

The Influence of Flexible Segments on Liquid Crystalline Properties in Terms of Solubility Parameters. An Attempt at Quantitative Interpretation

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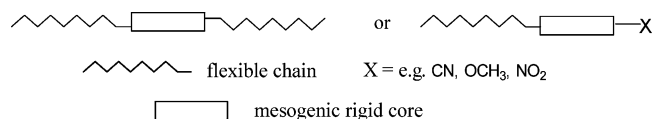
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The phase behavior of some rodlike block molecules has been reviewed with reference to the polarity of constituent segments. It was found that the ability of the mesophase formation is connected with differences in polar character between the flexible chains and rigid cores. Thus the polar poly(oxyethylene) group connected with the polar rigid core reduces mesophase stability but is advantageous when put together with some apolar building blocks. An attempt at quantitative estimation of the incompatibilities of different parts of molecules by means of Hansen solubility parameters δ and Flory interaction parameters χ has also been made. On the basis of χ parameters the Gibbs free energies of mixing of these segments were calculated. The changes of Gibbs free energy reflecting the compatibility of segments and their tendency to the phase separation and the volume fraction of mesogenic rigid core reflecting their ability to arrangement in one direction appear to be crucial in terms of type of the mesophase formation.

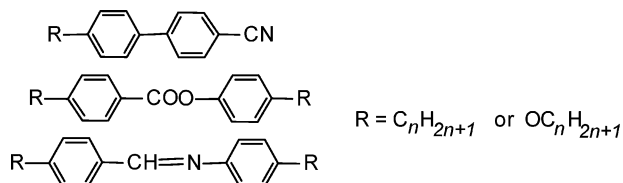
1. Introduction

When discussing the mesomorphic properties of matter, one often considers substances able to produce liquid crystalline phase belonging to one of two distinct classes of materials: the so-called amphiphilic and nonamphiphilic mesogens.¹ The simplest molecular architecture of amphiphilic molecules consists of a hydrophilic group connected to a lipophilic substructure. The remarkable feature of amphiphilic molecules is the tendency of their constituent parts to segregate in space into distinct microdomains¹—mixed with a polar or nonpolar solvent they form a variety of lyotropic organized phases. A typical example of amphiphilic molecules is soaps but also polyhydroxy compounds, carbohydrates or phospholipids, that are able to form lyotropic LC phases.²

The most common type of nonamphiphilic mesogens are rod-shaped anisometric molecules. Such compounds, giving rise to thermotropic mesophases, are called calamitic liquid crystals and are usually composed of a rigid part (two or more ring structures with or without linking group) and one or two flexible aliphatic chains attached directly to this rigid core.¹



Typical examples are

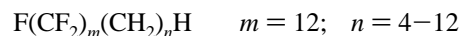


The molecule is therefore composed of several building elements (blocks) of different physicochemical properties (polarizability,

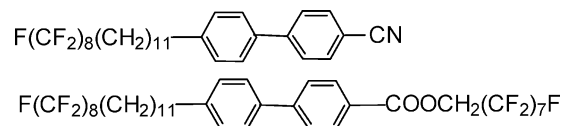
stiffness, shape). The organization of the rigid cores of rodlike molecules along a preferred direction is regarded as the main reason for the formation of nematic phase. Therefore their length-to-width parameter is of great importance in structure—property relationship. If this parameter is pretty large, the mesophase can exist even as the molecule consists only of some phenyl rings without any end substituents, e.g., quinquephenyl.

In a typical molecule of smectic mesogen the aromatic rigid cores and the flexible polymethylene chains are the incompatible subunits having tendency to segregate in separate domains. This effect is even more pronounced in the systems containing perfluorinated alkyl chains.^{3,4} The perfluorinated compounds are known to be chemically different compared with their hydrocarbon analogues (for example, they are incompatible in solubility terms). The fluorine atoms are of greater dimensions than the hydrogen atoms and favor all-trans conformations, and the actual configuration of the chain is helicoidal.⁵ As a consequence the perfluoroalkyl chains are much stiffer than their hydrocarbon analogues and their cross-section area (~ 0.27 – 0.35 nm²) is larger than that of alkyl chains (~ 0.18 – 0.22 nm²).⁶

The stiffness of perfluoroalkyl chain and its incompatibility with alkyl substituent result in smectic properties of partially perfluorinated aliphatic hydrocarbons.⁷



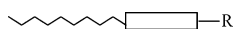
The combination of partially perfluorinated chains with rigid aromatic rings leads to block systems composed of at least three chemically different moieties, incompatible with each other, and enhances the stability of smectic phases.^{8,9}



The poly(oxyethylene) chain is another example of an incompatible segment applied as the flexible part of liquid crystalline structures, differing in chemical properties from the

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TABLE 1: Liquid Crystalline Properties of Monomesogenic 4-Substituted Benzoic Acid Derivatives of General Formula

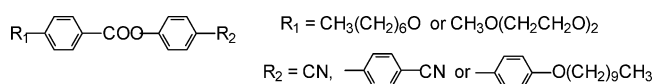
Containing Alkyl or Poly(oxyethylene) Chains¹⁹

No	Chemical formula	Block system	Philicity	Meso-phase	Phase transitions [°C]
1A	$\text{CH}_3(\text{CH}_2)_6\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	N-P ¹⁾	bi-	N	Cr 71.6 N 82 I ²⁾
1B	$\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	P-P	mono-	-	Cr 67.0 I
2A	$\text{CH}_3(\text{CH}_2)_6\text{O}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	N-P	bi-	N	Cr 89.0 N 246.0 I ²⁾
2B	$\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	P-P	mono-	N	Cr 107.7 N 202.8 I
3A	$\text{CH}_3(\text{CH}_2)_6\text{O}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{OC}_{10}\text{H}_{21}$	N-P-N	tri-	S	Cr 123.8 SmA 158.2 N 182.0 I
3B	$\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{OC}_{10}\text{H}_{21}$	P-P-N	bi-	S	Cr 112.2 SmA 124.7 N 161.5 I
4A	$[\text{CH}_3(\text{CH}_2)_6\text{O}-\text{C}_6\text{H}_4-\text{COOH}]_2$	N-P-N	tri-	S	Cr 92 SmC 98 N 146 I ²⁾
4B	$[\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2-\text{C}_6\text{H}_4-\text{COOH}]_2$	P-P-P	mono-	-	Cr 127.2 I

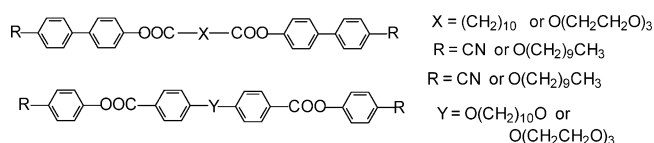
¹⁾ P, polar; N, nonpolar building block. ²⁾ Phase transition temperatures were taken from refs 24 and 25.

poly(methylene) substituent.^{10–12} According to literature reports, it destabilizes liquid crystalline phases in some cases¹³ but promotes in others.¹⁴ Poly(oxyethylene) substituents are useful as headgroups in nonionic surfactants with the interesting feature of complexing alkali metal cations;¹⁵ these complexes are thermotropic liquid crystalline polyelectrolytes. The other field of its application is the synthesis of ferroelectric liquid crystals, especially chiral side chain oligosiloxanes.^{16,17}

In our previous works we have compared the influence of polymethylene and poly(oxyethylene) chains or spacers on mesomorphic properties of some monomesogenic (containing one mesogenic rigid core) compounds¹⁸



and some bismesogenic derivatives (so-called dimers)^{19,20}



We have observed that in all these systems the replacement of poly(methylene) spacer or substituent by a poly(oxyethylene) one brings about essential changes in the type of mesophase in the presence of mesogenic rigid cores consisting of two aromatic rings. In this work we have made an attempt to demonstrate that this effect depends on the cohesion of rigid and elastic segments and their distribution in the calamitic system.

Although the concept of microsegregation of incompatible parts of mesogenic molecules as a driving force for the formation of liquid crystalline phase is now well established,^{6,10,21,22} the quantitative estimation of such interactions is difficult. The only

approach has been made by Tschierske et al.²³ who compared the polarity of some linking groups in nonconventional liquid crystalline molecules by means of solubility parameters. The possibility of taking into account the Flory parameter in qualitative estimations has been suggested as well.^{6,10}

We made an effort to develop this approach systematically to the above-described typical mesogenic systems by discussing the phase separation effects in terms of solubility parameters δ and Flory interaction parameters χ of constituent parts of simple block molecules. Subsequently this attitude was extended to some literature examples of liquid crystalline substances of similar structures.

2. General Characteristics of Investigated Compounds

The synthesis and characterization of compounds presented in Tables 1 and 2 were described elsewhere.^{18–20} The data for compounds **1A**, **2A**, and **4A** were taken from refs 24 and 25.

We employed the biphenyl, benzoyloxy phenyl, or benzoyloxybiphenyl rigid cores bearing different end groups: polar cyano or nonpolar oxydecyl substituents. The flexible alkyl and oxyethylene segments were chosen this way to ensure the same dimensions (comparable or the same number of atoms) in order to fix attention on the differences subsequent to polar or nonpolar character.

We applied chains consisting of 8 atoms (e.g., oxyheptyl and 4-[2-(2-methoxyethoxy)]ethoxy groups, Table 1) or spacers made up from 10, 12, or 14 atoms (bismesogenic compounds, Table 2). These segments are long enough to show the differences in polar character retaining at the same time the comparable conformations of appropriate chains.

The conformation of poly(methylene) chains (in alkyl or alkoxy groups) in solid phase is usually trans. This type of conformation we commonly take into consideration by calculating the molecular length. The long poly(oxyethylene) chain in

TABLE 2: Properties of Bismesogenic Compounds of General Formula

No	Chemical formula	Rigid core	End group	Block system	Phili-city	Meso-phase	Phase transi-tions [°C]
5A	OOC(CH ₂) ₁₀ COO		CN	P-N-P	tri-	N	Cr 145.0 N 185.0 I
5B			CN	P-P-P	mono-	-	Cr 154.0 I
6A	O(CH ₂) ₁₀ O		CN	P-N-P	tri-	N	Cr 166.0 N 191.5 I
6B	O(CH ₂ CH ₂ O) ₃		CN	P-P-P	mono-	-	Cr 202.0 I
7A	OOC(CH ₂) ₁₀ COO		C ₁₀ H ₂₁ O	N-P-N-P-N	penta-	-	Cr 162.5 I
7B			C ₁₀ H ₂₁ O	N-P-P-P-N	tri-	S	Cr 112.5 SmA 121.1 I
8A	O(CH ₂) ₁₀ O		C ₁₀ H ₂₁ O	N-P-N-P-N	penta-	N	Cr 117.6 N 136.2 I
8B	O(CH ₂ CH ₂ O) ₃		C ₁₀ H ₂₁ O	N-P-P-P-N	tri-	S	Cr 92.8 SmA 124.1 I

polymeric molecules adopts a trans–gauche–trans conformation for the monomer units, and as a consequence a helical structure containing seven monomer units and two turns is obtained.²⁶

The structure of shorter oligooxyethylene chains was investigated in molecules of nonionic surfactants of general formula CH₃(CH₂)_{*n*-1}(OCH₂CH₂)_{*m*}OH.²⁷ In bulk solid state for *n* ≥ 5, the molecular conformation greatly depends on oxyethylene chain length. As a number of oxyethylene units increases the conformation changes from a highly extended to a helical. This conformational transition takes place between *m* = 3 and *m* = 4, so the four or more units are necessary for establishing the helical structure. In regard to this we assumed that applied chains (two oxyethylene units) or spacers (three oxyethylene units) retain all-trans conformations. The calculated molecular geometry (semiempirical AM1, Hyper-Chem) confirmed this supposition.¹⁹ However this modeling does not reveal the differences in flexibility between alkyl and oxyethylene chains.

To avoid the changes in molecular shape connected with the odd–even effect, the flexible chains (oxyheptyl and 4-[2-(2-methoxyethoxy)]ethoxy groups, 8 atoms, Table 1) or spacers (compounds **5A,B** and **7A,B**, 14 atoms, Table 2) were selected to keep the same number of atoms (carbon + oxygen) in both substituents.

The length of tri(oxyethylene) spacer connected by means of oxygen atoms to mesogenic cores (compounds **8B** and **6B**, 10 atoms) differs from 1,10-dioxydecamethylene (compounds **6A** and **8A**, 12 atoms); however, the parity of spacers was the same in both cases.

3. Results and Discussion

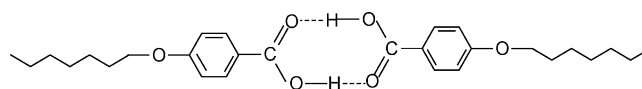
3.1. The Influence of the Polarity of Elastic Segments on Mesogenic Properties of Block Molecules. In this section we will summarize briefly the results of our studies on mesogenic

properties of some calamitic compounds consisting of two, three, and five building blocks, which will serve as a starting point for later discussion.

Let us consider first the simple system composed of one polar mesogenic rigid core and one or two flexible end groups (Table 1).

The compounds listed in Table 1 consisted of two- or three-ring mesogenic rigid cores. All of them are 4-substituted benzoic acid derivatives. Some of these compounds are cyanophenyl or cyanobiphenyl esters. The CN end group conjugated with phenyl rings belongs to the mesogenic core of polar character. Therefore, compounds **1A,B** and **2A,B** consist of two–rigid and flexible–parts; on the other hand compounds **3A,B** can be treated as consisting of three segments: a mesogenic rigid core and two flexible substituents.

In the case of substituted benzoic acids (**4A,B**) existing in the dimeric structures, one has to take into account the long lathlike structure with a three-ring core and two flexible chains. This way compounds **4A,B** form a three-block system, a central rigid part and two flexible chains.

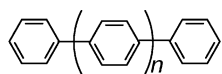


The above-mentioned constituent parts of molecules **1–4** are of different character. The mesogenic rigid cores (phenyl or biphenyl benzoates including polar CN end group or dimeric form of benzoic acid) are the most polar and polarizable parts of these block molecules. Owing to the presence of oxygen atoms, the poly(oxyethylene) chain is of polar character too, unlike the hydrocarbon substituents, which are examples of nonpolar segments. According to this criterion of polarity we

can distinguish the polar units (P, poly(oxyethylene) chains or mesogenic cores) and nonpolar ones (N, alkyl substituents). The aliphatic end groups are incompatible with mesogenic cores with respect to polarity and this way the calamitic molecules gain biphilic (nonpolar/polar: N–P, **1A**, **2A**) or triphilic (N–P–N, **3A**) character, which results in generation of mesogenic properties (Table 1).

The combination of poly(oxyethylene) substituents with polar mesogenic rigid cores gives rise to systems, which are monophilic with respect to the segment polarity (P–P, **1B**, **2B**; P–P–P, **4B**). One can expect, that the mutual solubility of polar mesogens and polar flexible segments in monophilic systems is much better than that in biphilic or triphilic ones. This is probably the reason for the lack of liquid crystalline properties in monophilic systems containing the two-ring core (**1B**) and 4-[2-(2-methoxyethoxy)]ethoxybenzoic acid (**4B**). The lack of liquid crystalline properties of 4'-[2-(2-allyloxyethoxy)]-ethoxy-4-biphenylcarboxylic acid (mp 189 °C) was observed by Hsiue.²⁸ This solubility effect is less pronounced in the case of mesogenic cores of higher length/width ratio i.e., a three-ring system, which generates a nematic phase while substituted with poly(oxyethylene) chains (**2B**). Its mesophase range (95.7 °C) and isotropization temperature (202.8 °C) are however of significantly smaller values than those of an analogous biphilic system (**2A**, 157 and 246 °C, respectively).

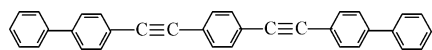
The above remarks are consistent with the observation that some molecules of poly(*p*-phenylenes)²⁴



$n = 3$ length/width ≈ 5.3 Cr 380 N 431 I

$n = 4$ length/width ≈ 6.2 Cr 435 Sm 465 N

or tolane oligomers²⁶



length/width = 6.35
Cr 296 SmA 302 N 347 I

form liquid crystalline phase if their length-to-width ratio is large enough to sustain the ordering of molecules. These molecules are of monophilic character too in terms of our concept. The critical ratio that stabilizes the nematic phase is 4.5, and the smectic phase in the absence of other than hydrogen substituents is more than 6, which means that the molecule should contain five or six phenyl rings connected by C≡C linking groups.²⁹ The essential problem in such a correlation is the suitable model series of compounds stable above their isotropization temperatures, which in the case of five or six phenyl rings are above 300 °C. Liquid crystalline molecules of lower mesophase range contain the alkyl chains, which add the flexibility to the rigid core structure that tends to reduce melting point. Additionally the long chains incompatible with cores facilitate the phase separation and lamellar packing required for smectic phase generation.

The mesogenic cores of compounds **1**, **2**, and **3** have length-to-width ratio about 3, 3.9, and 3.6, respectively, and the oxyheptyl end groups (**1A** and **2A**) are too short to result in phase separation and the formation of lamellar structures, but their flexibility diminishes the melting point enabling the existence of a nematic phase. They act as the internal solvent thereby making possible the alignment of molecules.

As can be seen from Table 1 the monophilic compound **2B** can be transformed into a biphilic one by the substitution of a

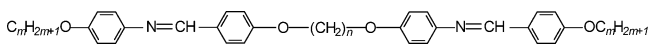
CN terminal group to alkyl nonpolar chain (**3B**). After this modification the biphilic (P–P–N) ester reveals a smectic phase owing to a longer (oxydecyl) flexible substituent, which enables microphase separation; however, the smectic phase formation is more efficient in triphilic systems (**3A**) than in biphilic analogues (**3B**).

The “philicity” concept can be extended to the more complex block molecules. For example the molecules presented in Table 2 are composed of three or five building blocks: they consist of two mesogenic cores (biphenyl or phenyl benzoate) linked by flexible chains: poly(oxyethylene) or polymethylene ones; some of them contain alkyl end groups additionally.

Taking into account the segment polarity, these molecules can be treated as monophilic (P–P–P, **5B**, **6B**), triphilic (P–N–P, **5A**, **6A**; N–P–P–P–N, **7B**, **8B**) and pentaphilic (N–P–N–P–N, **7A**, **8A**). Both monophilic systems do not generate mesophases. The triphilic systems give rise to the nematic phase in the case of triblock molecules terminated by mesogenic core with the CN end group (P–N–P). It is generally known, that the cyanophenyl esters and cyanobiphenyl derivatives as mesogenic moieties favor the nematic phase formation. As we have mentioned above, the appearance of nematic phase is considered as a result of ordering of mesogenic rigid cores according to preferred orientational direction. Probably the C≡N substituent located strictly in the long molecular axis, coplanar and conjugated with the phenyl rings enhances the length/width ratio and favors the interactions between rigid cores over the microphase separation processes.

The formation of the smectic phase was observed for compounds **7B** and **8B**, which can be considered as examples of triphilic derivatives too, although they have a five block structure, since they consist of one central polar part (poly(oxyethylene) spacer and mesogenic rigid cores as one building block) and two nonpolar decyl chains. Their methylene counterparts (**7A** and **8A**) are of pentaphilic character (alternate alkyl chains and polar mesogenic cores), and we have observed mesogenic properties only for one of them (**8A**). Therefore it seems that the multiple change of polarity restrains from smectic phase (**8A**) or in some cases even liquid crystalline character (**7A**).

The kind of destabilizing influence of the spacer's length on lamellar ordering was observed in the case of some other dimers of general formula^{30,31}



The early members of this series exhibit exclusively smectic behavior, but on increasing the spacer length, the tendency for nematic behavior predominates.

It should be noticed that alternating combinations of alkyl and perfluoroalkyl units also diminishes the mesogenic properties of calamitic liquid crystalline compounds.⁴

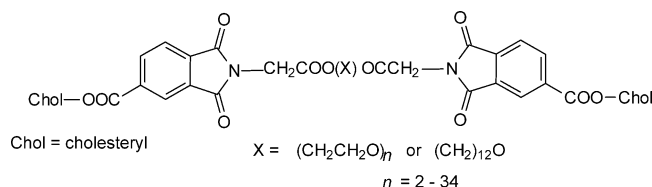
According to literature reports^{13,32,33} the poly(oxyethylene) spacers have an inherently low mesogenic propensity relative to the polymethylene segments. Our results give some explanations to this problem, indicating that the influence of spacer on mesomorphic properties depends on the type of other segments in the molecule. Polar poly(oxyethylene) spacers do not favor the stability of liquid crystalline phase when connected only with polar rigid cores,³⁴ because of monophilic character of the whole molecule. But if the molecular structure contains suitable segments of sufficiently nonpolar character, it could even enhance the mesophase stability. We have found that this condition can be also fulfilled by nonpolar mesogenic rigid core, e.g., cholesteryl moiety.³⁵ The poly(oxyethylene) spacer stabi-

TABLE 3: Liquid Crystalline Properties of Bismesogenic Esterimides³⁵

X	n^a	mesophase range (°C)
(CH ₂ CH ₂ O) _n	2	SmC 225 N* 235 I
(CH ₂ CH ₂ O) _n	4.5	SmC 216 N* 224 I
(CH ₂ CH ₂ O) _n	9	SmC 187 N* 195 I
(CH ₂ CH ₂ O) _n	13.5	Cr 52 SmC 157 I
(CH ₂ CH ₂ O) _n	34	Cr 35 SmC 110 I
(CH ₂ CH ₂ O) _n	45	Cr 54 I
(CH ₂) ₁₂ O		Cr 100 I

^a n represents the average number of oxyethylene units in the spacer.

lizes the existence of the liquid crystalline phase in the series of cholesteryl bisesterimides



Their mesogenic properties are presented in Table 3. The bisesterimides with poly(oxyethylene) spacer can be considered as compounds of triphilic character (N–P–N); they consist of two hydrocarbon (cholesteryl) mesogenic cores and a polar central part (two highly polar imide groups and a polar spacer). The liquid crystalline properties have been observed in the range 1–34 poly(oxyethylene) units in the spacer. On the contrary the bisesterimide with dodecamethylene spacer X = (CH₂)₁₂O, which, due to the presence of hydrocarbon spacer is a pentaphilic compound (N–P–N–P–N), does not form any mesophase.³⁵

We can conclude that the biphilic or triphilic character of the molecule, i.e., the presence of segments of different character, is responsible for a mesophase formation. If the differences are large enough to ensure the microphase separation, the smectic phases are favored over nematic. If the segments have similar properties, i.e., if the cohesion interactions between the same segments are almost equal to adhesion between different parts of molecule, the mutual solubility of elastic and rigid segments leads to isotropization.

3.2. Solubility Parameters of Elastic and Rigid Segments.

The question arises how to estimate the polarity of particular segments and their mutual interactions in calamitic block molecules. Taking the above discussion into account, we tried to apply the solubility parameters³⁶ (cohesion or Hildebrand parameters) as a measure of the cohesion interactions between particular segments of mesogenic molecules.

The solubility parameter is a numerical value that indicates the relative solvency behavior of a specific solvent. It provides an easy numerical method for quick prediction of the extent of interactions between materials, particularly liquids and polymers. The cohesion parameter approach to mixtures is that a material with a high cohesion parameter value requires more energy for dispersal than is gained by mixing it with a material of low cohesion parameter. In this case the materials are immiscible. On the other hand, two materials with similar cohesion parameter values gain sufficient energy on dispersal to permit mixing. The method is attractive for practical use because it predicts the properties of a mixed system knowing only the properties of the components.

The stabilizing or cohesive effect in condensed phases can be expressed in terms of the cohesive energy density (cohesive pressure)

$$c = -U/V \quad (1)$$

TABLE 4: Hildebrand Solubility Parameters for Selected Solvents³⁷

solvent	δ (MPa ^{1/2})
perfluorohexane	12.1
hexane	14.9
diethyl ether	15.1
benzene	18.8
chloroform	20.0

where c is the cohesive energy per unit volume, the cohesive energy density, U is the cohesive energy, the energy associated with the net attractive interactions, and V is the molar volume of the liquid.

The cohesive energy density could be derived from the heat of vaporization. It indicates the energy of vaporization per unit volume and is a direct reflection of the degree of van der Waals forces holding the molecules of liquid together. Since the solubility of two materials is only possible when their intermolecular attractive forces are similar, one might also expect that materials with similar cohesive energy density values would be miscible.

The cohesive energy density is the basis of the original definition of Hildebrand solubility parameter δ . This parameter was developed from regular solutions theory, but the concept has been extended to other systems. Hildebrand proposed the square root of the cohesive energy density as a numerical value indicating the solvency behavior of a specific solvent

$$\delta = c^{1/2} = (-U/V)^{1/2} \approx [(\Delta H - RT)/V]^{1/2} \quad (2)$$

where δ is the solubility parameter, ΔH is the molar enthalpy of vaporization, R is the gas constant, and T is the temperature (K).

Table 4 lists several solvents in order of increasing Hildebrand parameter.³⁷

As can be seen from Table 4 the δ values change gradually and point to the specific properties of perfluorinated hydrocarbons—their solubility parameters are the lowest, so they are immiscible with the majority of organic solvents. This difference reflects the disparity between the fluoroalkanes and other organic solvents and proves the usefulness of the application of cohesion parameters as a measure of interactions between particular segments of block molecules.

For volatile liquids (e.g., solvents) cohesive energy density and hence δ can be determined experimentally by measuring ΔH and V . In the case of more complexed compounds or polymers, solubility parameters can be correlated with the chemical structure of molecule. According to the additive method³⁸ the solubility parameters are calculated from a set of additive constants F , called molar attraction constants, by the relationship

$$\delta = [(\sum F)/V]^{1/2} \quad (3)$$

where $\sum F$ is the molar attraction constant summed over the groups present in the compound.

Values of molar attraction constants for most common groups in organic molecules can be estimated on the basis of vapor pressure and heat of vaporization data for a number of simple molecules. The solubility parameters δ values for typical building blocks of liquid crystalline molecules calculated according to the data compiled by Fedors³⁸ are presented in Table 5. It was necessary to define first the boundaries of building blocks in these calculations. We assumed that the mesogenic cores consist of phenyl rings and conjugated atoms (hybridization sp² or sp) of carbon, oxygen, or nitrogen.

TABLE 5: Hildebrand δ and Hansen δ_t Parameters Calculated for Building Blocks of Monomesogenic and Bismesogenic Compounds

building block	δ (Hildebrand) (MPa ^{1/2})	δ_t (Hansen) (MPa ^{1/2})
—OC ₁₀ H ₂₁	17.0	16.8
—OC ₇ H ₁₅	16.8	16.9
—O(CH ₂) ₁₀ O—	18.3	18.5
—O(CH ₂ CH ₂ O) ₂ CH ₃	17.8	19.8
—OOC(CH ₂) ₁₀ COO—	20.8	19.9
—O(CH ₂ CH ₂ O) ₃ —	19.6	22.0
—OOCO(CH ₂ CH ₂ O) ₃ COO—	23.1	24.1
—C ₆ H ₄ —C ₆ H ₄ —	24.6	24.2
—C ₆ H ₄ —COO—C ₆ H ₄ —C ₆ H ₄ —	25.5	25.0
—C ₆ H ₄ —C ₆ H ₄ —CN	26.3	25.0
—C ₆ H ₄ —COO—C ₆ H ₄ —C ₆ H ₄ —CN	26.4	25.0
—C ₆ H ₄ —COO—C ₆ H ₄ —	25.8	25.4
—C ₆ H ₄ —COO—C ₆ H ₄ —CN	27.0	25.6
—C ₆ H ₄ —COOH (dimeric form)	~31.3 ^a	~26.1 ^a
CH ₃ O(CH ₂ CH ₂ O) ₂ —C ₆ H ₄ —COO—C ₆ H ₄ —C ₆ H ₄ —	22.00	22.6
—C ₆ H ₄ —C ₆ H ₄ —OOC—O(CH ₂ CH ₂ O) ₃ —COO—C ₆ H ₄ —C ₆ H ₄ —	24.4	23.8
—C ₆ H ₄ —COO—C ₆ H ₄ —O(CH ₂ CH ₂ O) ₃ —C ₆ H ₄ —COO—C ₆ H ₄ —	24.4	23.8

^a Values approximated, because of lack of the appropriate data for dimeric form of carboxylic acids.

According to this definition the rigid core includes the oxycarbonyl group linked via carbon (sp²), but the ether oxygen atoms —O— (sp³) belong to the flexible chains or spacers.

In Hildebrand's development of the cohesion parameter approach to miscibility, the existence of polar interactions and specific interactions such as hydrogen bonding has been neglected. Numerous attempts have been made to improve the predictive ability of solubility parameters, but the most comprehensive approach has been that of Hansen³⁹ in which the solubility parameter is divided into three components: due to the dispersion forces δ_d , due to dipole forces δ_p , and due to hydrogen bonding (or in general due to donor–acceptor interactions) δ_h . The Hansen total cohesion parameter, δ_t

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (4)$$

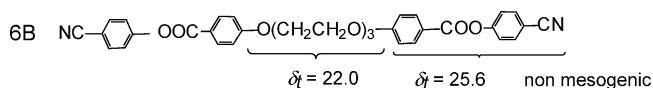
corresponds to the Hildebrand parameter δ , although these two quantities may not be identical because they are determined by different methods.

In this case methods based on structural contributions were developed too. The data of van Krevelen and Hoftyzer³⁹ were employed for the estimating of the Hansen parameters. δ_t for different building blocks are compiled in Table 5.

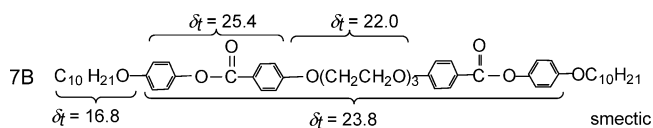
Comparing the values of δ_t and δ one can notice that only Hansen parameters are consistent with the differences in polarity between alkyl and poly(oxyethylene) chains: their values are located between those typical for alkyl substituents and characteristic for polar rigid cores. We will use mainly the Hansen (δ_t) parameters in the further discussion because of its greater accuracy. The Hildebrand (δ) ones will be employed only in the case of lack of other data.

The δ_t values of Hansen parameters for aromatic rigid cores were about 24–26 MPa^{1/2}, while for the flexible alkyl chains parameters were about 17–18 MPa^{1/2}, which in turn differ significantly from those of poly(oxyethylene), 20–24 MPa^{1/2}. On the basis of these results, we are able to support a hypothesis concerning the application of the solubility parameters for estimation of the incompatibility of segments in the molecule.

In the case of compatible segments (monophilic compound like **6B**, $\Delta\delta \approx 3.5$ MPa^{1/2}), the differences in the solubility parameters between particular parts of the molecule are not sufficiently large, the liquid crystalline phase cannot be formed.



For biphilic and triphilic molecules the smectic phase usually appears if this difference is about 7 MPa^{1/2}, i.e., in the presence of a sufficiently long alkyl substituent



The precise limiting values depend on the structure and philicity of the compound. The mesogenic properties of rigid cores play an important part—with increasing of the length of this core the tendency to parallel orientation of molecules prevails and nematic phase can appear. The alternate, with respect of polarity, character of the pentaphilic compounds does not favor the smectic phase formation, irrespective of differences in solubility parameter values of particular segments. This problem will be discussed later.

3.3. Segment Compatibility in Terms of the Flory Interaction Parameters and Changes of Gibbs Free Energy in the Course of Mesophase Formation. The problem of compatibility as miscibility on a molecular scale is a fundamental subject in polymer chemistry. It plays the major role in the molecular state of dispersion, in the morphology of two phase mixtures, and in the adhesion between phases and consequently influences most properties and applications. Flory and Huggins employed most of the crucial assumptions of regular solutions theory and thus a simple form for the change of Gibbs free energy (ΔG_{mix}) for the formation of polymer blends was obtained⁴⁰

$$\Delta G_{\text{mix}} = RT(N_A^{-1} \Phi_A \ln \Phi_A + N_B^{-1} \Phi_B \ln \Phi_B + \Phi_A \Phi_B \chi_{\text{mix}}) \quad (5)$$

where Φ_A and Φ_B are volume fractions of solvent and polymer, N_A and N_B are degree of polymerization, and χ_{mix} is the interaction parameter χ .

The Flory–Huggins equation is based on modified lattice theory which takes into account the large differences in the size between molecules of polymers (or between solvent and polymer) in addition to intermolecular interactions. The interaction parameter χ is empirical and can be determined experimentally, but it can be calculated too on the basis of Flory–Huggins and Hildebrand–Scatchard theories in terms of solubility parameters⁴⁰

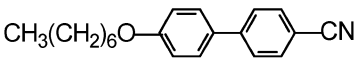
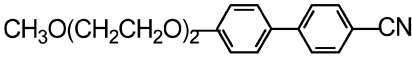
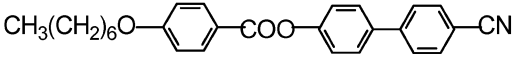
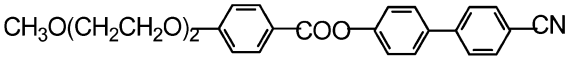
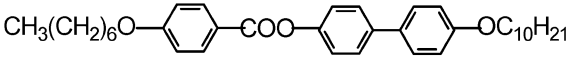
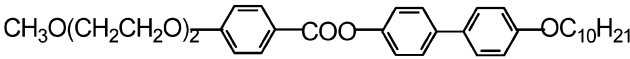
$$\chi_{\text{mix}} = (\delta_A - \delta_B)^2 V_r (RT)^{-1} \quad (6)$$

where V_r is the reference volume, an average volume of repeated units, and δ_A and δ_B are solubility parameters for A and B.

Parameter χ plays an important role in the theory of polymer solutions. It provides a measure of the thermodynamic affinity of a solvent to the polymer, or a measure of the quality of the solvent. The smaller χ is, the more stable the solution is relative to the pure components and the more likely that the system is miscible over a wide range of concentrations. On the basis of χ values, solvents may be classified as good $\chi < 1/2$ or poor $\chi > 1/2$ solvents. For very poor solvents χ may be higher than unity and for very good ones may be negative.

In our opinion the estimation of the compatibility of the segments in liquid crystalline molecules by means of parameter χ

TABLE 6: Interaction Parameters, Volume Fractions of Mesogenic Rigid Cores and Changes of Gibbs Free Energy for Selected Monomesogenic Compounds¹

No	Chemical formula	Block system	χ^2_{MX}	χ^2_{MY}	$\Phi_{mes}^{3)}$	ΔG [kJ/mol]
1A		N-P nematic	4.28		0.52	+0.93
1B		P-P -	1.68		0.57	-0.67
2A		N-P nematic	4.37		0.60	+0.93
2B		P-P nematic	1.90		0.65	-0.53
3A		N-P-N smectic	4.03	4.78	0.28	+0.86 ⁴⁾
3B		P-P-N smectic	1.51	4.78	0.30	+0.21 ⁵⁾

¹ Compounds **4A** and **4B** were omitted because of lack of appropriate data for dimeric form of carboxylic acids. ² X = CH₃OCH₂CH₂OCH₂CH₂O or CH₃(CH₂)₆O; Y = CH₃(CH₂)₉O; M, mesogenic rigid core. ³ Φ_{mes} volume fraction of mesogenic rigid core calculated according to ref 38. ⁴ ΔG was calculated under the assumption, that both alkyl substituents interact with mesogenic rigid core; the interaction parameter amounts then to 4.80. ⁵ ΔG was calculated under the assumption, that the molecule consists of polar (mesogenic core and 4-[2-(2-methoxyethoxy)]ethoxy chain) and apolar (oxydecyl chain); the interaction parameter between them amounts to 3.17.

is possible because one can find some analogies between bis-mesogenic liquid crystals and polymeric compounds. The transition properties of dimer depend critically on the length and parity of the flexible spacer in a manner strongly reminiscent to that observed for semiflexible main chain polymers, and this similarity has resulted in their use as model compounds for the polymeric systems. This analogy can be extended to other polyphilic block molecules as well, because considering the interactions between polymer molecules, which consist of a number of chemical units linked together in some fashion, it is necessary to investigate the interactions between the segments defined in terms of identifiable chemical units. The similarity refers to the restrained mobility of polymer molecules and of molecules in liquid crystalline phase (particularly in lamellar ordered phases) too.

Contrary to solubility parameters, the χ parameters reflect the interactions **between** two distinct parts of molecules taking into considerations the differences in their dimensions. Furthermore, with introduction of χ values to the equation (5), changes of Gibbs free energy of mixing of molecules (ΔG_{mix}) can be calculated. Substances are miscible if this change is of negative value. In relation to liquid crystalline block molecules the miscibility (i.e., compatibility) of segments implies the lack of mesogenic properties as a consequence.

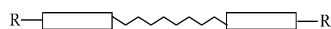
The first two terms of the right-hand side in the Flory–Huggins equation (5) are related to the entropy of mixing, and the third term containing the parameter χ is assigned to the enthalpy of mixing. For polymers having large or infinite molar mass, the entropic contribution is small and the miscibility of the system depends on the value of the enthalpy of mixing (it can be achieved when χ is negative). In the case of molecules of smaller dimensions the entropic term is of considerable negative value diminishing thus the significance of χ . The interaction parameters χ and changes of Gibbs free energy of mixing for esters of 4-substituted benzoic acid and bismesogenic compounds are collected in Tables 6 and 7.

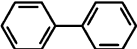
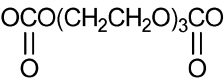
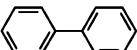
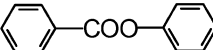

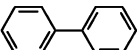
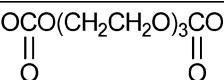
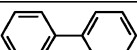

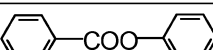
In the case of nonmesogenic monophilic compound **1B** the ΔG is negative (−0.67 kJ/mol) and the χ parameter is of rather low value compared with other data from Table 6, reflecting

the compatibility between both segments. The appearance of smectic phase in **3A** and **3B** results from incompatibility due to the presence of decyloxy chains (positive ΔG value and $\chi_{MY} = 4.78$ in both cases).

Compounds **1A** and **2A** form only nematic phase despite of their ΔG and χ values comparable to those of **3A**. We have suggested earlier that in these cases the tendency to order mesogenic cores of high length-to-width ratio in one direction prevails. Considering our calculations presented in Table 6, we suggest now that this effect is quantitatively connected with the volume fraction of mesogenic rigid cores Φ_{mes} calculated additively according to ref 38. This parameter complements the length-to-width ratio especially in the case of long aliphatic chains because is not dependent upon their conformations. The ordering interactions between the mesogenic cores predominates over the microphase separation if the volume fraction exceeds 0.5—these are examples of biphilic compounds **1A** and **2A**. If this volume fraction is sufficiently high, it enables the nematic phase formation even in the case of monophilic compound **2B** ($\Phi_{mes} = 0.65$), irrespective of negative ΔG value.

This assumption was confirmed by the data obtained for bismesogenic compounds (Table 7). The monophilic dimers **5B** and **6B** do not form any mesophase ($\Delta G \sim -1$ kJ/mol and $\chi = 0.04$ or 0.68, respectively). The smectic phase exists in triphilic compounds **7B** and **8B**, but in these cases interactions between end oxydecyl groups and the central polar parts of molecules are crucial ($\Delta G \sim +1$ kJ/mol and $\chi = 3.18$ or 4.49, respectively). For compound **6A** the interaction parameters are comparable with those for **7B**, but due to the lower positive ΔG value (+0.58 kJ/mol) and greater volume fraction of mesogenic core ($\Phi_{mes} = 0.63$), the nematic phase appears. The influence of $\Phi_{mes} > 0.5$ in the case of nematic phase formation is strongly marked if ΔG is of slightly negative value (**5A**, $\Delta G = -0.26$ kJ/mol), but fails if ΔG reaches ca. −1 kJ/mol (**5B**, **6B**). Pentaphilic compound **7A** ($\Delta G = -0.06$ kJ/mol) independently of high χ values (1.16 and 3.19) does not form a smectic phase. It is probably the result of diffusion forced by the alternation of chemically different segments, which hinders the phase separation processes for low molecular weight

TABLE 7: Interaction Parameters, Volume Fractions of Mesogenic Rigid Cores and Changes of Gibbs Free Energy Calculated for Selected Bismesogenic Compounds of General Formula

No	Chemical formula			Block system	χ^1_{MX}	χ^1_{MY}	$\Phi_{mes}^{2)}$	ΔG [kJ/mol]
	Spacer	Rigid core	End group					
5A	OOC(CH ₂) ₁₀ COO		CN	P-N-P nematic	1.71		0.57	-0.26
5B			CN	P-P-P	0.04		0.63	-1.24
6A	O(CH ₂) ₁₀ O		CN	P-N-P nematic	3.22		0.63	+0.58
6B	O(CH ₂ CH ₂ O) ₃		CN	P-P-P	0.68		0.72	-0.83
7A	OOC(CH ₂) ₁₀ COO		C ₁₀ H ₂₁ O	N-P-N-P-N	1.16	3.19	0.27	-0.06 ³⁾
7B			C ₁₀ H ₂₁ O	N-P-P-P-N smectic	5 · 10 ⁻⁴	3.18	0.29	+0.78 ³⁾
8A	O(CH ₂) ₁₀ O		C ₁₀ H ₂₁ O	N-P-N-P-N nematic	2.77	4.49	0.31	+0.42 ³⁾
8B	O(CH ₂ CH ₂ O) ₃		C ₁₀ H ₂₁ O	N-P-P-P-N smectic	0.54	4.49	0.34	+0.93 ³⁾

¹ X, spacer; Y, oxydecyl substituent; M, mesogenic rigid core. ² Φ_{mes} volume fraction of mesogenic rigid core calculated according to ref 38. ³ ΔG values were calculated under the assumption that the molecule consists of a central part (two mesogenic cores and the spacer) and two end groups (oxydecyl chains).

compounds. In some cases this effect can be reduced by other intermolecular forces, e.g., donor–acceptor interactions⁴¹ or for polymer molecules by the ordering influence of polymer chain. Pentaphilic dimer **8A**, having positive change of free energy of mixing ($\Delta G = +0.42$ kJ/mol) generates only nematic phase.

From the results of our calculations presented in Tables 6 and 7 arises that the smectic phase can be formed as long as the change of Gibbs free energy is of positive value and volume fraction of mesogenic rigid core does not exceed 0.5. The positive or slightly negative ΔG values favor the nematic phase in biphilic or triphilic systems on condition that the volume fraction of a mesogenic rigid core amounts more than 0.5. The block molecules do not form any mesophase if ΔG is of high negative value (it implies the miscibility of segments in the case of monophilic compounds) or if they consist of five alternating parts, in respect of polarity (it implies the forced diffusion of incompatible segments even though ΔG is about 0). On this score the poly(oxyethylene) spacers compatibility with aromatic rings (compounds **7B** and **8B**) can play an important part in molecular architecture of mesogenic molecules.

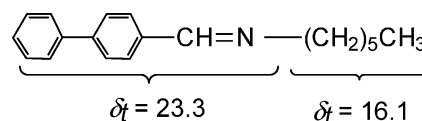
3.4. Interaction Parameters and Changes of Gibbs Free Energy for Selected Examples of Liquid Crystalline Compounds. To prove our hypothesis, similar calculations for some other mesogenic molecules were carried out. We concentrated our attention on some literature examples of compounds with short rigid cores creating the smectic phase.

We have considered some partially fluorinated compounds of similar structure first. The low values of the solubility parameters for perfluorinated hydrocarbons intensify the polyph-

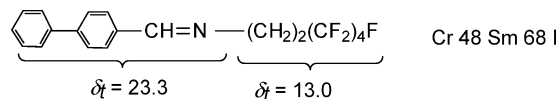
TABLE 8: Interaction Parameters, Volume Fractions of Mesogenic Rigid Cores, and Changes of Gibbs Free Energy for 4-Phenylbenzylideneamine Derivatives

chemical formula	phase transitions (°C)	χ	Φ_{mes}	ΔG (kJ/mol)
C ₆ H ₅ –C ₆ H ₄ –CH=N–(CH ₂) ₅ CH ₃	nonmesogenic	2.48	0.52	–0.07
C ₆ H ₅ –C ₆ H ₄ –CH=N–(CH ₂) ₂ (CF ₂) ₄ CF ₃	Cr 48 Sm 68 I	6.04	0.44	+ 0.80

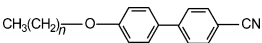
ilic character of partially fluorinated molecules and can be determinant for mesogenic properties. It is clearly visible in the case of relatively short mesogenic rigid cores.⁴² The *N*-hexyl-(4-phenylbenzylidene)imine is not a liquid crystalline compound



whereas its partially fluorinated analogue reveals smectic properties (Table 8)



The introduction of a perfluorinated chain increases the difference between solubility parameters of the segments. As a result the interaction parameter χ increases more than 2-fold (from 2.48 for the former to 6.04 for the latter; in these calculations

TABLE 9: Interaction Parameters, Volume Fractions of Mesogenic Rigid Cores, and Changes of Gibbs Free Energy for Some Cyanobiphenyl Derivatives


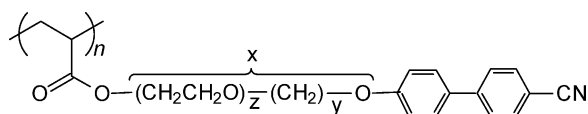
<i>n</i>	phase transitions ²⁵ (°C)	δ_t (MPa ^{1/2})	χ_{MX}	Φ_{mes}	ΔG (kJ/mol)
4	Cr 53 N 67.5 I	17.1	2.90	0.56	+0.071
5	Cr 58 N 76.5 I	17.0	3.18	0.52	+0.25
6	Cr 53.5 N 75 I	16.9	3.45	0.49	+0.42
7	Cr 54.5 Sm 67 N 80 I	16.9	3.70	0.46	+0.57

semifluorinated chains were treated as one part of the molecule because the hydrocarbon segment was made from two methylene units and the fluorinated part was the predominant one) and Gibbs free energy of mixing becomes of positive value. This, combined with relatively short mesogenic core, favors lamellar structure.

Another problem is the correlation between the dimensions of an alkyl substituent and the appearance of the smectic phase. It is commonly known that the generation of the smectic phase (lamellar arrangement of the molecules) is facilitated in the presence of relatively long terminal alkyl chains. E.g., in the series of mesomorphic cyanoalkoxybiphenyl derivatives (Table 9) the first three homologues form a nematic phase; the smectic phase appears in the case of octyloxy or longer substituents.²⁵

Comparing the solubility parameters, one can hardly find the difference—the values of δ_t lower slightly (1% within the data in Table 8) with the length of the alkyl chain, but the Flory interaction parameter taking into considerations the data for both interacting segments ($\Delta\delta_t$ and V_t) illustrates clearly the increasing incompatibility between them. It results in increasing ΔG values. At the same time the molar volume fraction of the mesogenic core decreases, leading to the microphase separation and formation of the smectic phase.

The last example concerns polymeric liquid crystals: Akiyama and co-workers⁴³ have investigated the influence of segmented spacer on mesogenic properties of side chain liquid crystal polymers. They have synthesized some liquid crystalline polyacrylates having 4-cyanobiphenyl as a typical mesogenic group and a spacer composed from poly(oxyethylene) and poly(methylene) segments. The appearance and the type of mesophase was dependent on constituent parts of the spacer. The segments—poly(oxyethylene) and poly(methylene)—differ in polarity, so we tried to interpret the results in terms of interaction parameters.



We have calculated interaction parameters, volume fractions of mesogenic rigid cores, and changes of Gibbs free energy values for some polymers synthesized by Akiyama; they are presented in Table 10.

In agreement with our previous results, the poly(oxyethylene) spacer connected with the cyanobiphenyl rigid core does not favor the liquid crystalline phase formation—in the case of miscible segments the calculated ΔG values were about -1.5 kJ/mol. On exchange of this spacer to a poly(methylene) one, the authors obtained LC phases—nematic for the shorter spacer ($y = 4$, $\Delta G = -1.09$, $\Phi_{mes} = 0.65$) or smectic in the case of a longer one ($y = 11$, $\Delta G = +0.16$, $\Phi_{mes} = 0.41$). The smectic phase can be also generated by adding to the poly(oxyethylene) spacer a poly(methylene) segment incompatible with other parts

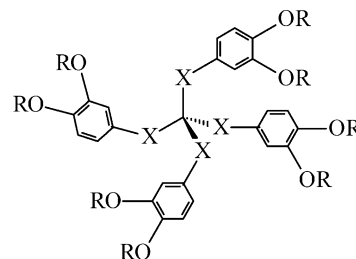
TABLE 10: Interaction Parameters, Volume Fractions of Mesogenic Rigid Cores, and Changes of Gibbs Free Energy for Selected Polyacrylates

<i>z</i>	<i>y</i>	liquid crystalline phases	χ	Φ_{mes}	ΔG (kJ/mol)
3	0		0.29	0.54	-1.53
4	0		0.25	0.47	-1.56
0	4	nematic	0.91	0.65	-1.09
0	6	nematic	1.78	0.56	-0.61
0	11	smectic	3.06	0.41	$+0.16$
3	4	unidentified mesophase	1.54^a	0.42^a	-0.75^a
3	6	smectic	2.11^a	0.38^a	-0.39^a
3	11	smectic	3.41^a	0.31^a	$+0.30^a$

^a Φ_{mes} , ΔG , χ and were calculated as the mean values for the whole spacer.

of the molecule. As a result, a triphasic mesogenic molecule is obtained. We suppose that the role of this additional spacer placed between a polymer backbone and the mesogenic core is not only the decoupling and enhancement of ordering the mesogenic group but the introduction of the polyphlicity essential to phase separation and the formation of lamellar phase. ΔG changes are of positive ($z = 3$, $y = 11$) or slightly negative ($z = 3$, $y = 6$) values. The negative value can arise from the influence of the polymeric chain, which facilitates some additional arrangement and separation of more or less compatible segments. Besides, the elongation of the spacer results in decreasing of the volume fraction of the mesogenic rigid core and thus facilitates the phase separation.

There exist however several groups of nonconventional thermotropic liquid crystals with tetrahedral geometry, for example, some dendritic molecules forming the columnar mesophase, whose liquid crystalline properties can be explained only on the basis of microsegregation processes, because they possess neither anisometric structure nor strong amphiphilic character. A good example is the series of pentaerythritol derivatives synthesized by Tschierske et al.²³



X = CH₂OCO, CH₂NHCO, CH₂OCH₂, none

R = C_nH_{2n+1} n = 6,8,9,10,11,12,16

Most of them display a columnar mesophase although they do not have disklike rigid units. Their mesogeneity is driven by self-organization of incompatible molecular parts differing in polar character, and this process influences the conformation of individual molecules, because only the more or less flat shape enables the microphase separation leading to columnar phase. The polarity of central part of molecules (CX₄) was estimated by the authors on the basis of solubility parameters; its increase promoted the mesophase stability, confirming the role of incompatibility of segments. On the contrary, the increase of rigidity of central part disfavors the mesophase formation hindering the suitable conformations of molecules.

We evaluated the solubility parameters of constituent parts of the polar core -X-C₆H₄- according to the methods applied earlier: for -CH₂COO-C₆H₄- it amounts about 27.1 MPa^{1/2}. Therefore the difference between, for example, decyloxy chain

(Table 5) amounts about 10 MPa^{1/2}, and the appropriate χ parameter is 5.7. This high incompatibility between the components is determinant for self-aggregation, but this time the smectic lamellar ordering of eight alkoxy chains is not possible because of small flexibility of central building block and the disklike arrangement is more probable.

4. Concluding Remarks

We showed, that in the case of relatively simple calamitic block compounds the generation of mesophase is influenced not only by their length-to-width ratio but also by the mutual miscibility of segments (resulting from the difference in polarity of flexible and rigid parts) and relative share of rigid and flexible parts, which can be expressed by means of their volume fractions.

The differences in polar character of elastic and rigid segments favor the formation of the mesophase. The best mesogenic properties show the bi- or triphilic (consisted of two or three alternating segments of different polarity) block compounds. The molecules of monophilic character (consisting of blocks compatible in respect of polarity) do not generate the liquid crystalline phase because the flexible segments act as internal solvent hindering thereby the arrangement of molecules.

We chose a group of very simple compounds, representative for typical calamitic liquid crystalline molecules for which the mutual compatibility of segments can be compared by means of easy calculated Hansen solubility parameter δ_i and Flory interaction parameters χ . Some of these examples were bismesogenic compounds, which establish bridges between low molecular liquid crystals and liquid crystalline polymers, so the application of concepts developed for polymer chemistry seems to be valid. To summarize the data presented above, we can conclude that the changes of Gibbs free energy together with the volume fraction of mesogenic rigid core allow us to predict the mesophase formation. Our considerations give some valuable directions for an appropriate design of simple mesogenic block molecules:

The mesophase cannot be formed if the difference between the solubility parameters of rigid and elastic segments amounts less than about 4 MPa^{1/2} for the sake of segments compatibility. For such miscible segments the change of Gibbs free energy of mixing (ΔG_{mix}) calculated on the basis of interaction parameters χ is of negative value.

On the contrary, calamitic block molecules consisting of incompatible (differing with respect to polarity) segments generate the mesophases and the ΔG_{mix} changes are of positive value indicating the immiscibility of the components.

The increasing positive values of ΔG_{mix} favors the formation of smectic phases, but the type of the mesophase depends also to a high degree on relative volume fraction of mesogenic rigid core and flexible chain. The smectic phase arises unless this parameter does not exceed 0.5. The greater than 0.5 contribution of rigid core favors the formation of nematic phase because the tendency to ordering of mesogenic rigid cores in one direction predominates other interactions.

The nematic mesophase can be formed even if ΔG_{mix} is of slightly negative value on the condition that the Φ_{mes} is significantly higher (≥ 0.6) than the fraction of flexible segment. In these systems the concentration of a flexible chain acting as a "poor" internal solvent is probably too low to disturb the rigid cores organization.

These observations allow us to give an explanation of the diverse influence of the poly(oxyethylene) segment on mesogenic properties of molecules. It is advantageous if the

molecule consists of some apolar building blocks besides the poly(oxyethylene) chain; this way the molecule gains bi- or triphilic character. On the contrary, the poly(oxyethylene) segment put together only with polar mesogenic rigid cores is ineffective in the mesophase generation giving rise to a monophilic molecule.

We are fully aware that this paper can be only considered as a starting point for precise quantitative description of the role of incompatibility of constituent parts of block molecules in self-aggregation processes in liquid crystalline phases. Our approach considers the incompatibility resulting from polarity of particular segments but does not take into account the rigid-flexible incompatibility. The other important limitation of the method developed above concerns the temperature conditions: the calculations were made on the basis of the standard (25 °C) data but applied to the discussion of liquid crystalline properties which generally appear in much higher temperatures. Therefore the experimental results and the calculations are more compatible if the mesophase exists at low temperature. Furthermore the method does not take into consideration steric effects or the functional group distribution in the segments, which are important in the mesophase formation besides the microphase separation processes.

References and Notes

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