


FIGURE 5 Scheme of X-ray experiment and X-ray diagram.

shows that the optical properties of the oriented layer in both phases (below and above T_1) are practically identical. As has already been mentioned above, this transition is accompanied with a narrowing of the outer ring (Figure 2). The textural change results only in a formation of the system of longitudinal stripes on the "fan" surface (Figure 3c). From the sharpness of the outer maximum with $d = 0.436$ nm the crystallization of the mesogenic groups in these polymers has been proposed in Ref. 5. The following sequence of phase transitions has been suggested.

$$C \xleftrightarrow{T_1} S_A \xleftrightarrow{T_{cl}} I$$

From calorimetric data presented in Table I the first transition enthalpies at T_1 appear to be one order lower in comparison with the crystal ↔ smectic transition enthalpies, and in most cases lower than the second transition enthalpies ΔH_2. These data brought us to examine all the sets of experimental results from the point of view of a smectic polymorphism. One can assume the formation of a smectic phase with structured layers below the temperature T_1. Only one outer maximum with $d = 0.436$ nm can be related to the ordering of the mesogenic side chains in every layer, as is known for solid smectic B.[6-8] This interpretation is a hypothetical one but it can explain small values of ΔH_l, and the stability of the pseudo-isotropic phase by the cooling of a polymer. The next scheme of phase transition in polymeric azomethynes But-*m*-PA and PMA

$$S_{B(?)} \xleftrightarrow{T_l} S_A \xleftrightarrow{T_{cl}} I$$

is in agreement with the optical uniaxiality of both smectic phases.

As has been already shown, the mesophase types in all the polymers studied are the same. The difference is in the arrangement of the side chains in the smectic layer. The interplanar spacings d_l in polymers with $m = 6.11$ are related to the calculated length L of the side groups (Table I). From this observation, the antiparallel packing of side chains typical for smectics can be suggested (Figure 6a). Unlike the normal arrangement of the mesogenic groups regarding the layer plane in polymethacrylates, there is a small tilt in the polyacrylic derivative—But-11-PA. As for the interplanar spacing d_l—it is practically equal to that of But-*m*-PMA because of the small value of the tilt angle.

If the mesogenic fragment size significantly exceeds the spacer length (in But-3-PA), the packing like a double layered structure, well-known for amphiphilic compounds, appears. (Figure 6b). The stability of such a structure is

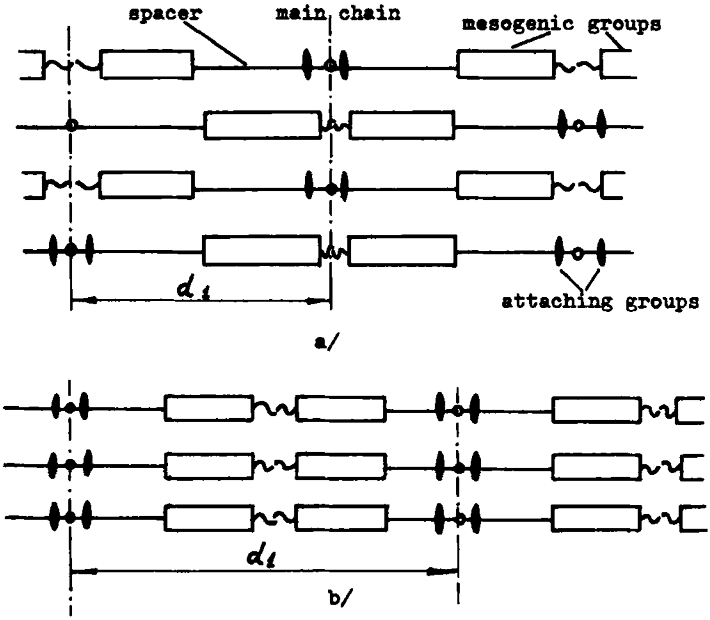


FIGURE 6 Chain packing of macromolocules with various length of methylene group $m = 6.11$ (a) and $m = 3$ (b). Projections along main chain axis.

obviously due to the chemical bonding of mesogenic groups with polymer main chains.

In summary, the existence of a smectic phase as a result of studying the structure and properties of polymeric comb-like liquid crystalline azomethynes has been established. For the first time the characteristic optical textures of polymeric smectics have been obtained and characterized. The preparation of oriented polymeric films having the optical properties specific for uniaxial single crystals proved to be possible. The structure of these films has also been studied.

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