Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Synthesis and comparative structural investigation of crystalline and liquid-crystalline phases of low molecular mass compounds and side group polymers I. Low molecular mass compounds

Karin Hans[a]; Peter Zugenmaier[a]
[a] Institut für Physikalische Chemie der TU Clausthal, Clausthal-Zellerfeld, F.R. Germany

To cite this Article Hans, Karin and Zugenmaier, Peter(1990) 'Synthesis and comparative structural investigation of crystalline and liquid-crystalline phases of low molecular mass compounds and side group polymers I. Low molecular mass compounds', Liquid Crystals, 8: 1, 95 — 108

To link to this Article: DOI: 10.1080/02678299008047333

URL: http://dx.doi.org/10.1080/02678299008047333

LIQUID CRYSTALS, 1990, VOL. 8, NO. 1, 95–108

Synthesis and comparative structural investigation of crystalline and liquid-crystalline phases of low molecular mass compounds and side group polymers

I. Low molecular mass compounds

by KARIN HANS and PETER ZUGENMAIER
Institut für Physikalische Chemie der TU Clausthal, D-3392 Clausthal-Zellerfeld, F.R. Germany

(*Received 27 July 1989; accepted 27 December 1989*)

Low molecular mass compounds and analogous side group polymers with a thermotropic phase behaviour crystalline–smectic liquid–crystalline–isotropic have been synthesized for a comparative structural study. As characteristic features of the compounds a biphenyl group has been chosen for the mesogenic core and alkoxy parts of various lengths as terminal and spacer groups. The phase behaviour has been studied with differential calorimetric (DSC) measurements and polarization microscopic observations. The low molecular mass compounds form crystalline phases at room temperature and exhibit predominantly mosaic textures in the polarization microscope at elevated temperatures indicating high order of the packing of the molecules. The arrangements of the molecules in the crystalline and liquid-crystalline phase can best be described as layered structures according to X-ray diffraction measurements. A structural analysis of a solution grown single crystal provides valuable information on the conformation and packing of the compounds investigated in this study.

1. Introduction

Two basic structural features are inherent in polymers with mesogenic side groups: the polymeric main chain, which is responsible for the macromolecular properties, and the mesogenic side group for the formation of liquid-crystalline phases. Correspondingly, the structure of crystalline and liquid-crystalline phases have to be considered with regards to main chains and side groups and their interrelations. Models to be proposed have to state the conformation of the main chain, which might be more or less ordered or disordered, and the packing of the side groups in the corresponding phases. How are the layers arranged in a smectic phase and what is the state of order? The relationship between main chain and side group has to be described, and also the differences between crystalline and liquid-crystalline phases. At present, the proposed models are strongly dependent on the method used in the investigations, and differences are detected for various kinds of main chain skeleton. A wider range of compounds may be useful for structural investigations to clarify some of the features of the models.

Three different types of fundamental changes were introduced on the molecular level of the samples to provide more insight into structural details of liquid-crystalline phases.

(i) The chemical constitution of the main chain was altered and experimental data were gathered for a polyacrylate (PAc) and polymethacrylate (PMAc) with the same mesogenic side group. A change in the side group length at the same main chain completed this investigation.
(ii) Low molar mass mesogenic compounds were synthesized, the same kind as that which had been attached to the polymeric backbone, and extensively studied.
(iii) The crystal structure was investigated at the low molar mass and polymeric level for reasons of comparison with structural features of liquid-crystalline phases.

2. Compounds

The synthesized compounds are listed in figures 1 and 2 with their abbreviations. Some of the monomers and almost all of the polymers exhibit thermotropic crystalline–liquid-crystalline phase behaviour with favourable transition temperatures in the low temperature range for obtaining the necessary experimental data. A few of the sixteen monomeric, one dimeric and nine polymeric compounds have been described in the literature [1]. They differ in the rigid core, the lengths of the terminal groups, the acid residue, and the kind and average length of the polymeric chain, respectively.

A large variety of structures and properties became available by the systematic changes of the chemical constitution of various parts of the molecules. Three different mesogenic cores have been employed: biphenyl (-Bi-6*n*), naphthalin (-Np-6Br) and benzophenone (-Bp-6Cl) derivatives. Some methacrylates (MoMAc-Bi-6*n*, PMAc-Bi-6*n*; $n = 0, 1, 2, 5, 6$) of the biphenyl type of compounds are known [1]. These compounds serve as references and suggest that the newly synthesized structures may exhibit smectic phases, a prerequisite for a successful study within the scope described previously. The polymers PMAc-Bi-61 and PMAc-Bi-62 have been investigated previously and a few structural details of the partial crystalline phases have been revealed but not enough to propose a structural model [2, 3]. Therefore, the synthesis of further similar compounds of this type by a variation of lengths of side groups and of the polymeric chain should help to establish structural models [4].

All low molar mass compounds possess a hexyloxy residue which serves as a spacer between the side group and the corresponding main chain. The olefinic double

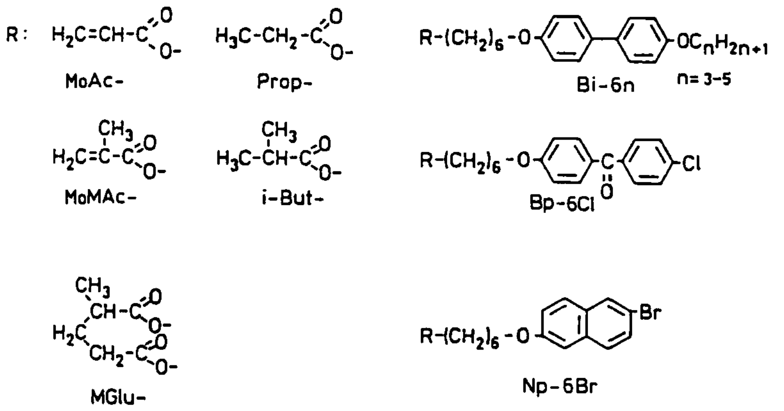


Figure 1. Low molecular mass compounds and abbreviations used.

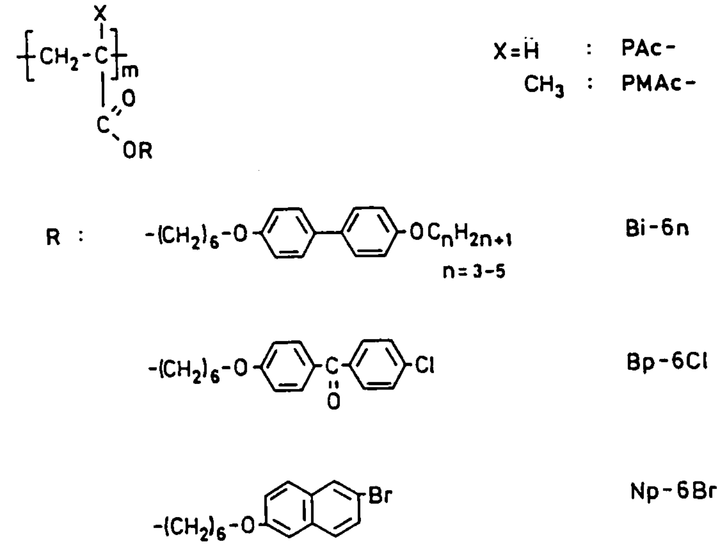


Figure 2. Polymeric compounds and abbreviations used. Different initiator concentration led to two polymers with different molar masses called PMAc-Bi-63*n* (0·5 mol % initiator) and PMAc-Bi-63 (2 mol % initiator).

bonds in the small molecules can be polymerized to produce the analogous side group polymers. The saturated low mass compounds have been synthesized for reasons of comparison and to investigate the influence of single and double bonds in the acid residue.

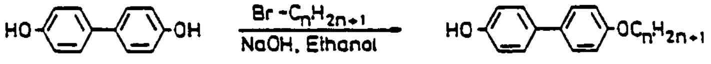
Esterification of the dicarbonic acid 2-methylglutaric acid led to the dimer (MGlu-Bi-65), comparable with the acrylates, and an interesting sequence monomer–dimer–polymer has been achieved. The molecular structure of this dimer contains a chiral carbon centre. Since the starting material was obtained by a non-stereoselective reaction the end product represents a racemic mixture.

The polymeric compounds have been synthesized by radical polymerizations of the unsaturated monomers. The initiator 2,2′-azo-bis-isobutyronitrile (AIBN) has been used in various concentrations:

0·5 mol % AIBN:	PMAc-Bi-63*n*,
1 mol % AIBN:	PAc-Bi-64, PMAc-Bi-64, PMAc-Bi-65,
2 mol % AIBN:	PAc-Bi-63, PMAc-Bi-63, PAc-Bi-65, PAc-Bp-6Cl, PAc-Np-6Br, PMAc-Np-6Br.

3. Synthesis

The syntheses of the compounds have been carried out in three steps according to procedures described in the literature [1]. In a first step 4,4′-biphenyldiol (**1**) was reacted to give 4-*n*-alkoxy-4′-hydroxy-biphenyl (**2**) according to the Williamson ether synthesis.

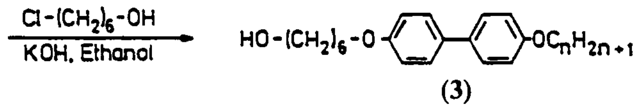


(1) (2)

The separation of the components in the reaction mixture ((**1**), (**2**) and the biether) was achieved by using the different solubility in NaOH solutions (**1**) soluble in the cold, (**2**) soluble in the heat, biether insoluble). The yield of the desired product (**2**) amounted to 30–40 per cent after recrystallization from ethanol. This first step was omitted in the reaction of naphthalin and benzophenone derivatives.

The second step also consisted of a Williamson ether reaction. The 'spacer' was added to (**2**) and 4-*n*-alkoxy-4′-(*ω*-hydroxy hexyloxy) biphenyl (**3**) obtained.

(2)

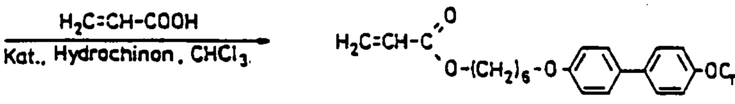


(3)

Analogous reactions were carried out with 4-chloro-4′-hydroxy-benzophenone to result in 4-chloro-4′-(*ω*-hydroxy hexyloxy)-benzophenone and with 2-bromo-6-naphtol to obtain 2-bromo-6-(*ω*-hydroxy hexyloxy)-naphthalin. A yield of *c*. 70 per cent was achieved after recrystallization from ethanol.

Finally an azeotropic esterification with acrylic acid was performed in a third step which led to 4-(acryloyloxy)-hexyloxy-4′-*n*-alkoxy-biphenyl (**4**), or with methacrylic, propionic, *i*-butyric and 2-methylglutaric acid to the desired low molecular mass compounds.

(3)



(4)

The reaction mixture was purified by column chromatography (stationary phase: silica gel and CH_2Cl_2, fluid: CH_2Cl_2) and a yield of 40–70 per cent (after recrystallization in ethanol) obtained for the product.

The radical polymerizations of the acrylates and methacrylates were carried out with 2,2′-azo-bis-isobutyronitrile as initiator in toluene (concentration 10 per cent) for 6 hours (biphenyl derivatives) or for *c*. 20 hours (naphthalin and benzophenone derivatives) under N_2 atmosphere at 60°C. The purification was achieved through reprecipitation in methanol and aceton several times. Finally the samples have been dried for 1 or 2 days in high vacuum. The compounds have been characterized by elemental analysis (table 1). IR- and ^{1}H-NMR (figure 3) spectroscopy, and the purity

Table 1. Elemental analysis of some of the synthesized compounds. Theoretical (theor.) and experimental (exp.) determined ratios of carbon (C) and hydrogen (H).

Compound	% C (theor.)	% C (exp.)	% H (theor.)	% H (exp.)
MoAc-Bi-63	75·36	75·53	7·91	7·86
PAc-Bi-63	75·36	75·45	7·91	7·93
PMAc-Bi-63	75·73	75·84	8·13	8·27
MoAc-Bi-64	75·73	75·61	8·13	8·24
PAc-Bi-64	75·73	75·46	8·13	8·01
PMAc-Bi-64	76·06	76·00	8·35	8·47
Prop-Bi-65	75·70	75·68	8·80	8·85
i-But-Bi-65	76·02	75·96	8·98	9·01
MoMAc-Bi-65	76·38	76·50	8·55	8·59
MGlu-Bi-65	75·88	75·73	8·57	8·54
PAc-Bi-65	76·06	75·89	8·35	8·31
i-But-Np-6Br	61·08	61·15	6·41	6·54
MoMAc-Np-6Br	61·39	61·49	5·93	5·98
MoAc-Bp-6Cl	68·30	68·40	5·99	5·89

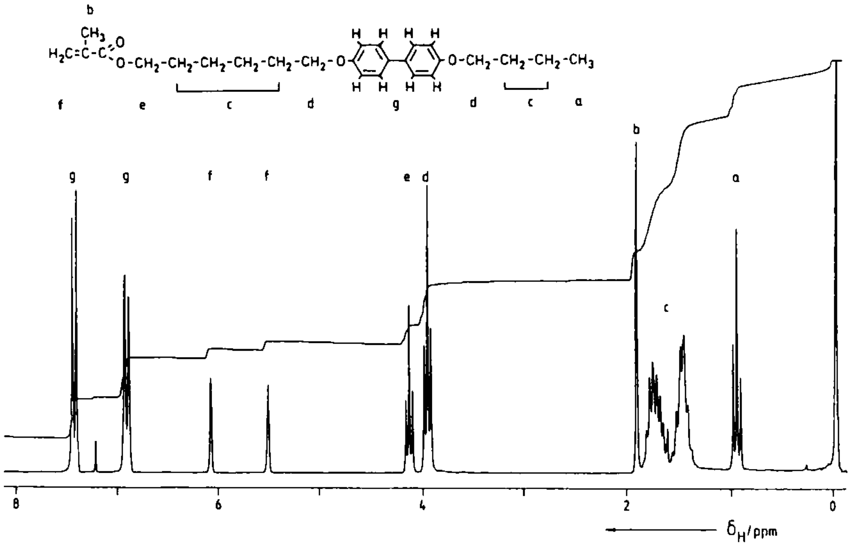


Figure 3. ^{1}H-NMR spectrum of the compound MoMAc-Bi-64 as an example for a monomer in $CDCl_3$ with TMS as reference.

necessary for further investigations verified [4]. A determination of molar mass by vapour osmotic measurement (solvent $CHCl_3$) resulted in 20 200 g mol^{-1} for PMAc-Bi-63 (degree of polymerization DP $\approx$ 50) and 24 600 g mol^{-1} for PMAc-Bi-64 (DP $\approx$ 60).

4. Phase behaviour

An overview of the phase behaviour with transition temperatures is represented in table 2. These data have been determined by differential scanning calorimetry (DSC), polarization microscopic and X-ray investigations. Some of the monomers with the biphenyl core form smectic phases. An increasing tendency for the formation of smectic phases is observed with a prolongation of the terminal group. The polymers with these monomers as side groups exhibit at least one smectic phase at elevated temperatures with one exception and are partial crystalline at room temperature. The compounds with the biphenyl mesogen fulfil the required prerequisite for the structural investigations intended.

The melting temperature of the naphthalin and benzophenone compounds are lower than those of the biphenyl derivatives, as expected from a comparison of the melting behaviour of the starting materials. Liquid-crystalline phases have not been detected although comparable cyano and bromo biphenyl compounds have led to liquid-crystalline materials [5–7]. The more rigid mesogenic core (naphthalin, benzophenone group) and/or stronger packing interactions seem to hinder the formation of liquid-crystalline phases. The polymeric naphthalin compounds are amorphous. PAc-Bp-6Cl is partial crystalline. Since these materials are not suitable for the planned structural investigations, no further studies have been undertaken.

Only results on the low molecular mass materials will be presented in this paper, those of the polymeric compounds in connection with the corresponding monomers will be published elsewhere.

The clearing temperature T_c of the monomeric biphenyl compounds is observed in the range of 356–368 K. The methacrylates in contrast to the corresponding

Table 2. Overview of the phase behaviour of the synthesized compounds determined by DSC, polarization microscope and X-ray investigations. Phase transition temperatures in K by DSC-measurements (heating rate 5 K min^{-1} (monomer), 10 K min^{-1} (polymer); C, crystalline; g, glass; CS, crystalline or higher ordered smectic; S, smectic; I, isotropic; sh, shoulder; +, phase behaviour strongly dependent on heating rate; annealing and number of heating cycles; x, transition determined by polarization microscopic method).

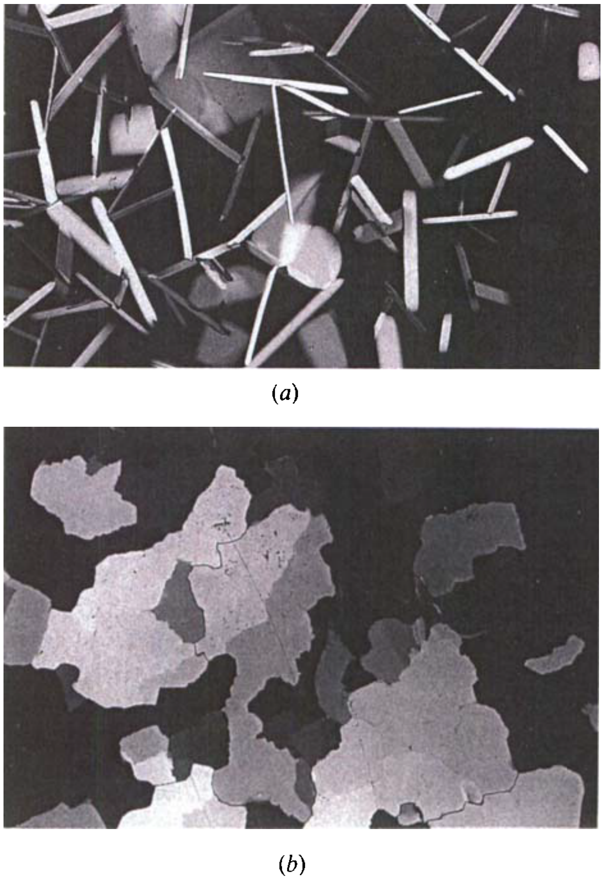
Compounds	Phase behaviour								
MoAc-Bi-63	C	368	I						
MoMAc-Bi-63	C	363	I						
MoAc-Bi-64	C	342	S	368	I				
MoMAc-Bi-64	C	(358	sh)	361	I				
MoAc-Bi-65	C	321·5	CS	327	S	361	I		
Prop-Bi-65	C	337	C	362	I				
MoMAc-Bi-65$^+$	C	310	CS	334·5	CS	344	S	356	I
i-But-Bi-65	C	(356	sh)	357	I				
MGlu-Bi-65	C	380	S	384·5	I				
PAc-Bi-63	C	414	S	437·5	I				
PMAc-Bi-63	C	408	S	428·5	I				
PMAc-Bi-63*n*	C	406·5	S	428·5	I				
PAc-Bi-64	C	407	CS	412	S	441	I		
PMAc-Bi-64	C	399·5	S	430	I				
PAc-Bi-65	C	413	S	438	I				
PMAc-Bi-65	C	428	I						
MoAc-Np-6Br$^+$	C	328	I						
Prop-Np-6Br$^+$	C	315·5	I						
MoMAc-Np-6Br$^+$	C	312·5	I						
i-But-Np-6Br$^+$	C	293	I						
PAc-Np-6Br$^\times$	g	310–320	I						
PMAc-Np-6Br$^\times$	g	310–320	I						
MoAc-Bp-6Cl$^+$	C	347	I						
Prop-Bp-6Cl	C	333	I						
MoMAc-Bp-6Cl$^+$	C	324	I						
i-But-Bp-6CL	C	316	I						
PAc-BP-6CL	C	342	I						

acrylates always melt at temperatures about 5–7 K lower due to the branching in the acid residue. The clearing temperatures of the saturated and equivalent unsaturated substances are almost equal. However, the latter compounds show additional phase transitions. The dimer (MGlu-Bi-65) exhibits a T_c at 23 K higher than the corresponding monomer and this difference augments to 53 K for the polymeric material.

All monomeric samples except MoMAc-Bi-65 represent approximately the same phase behaviour at cooling and subsequent heating. The monomer MoMAc-Bi-65 in contrast shows two phase transitions on cooling and three or four transitions on heating depending on the heating rate. It thus shows a complex phase behaviour, and the associated structural changes are difficult to visualize.

The monomers of the biphenyl mesogen form a second crystalline modification or a smectic phase of higher order (Prop-Bi-65, MoAc-Bi-64, MoAc-Bi-65, MoMAc-Bi-65) at higher temperatures. Clearly, an increasing tendency for the formation of smectic phases is observed with increasing length of the terminal groups. The enthalpy difference accounts to 42–63 J/g at T_c and 3–22 J/g for the other transitions with the exception of MoMAc-Bi-65 with 57 J/g. The high enthalpy differences at the isotropic–anisotropic transitions suggest that ordered structures are formed from the isotropic melt. Mosaic textures are observed in the polarization microscope below this transition and similarly support that highly ordered structures are produced below the isotropic–anisotropic transition.

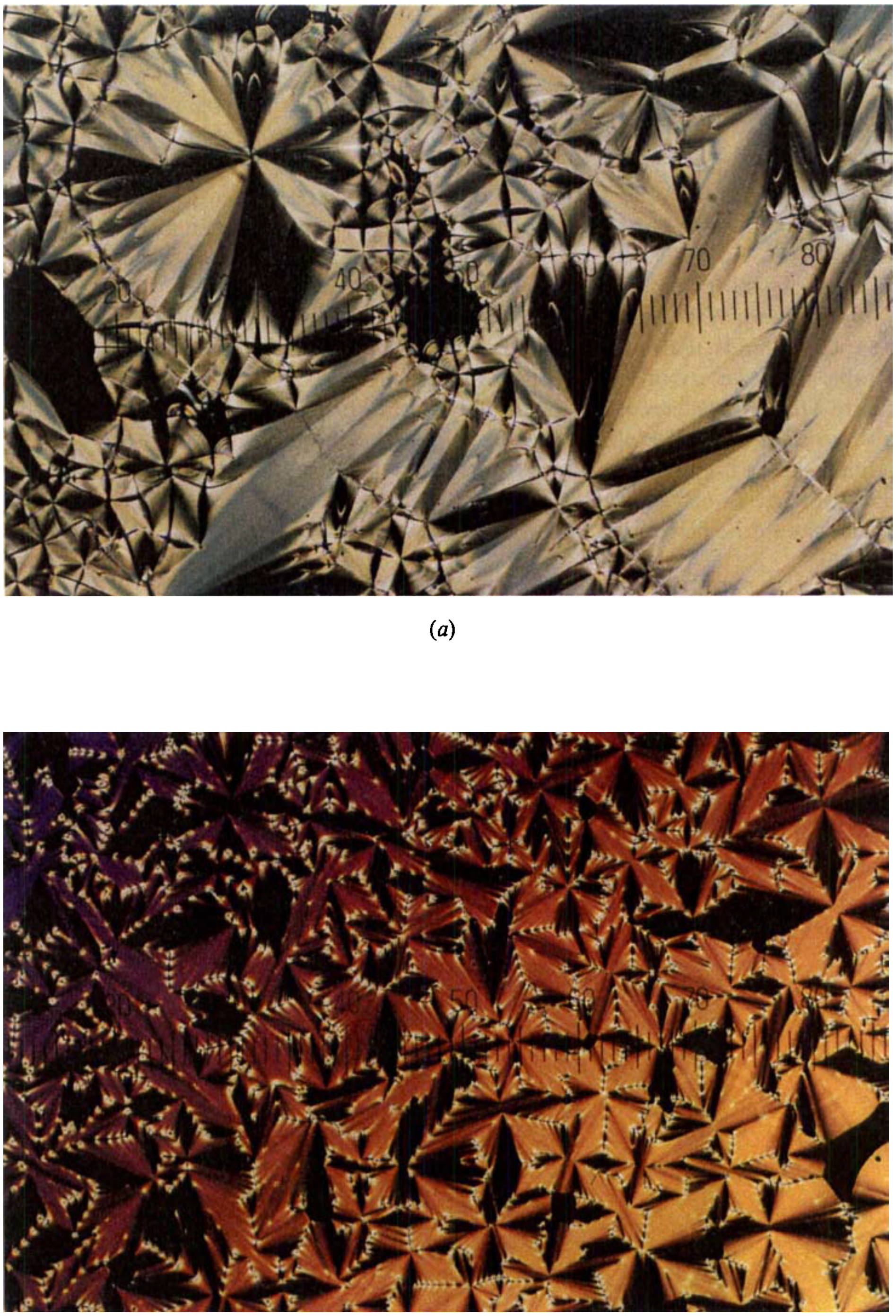
The formation of liquid-crystalline phases can be recognized by an observation of the microscopic mobility of original samples, which have not yet been molten, below the clearing temperature at heating. The compound Prop-Bi-65 gains its mobility only at the transition into the isotropic phase. In contrast, powder-like samples of MoAc-Bi-64, MoAc-Bi-65 and MoMAc-Bi-65 already show some mobility at temperatures below T_c and form somewhat larger, connected anisotropic areas, indicative of liquid crystal formation. Elements of distinct textures are visible after annealing. Far more characteristic textures are observed on cooling from the isotropic phase for these compounds. Extremely well formed monodomains with a morphology comparable to single crystals may appear at the isotropic–anisotropic phase transition (figure 4 (*a*)). Mosaic textures are normally formed below this transition (figure 4 (*b*)) and are signs of high molecular order besides the formation of the regular monodomains in the high temperature region of the monomers MoAc-Bi-64, MoAc-Bi-65 and MoMAc-Bi-65. A clear association to one of the higher ordered smectic phases cannot be performed (cf. also X-ray investigations). A uniaxial phase can be



(*a*)

(*b*)

Figure 4. Polarization microscopic exposures of MoAc-Bi-64 (× 70) (*a*) isotropic–anisotropic phase transition, 368·5 K; monodomains, (*b*) sample annealed, 363 K; mosaic texture typical for higher order smectic phases.



(*a*)

(*b*)

Figure 5. Polarization microscopic exposures of MGlu-Bi-65, smectic phases (S_A) (magnification: 10 bars ≙ 0·17 mm); (*a*) focal-conic textures at 380·5 K, (*b*) focal-conic fan texture at 380·4 K.

excluded, however, since homeotropic areas in textures have not been found under any conditions.

The dimer MGlu-Bi-65 also exhibits a distinct domain formation at the isotropic–smectic phase transition analogous to the behaviour of the monomeric compounds. The appearance of domains has also been observed for some polymers [8]. In contrast to the monomers, the dimer forms a low ordered smectic phase of the S_A type, since exclusively focal-conic textures have been produced and especially as natural textures. Sites and arrangements of the focal-conic domains are strongly dependent on the thickness of the samples.

The focal-conic domains with their elliptical bases are placed predominantly in the preparation plane for relatively thick samples and to some extent perpendicular to this plane as represented in Figure 5(*a*). Decreasing the sample thickness results in a predominant orientation of the hyperbolae in the preparation plane. They almost always combine to fans in relatively thin samples and characteristic focal-conic fan textures are created in various colour (figure 5(*b*)).

5. X-ray investigations

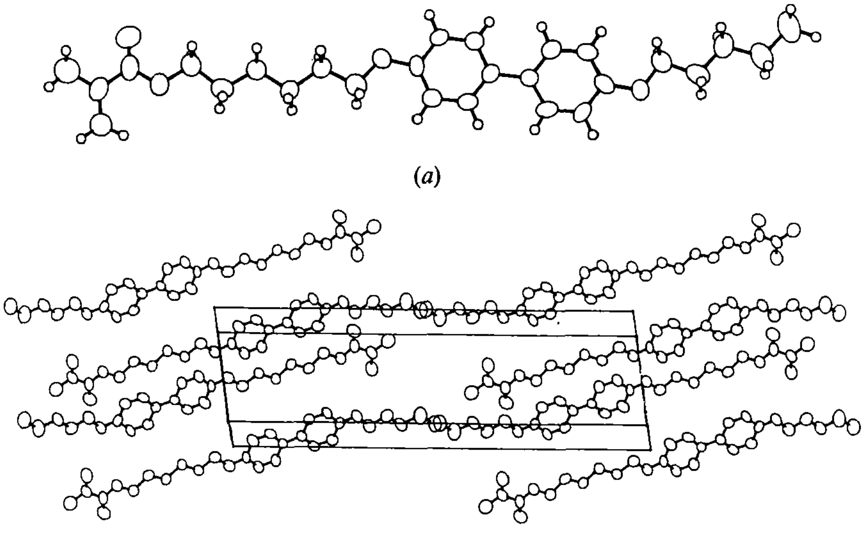
X-ray investigations have been carried out on all compounds as synthesized before melting in a vacuum flat film and Kratky camera with a position sensitive counter at room temperature. The diffraction diagrams served to evaluate structural models for the prevailing crystalline phase of the biphenyl derivatives at this temperature. A single crystal was grown for MoMAc-Bi-65 and the structure solved with data from a four circle diffractometer. The characterization was completed at elevated temperatures and X-ray exposures taken of the crystalline or smectic phases of the compounds MoAc-Bi-64, MoAc-Bi-65, MoMAc-Bi-65, Prop-Bi-65 and the dimer MGlu-Bi-65 just below the anisotropic–isotropic phase transition.

6. Crystalline phases at room temperature

Single crystals of MoMAc-B-65 have been grown out of solution, and the structure solved with the X-ray data of a four circle diffractometer [9]. The unit cell is triclinic with $a = 7{\cdot}9328\ (\pm 14)$ Å, $b = 29{\cdot}2531\ (\pm 28)$ Å, $c = 5{\cdot}5372\ (\pm 20)$ Å, $\alpha = 87{\cdot}033\ (\pm 15)^\circ$, $\beta = 108{\cdot}120\ (\pm 20)^\circ$, $\gamma = 97{\cdot}411\ (\pm 11)^\circ$ and contains two molecules; space group $P\bar{1}$ and $R = 6{\cdot}4$ per cent for 1161 observed reflections. The conformation of the compound is represented in figure 6(*a*), the packing within the unit cell is shown in figure 6(*b*). Surprisingly, the biphenyl mesogen is almost planar and the carbon and oxygen atoms of the spacer and terminal group are also placed in two planes, respectively. These three planes are slightly twisted. The model of the molecule is best represented by an all trans conformation.

The molecules are packed in an antiparallel fashion and are slightly tilted towards the unit cell axis. The arrangement of the molecules can be described by a single layer structure with a partial overlap of the terminal group of molecules belonging to adjacent layers. Since two molecules of adjacent layers (or in the unit cell) are related by a symmetry element (centre of inversion) in the crystalline state, the approximate length of the molecule suffices for the description of the layer spacing or the length of one unit cell dimension. This may be different, if such a symmetry element is missing.

Although this solution grown crystal structure of MoMAc-Bi-65 represents a different modification than that observed in the powdery sample investigated by the



(a)

(b)

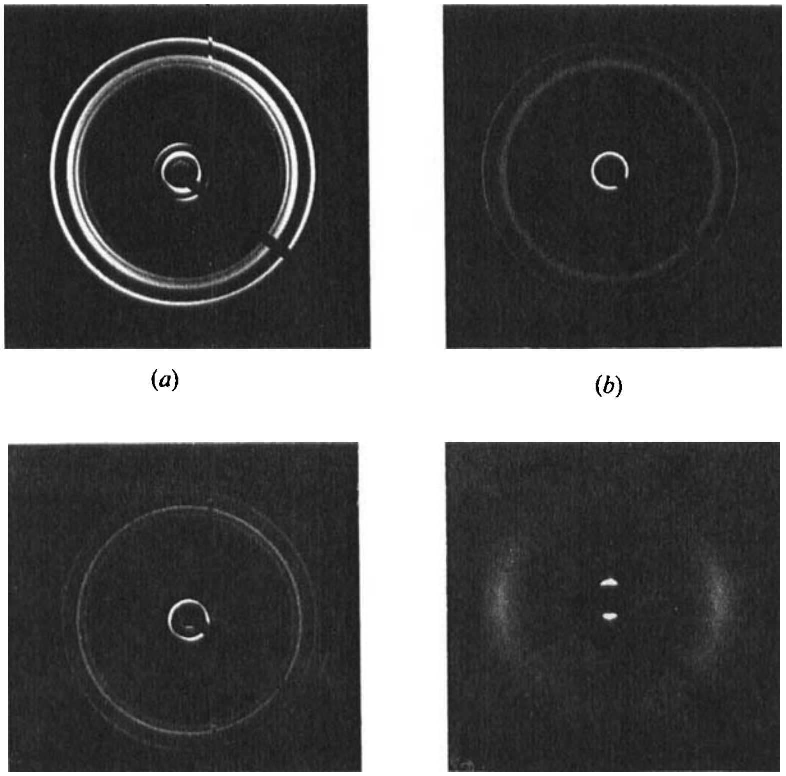
Figure 6. Conformation and packing of the crystalline MoMAc-Bi-65 at room temperature: (a) conformation of a single molecule, (b) packing in a triclinic unit cell, space group P$\bar{1}$.

flat film technique, many features of the conformation and packing may be realized in this crystal structure and in the other monomeric and polymeric materials in the crystalline and liquid-crystalline phases.

The X-ray pattern of two compounds, the monomer MoAc-Bi-65 and the dimer MGlu-Bi-65 are shown in figure 7 at room temperature and at elevated temperatures. The *d* spacings of the reflections of the crystalline monomeric compounds are collected in table 3 at room temperature. The underlying structure can be interpreted as a layered structure, since a periodic sequence of *d* spacings is present in the small angle scattering region and indicative of the thickness of a molecular layer. The layer is extremely well developed for the acrylates and reflections are observed up to the eighth diffraction order. This number is reduced to the fourth or sixth order for the methacrylates and even more for the saturated derivatives. Only one reflection is observed for *i*-But-Bi-65 in the small angle region.

The first order *d* spacing in the small angle region of the X-ray diffraction corresponds to the layer thickness and is correlated to some extent with the lengths of the molecules. The measured layer thickness lies in the range of 45–51 Å for the acrylates and 24–30 Å for the other monomeric materials. The lengths of the molecules considered here can be estimated to 22–29 Å with the use of models. Structures with double layers have to be considered for the acrylates to account for the large *d* values. The other compounds crystallize in single layer structures. A decisive conclusion cannot be reached for MoAc-Bi-64 and MoMAc-Bi-64.

The lateral molecular packing within the layers causes characteristic reflections with *d* spacings below 7–5 Å in the wide angle scattering region. A comparison of these reflections leads to strong similarities among the acrylates and for the methacrylates MoMAc-Bi-63 and MoMAc-Bi-65 with an odd number of C atoms in the terminal group. The packing of MoMAc-Bi-64 resembles the corresponding acrylate MoAc-Bi-64. An odd–even effect for the C-number of the terminal groups is observed concerning structural features, and similarities found between the acrylates MoAc-Bi-63



(*a*) (*b*)

(*c*) (*d*) ⟶

Figure 7. X-ray flat film exposures of some low molecular mass biphenyl derivatives; (*a*) monomer MoAc-Bi-65, , powdery sample at room temperature, (*b*) monomer MoAc-Bi-65, powdery sample heated to 355 K, (*c*) dimer MGlu-Bi-65, powdery sample at room temperature, (*d*) dimer MGlu-Bi-65, magnetic field oriented smectic phase (S_A) at 383 K (the direction of the magnetic field is indicated by an arrow).

and MoAc-Bi-65 as well as between the methacrylates MoMAc-Bi-63 and MoMAc-Bi-65 as also indicated by a comparison of the reflections in the small angle region.

The influence of different building blocks in the molecule on the structure is reflected in the X-ray exposures of the low molecular mass biphenyl derivatives by the appearance of characteristic small and wide angle diffraction peaks. The mesogenic stiff core with the flexible terminal groups lead to layered structures. The formation of layers is favoured by the double bond in the acid group as demonstrated by a comparison of the number of small angle reflections between unsaturated and saturated compounds. An additional methyl group at the acid residue disturbs the layered structure of the unsaturated derivatives with planar end groups by far more than the structure of the saturated compounds (compare acrylates with methacrylates and Pro-Bi-65 with *i*-But-Bi-65). The acrylate derivatives form predominantly double layers, the remaining compounds single layers. The thickness of the layers is influenced by the acid group as well as by the length of the terminal group (continuous increase for the acrylates). Similarities are found in the packing of the molecules within the layers for odd C numbers in the terminal groups for acrylates and methacrylates, which are reduced for even C number compounds (MoAc-Bi-64, MoMAc-Bi-64).

Table 3. *d* spacings in Å of X-ray reflections of low molecular mass biphenyl derivatives at room temperature; *n* and *n′* denote reflections of *n* and *n′* order in the small angle region, respectively. (*n*) represents a further, possible indexing. Estimated relative intensities: si, very strong; i, strong; s, weak; ss, very weak.

Compounds		-Bi-63	*n*, *n′*		-Bi-64	*n*, (*n*)		-Bi-65	*n*, *n′*
MoAc							s	51·0	*1*
	si	22·7	*2*	si	23·9	*2* (*1*)	si	24·8	*2*
	i	15·2	*3*				i	16·5	*3*
	s	11·3	*4*	s	12·0	*4* (*2*)	s	12·3	*4*
	ss	9·1	*5*	ss	9·7	*5*	ss	9·9	*5*
	i	7·5	*6*	i	8·0	*6* (*3*)	s	8·3	*6*
	ss	6·4	*7*	s	7·1	*7*	s	7·1	*7*
				s	6·4				
	ss	5·7	*8*	s	6·0	*8* (*4*)	s	6·2	*8*
	i	4·8		i	4·7		s	4·8	
				si	4·5		si	4·5	
	si	4·4					si	4·3	
	si	4·2		si	4·2		si	4·2	
	s	3·8		s	3·8		s	3·8	
	si	3·7		si	3·7		si	3·7	
MoMAc-	si	24·9	*1*	si	25·1	*1* (*2*)	si	29·2	*1*
	s	20·5	*1′*						
	i	12·4	*2*	i	12·5	*2* (*4*)	i	14·5	*2*
	s	10·2	*2′*						
				ss	9·8	(*5*)			
	i	8·3	*3*	i	8·2	*3* (*6*)	i	9·7	*3*
	s	6·9	*3′*				s	7·7	*1′*
	s	6·2	*4′*				s	7·3	*4*
	si	5·1					si	5·2	
	i	4·8		s	4·8		i	5·0	
				i	4·6				
				si	4·3				
				si	3·8		si	3·8	
	si	3·6					si	3·6	
	Prop-Bi-65		*n*	*i*-But-Bi-65		*n*			
	si	26·3	*1*	si	27·0	*1*			
	ss	13·0	*2*	ss	12·0				
	s	8·7	*3*	s	8·3				
				ss	6·3				
	si	4·5		si	4·5				
	si	4·2		si	4·2				
	si	3·8		si	3·8				

The following structural models can be proposed and are based on the length of the molecules derived from the known conformation of MoMAc-Bi-65. The calculated lengths of the acrylate molecules, forming double layers, are larger than the measured *d* spacings. A tilt of the molecules in the layers, most probably packed in an antiparallel fashion, as well as a partial overlap, explains this structural feature, which also occurs in the single layers of MoMAc-Bi-63 and MoMAc-Bi-64. The length of the molecules and layer thickness approximately agrees for Prop-Bi-65. The molecules may then be arranged perpendicular to the single layer surfaces. A similar packing has to be assumed for *i*-But-Bi-65. The flat film X-ray exposure of a crystalline, powdery sample of the dimer MGlu-Bi-65 only shows a few reflections (figure 7 (*c*)) and appears quite different from the exposures of the crystalline monomeric compounds. The *d* spacings of the small angle reflections favour a single layer structure. The layer thickness of 26·2 Å is of approximately the same size as the saturated, monomeric compound Prop-Bi-65.

7. Phases at higher temperatures

Powdery samples of the materials MoAc-Bi-64, MoAc-Bi-65 (figure 7 (*b*)), MoMAc-Bi-65 and Prop-Bi-65 have been heated to just below the anisotropic-isotropic phase transition, and X-ray exposures taken at that temperature. The X-ray diagrams exhibit a distinct, reduced number of reflections as compared to the crystalline phase at room temperature. However, more reflections in the wide angle region are observed than usually for known higher ordered smectic phases as, for example, S_E, S_G, S_H. The sample of Prop-Bi-65 shows a coarse-grained X-ray pattern with many reflections at higher temperature from which a second crystalline modification for this compound is concluded.

In contrast, the X-ray exposure at the elevated temperature of the dimer MGlu-Bi-65 represents a little ordered phase with very few reflections in the small angle scattering region and a diffuse wide angle peak (figure 7 (*d*)). The kind of orientation of the molecules in a magnetic field [4] and the X-ray pattern described are indicative of a S_A phase with perpendicular arrangements of the molecules to the smectic layers.

A comparison of *d* spacings of the strong X-ray reflections for the monomers between the high temperature phase and the crystalline modifications at room temperature shows an increase in *d* value of the small angle reflections representative of the layer thickness for the acrylates, and a decrease for Prop-Bi-65 and MoMAc-Bi-65. This increase may be due to a changing tilt angle of the rodlike molecule towards zero with respect to the unit cell axis or to a decreasing overlap of a pair of antiparallel arranged molecules. The *d* spacings of the reflections representing the lateral packing (wide angle reflections) are quite comparable for all monomers in the high temperature forms.

The comparison of monomeric, dimeric and finally polymeric compounds exhibits a distinct decrease in the order of the underlying structure, which was detected for the crystalline phase at room temperature, as well as for the high temperature forms in polarization microscopic (textures) and X-ray investigations.

This work was supported by a grant from Deutsche Forschungsgemeinschaft.

References

[1] Finkelmann, H., Happ, M., Portugall, M., and Ringsdorf, H., 1978, *Makromolek. Chem.*, **179**, 2541.

[2] Hahn, B., Wendorff, J. H., Portugall, M., and Ringsdorf, H., 1981, *Colloid Polym. Sci.*, **259**, 875.

[3] Hans, K., 1985, Diplomarbeit, Institut für Physikalische Chemie der TU Clausthal, Clausthal-Zellerfeld.

[4] Hans, K., 1988, Dissertation, TU Clausthal, Clausthal-Zellerfeld.

[5] Kostromin, S. G., Sinitzyn, V. V., Talroze, R. V., Shibaev, V. P., and Platé, N. A., 1982, *Makromolek. Chem. rap. Commun.*, **3**, 809.

[6] Shibaev, V. P., Kostromin, S. G., and Platé, N. A., 1982, *Eur. Polym J.*, **18**, 651.

[7] DEMUS, D., and ZASCHKE, H., 1984, *Flüssige Kristalle in Tabellen II* (VEB Deutscher Verlag für Grundstoffindustrie).
[8] HANS, K., and ZUGENMAIER, P., 1988, *Makromolek. Chem.*, **189**, 1189.
[9] The single crystal analysis was carried out by Dr. V. Enkelmann, Max-Planck-Institut für Polymerforschung, Mainz, and will be published elsewhere.