Conformational Effects in Mesogenic Fragments in Liquid-Crystalline Side-Chain Polymers and Networks

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ABSTRACT: Side-chain liquid-crystalline polymers (linear and cross-linked) containing alkoxycyanobiphenyl as a mesogenic fragment were studied in solution and in bulk by FTIR spectroscopy. It was found for linear polymers that the transition from solution to bulk is accompanied by the appearance of new bands (satellites) at both sides of the C≡N mode in the FTIR spectrum. Introducing nonmesogenic fragments into copolymer together with the network formation does not affect their number and frequencies but changes their relative intensities. The appearance of satellites is assumed to be connected with the appearance of conformational inhomogeneity of the aromatic cores of mesogenic fragments by the interaction of their dipoles. This assumption was confirmed by quantum chemistry calculations of model molecules.

Introduction

The short distance character of intermolecular forces determining the stability of the liquid-crystalline (LC) state is the main reason for additive contributions from different molecular fragments into mesophase properties. This allows one to single out and analyze the role of different intramolecular degrees of freedom in the thermodynamical and physical properties of the LC state.

As had been found before for low molecular weight liquid crystals,[1−5] a change of conformation in mesogenic molecules substantially affects phase transition points and LC polymorphism. At the same time, transitions between different LC phases and the change of molecular ordering within a single phase are also accompanied by the change of conformation in molecular fragments.

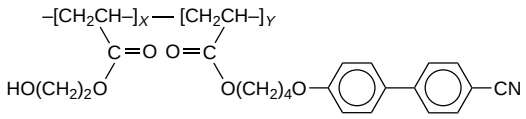
Of particular interest are conformational effects in conjugated mesogens which influence the conjugation strength and length. The most marked consequences of conformational effects could be expected in LC polymers containing such mesogenic groups as biphenyl, stilbene, or azomethyne[6] in the backbone or side chain.

The main goal of this paper is to investigate the relationship between the structure of side-chain linear and cross-linked LC polymers and the conformation of the mesogenic fragment—alkoxycyanobiphenyl—as related to the change of the LC structure when nonmesogenic fragments or cross-links are introduced into the mesogen-containing macromolecules.

FTIR spectroscopy combined with quantum chemistry calculations was used for the study because they both are known to be important and informative tools of the analysis of orientational and statistical properties of liquid crystals or the conformational structure of different molecular fragments.

Experimental Section

A mesogen-containing monomer was synthesized according to ref 7. Homopolymers and random copolymers having the structure



where X:Y = 0:100 and 10:90 were prepared by radical copolymerization of corresponding monomers in chlorobenzene at 65 °C for 35 h. 2,2′-Azobis(isobutyronitrile) (0.1% of the total weight of the monomers) was used as an initiator. The polymers were precipitated from a mixture of 1,2-dichloroethane and acetonitrile (4:1 v/v) into methanol. The yield of homo- and copolymers was 60%.

The copolymers were identified by FTIR spectroscopy. The composition of the copolymers was determined by UV spectroscopy using the value of the extinction coefficient measured for the homopolymer (296 nm).

The molecular mass characteristics of the copolymers were determined by gel-permeation chromatography using a Waters liquid-phase chromatograph equipped with a R401 differential refractometer.

Cross-linking was performed either with the cross-linking agent or by γ-irradiaion. For chemical cross-linking the powdered copolymer was dissolved in a mixture of 1,2-dichloroethane and acetonitrile (4:1 v/v), and a solution of a cross-linking agent, 4,4′-methylenediphenyl diisocyanate (MDI), in the same mixture of solvents was added. After a homogeneous solution was obtained, the mixture of solvents was distilled off. The copolymer containing the cross-linking agent was dried in a vacuum at room temperature. After complete removal of the solvent, the sample was placed in a thermal chamber, where the cross-linking proceeded for 1 h at 90 °C. The reaction was monitored by the disappearance of the melting peak due to the cross-linking agent (DSC) and by swelling of the samples in the 1,2-dichloroethane/acetonitrile mixture.

Under the conditions of complete consumption of the sol fraction and cross-linking agent, the cross-linking density was calculated from the stoichiometric ratios using the formula[8]

$$M_c = m_{cop}/2\upsilon_{mdi}$$

where m_{cop} is the weight of the copolymer and υ_{mdi} is the number of moles of the cross-linking agent.

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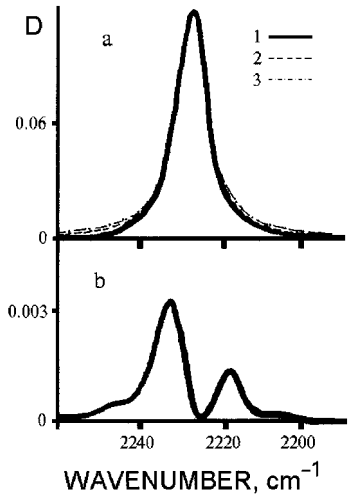


Figure 1. FTIR spectra of solutions of homopolymer (a: 1−5 wt %, 2−20 wt %) and copolymer (a: 3−20 wt %) and differential spectrum of the copolymer (b: the 20 wt % spectrum with respect to the 5 wt % one).

To perform cross-linking under the action of γ-radiation, film of a copolymer was placed in the ampules, which were evacuated for 1 h at a temperature of isotropic melt at 0.133 Pa. The ampules were sealed and irradiated (^{60}Co) at doses from 0.1 to 3 MGy at room temperature. The dose rate was 0.048 MGy/h. The gel dose was determined by the standard technique[9] from the gel fraction versus dose plots. To characterize the cross-linking density in the networks formed under the action of γ-radiation, the parameter M_w/M_c was calculated according to ref 8.

FTIR spectra of thin solid films as well as linear polymer solutions in an acetonitrile/dichlorethane mixture (1:4, v/v) placed in NaCl cells (0.03 mm thickness) were recorded with an IFS-113v (Bruker) spectrometer.

The set of combined modified FT-IR Brucker utility programs was used for the calculation of the spectrum second derivative. This permitted evaluation of the number and position of components of the composite $\nu_{C\equiv N}$ experimental band in the IR spectra. The individual components were approximated by a Gaussian function. A half-width of a single $\nu_{C\equiv N}$ band measured in the spectrum of the 5% polymer solution was used as a measure for the half-width of all the satellites. The above data were used for the procedure of spectra deconvolution by means of the standard Brucker programs BASINFO and BANDSIM.

Quantum chemistry calculations were carried out with the help of the MOPAC-6 program with the AM1 Hamiltonian[9] with full optimization of geometrical parameters.

Results and Discussion

Acrylic polymers containing cyanobiphenyl mesogenic groups are of great interest for studying the conformational structure of the mesogen by means of IR spectroscopy because the C≡N stretch is an individual mode and any vibration in the 2260−2190 cm^{-1} range should be unambiguously assigned to $\nu_{C\equiv N}$.[10−12]

FTIR spectra of linear homo- and copolymer solutions are shown in Figure 1. For solutions containing 5 wt % of a corresponding polymer one can observe a single $\nu_{C\equiv N}$ band at 2228 cm^{-1} (Figure 1a, curve 1) which can be very well described by the Gaussian curve. When the concentration is increased up to 20 wt %, this band is slightly broadened (Figure 1a, curves 2 and 3), but its half-width still remains unchanged. In the differential spectrum there appear several features of low intensity corresponding to the nitrile vibrations of mesogen fragments with frequencies different from those in spectra of less concentrated solutions (Figure 1b and Table 1).

Table 1. Relative Intensity (%) of the $\nu_{C\equiv N}$ Central Mode and Its Satellites (cm^{-1}) for Different Polymer Systems

	component frequencies					
polymer system	2243 ± 0.5	2233	2228	2217	2208	2198
Homopolymer						
5 wt % solution			100			
20 wt % solution	1.5	2.2	95.5	0.8		
solid film (nematic LC)	2.4	15.9	45.2	31.3	3.8	1.4
γ-Cross-Linked Homopolymer						
$\bar{M}_w/\bar{M}_c = 11.6$	5.6	17.7	22.0	24.9	20.3	9.5
Copolymer						
5 wt % solution			100			
20 wt % solution	1.5	2.5	95.1	0.8	0.2	
solid film (nematic LC)	1.9	16.8	39.7	33.6	5.6	2.3
Cross-Linked Copolymer						
chemical cross-linking						
$\bar{M}_w/\bar{M}_c = 0.5$[a]	3.2	23.7	37.5	31.2	3.2	1.2
$\bar{M}_w/\bar{M}_c = 2.3$	6.8	23.6	33.2	29.6	4.3	2.6
$\bar{M}_w/\bar{M}_c = 11.2$	9.0	27.0	32.5	24.9	4.5	2.1
γ-cross-linking						
$\bar{M}_w/\bar{M}_c = 11.6$	2.6	17.6	27.9	26.6	13.4	8.5

[a] Actually this system is branched rather than cross-linked.

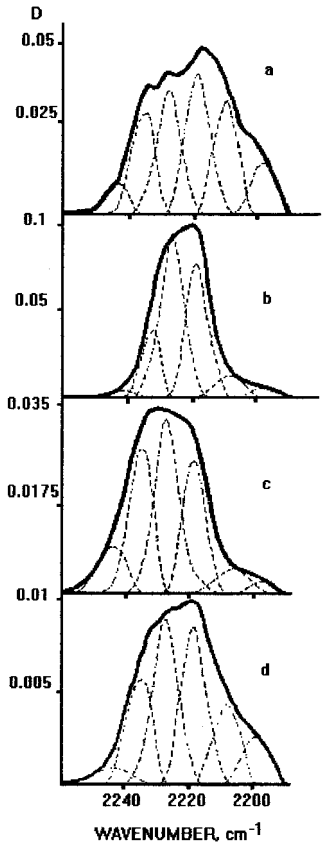
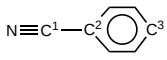
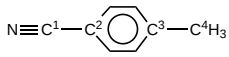
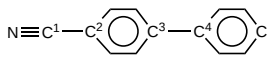
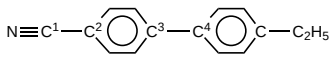
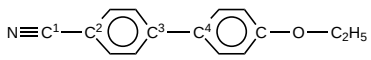


Figure 2. $\nu_{C\equiv N}$ band absorption profile in FTIR spectra of solid below polymer films below T_g: γ-cross-linked ($\bar{M}_w/\bar{M}_c$ = 11.6) homopolymer (a); linear copolymer (b); chemically cross-linked (M_w/M_c = 11.2) copolymer (c); γ-cross-linked ($\bar{M}_w/\bar{M}_c$ = 11.6) copolymer (d).

In contrast to solutions, the $\nu_{C\equiv N}$ mode for solid homo- and copolymer films as well as cross-linked samples becomes more complex (Figure 2). The presence of several extremes in the $\nu_{C\equiv N}$ spectral band shows that this band is a complex one. To evaluate the number and position of components, the second derivative of the spectral band contour was calculated. It is given in Figure 3 for a γ-cross-linked sample as an example. Due

Table 2. Model Molecules and Their C≡N Frequencies

molecule		frequency (cm^{-1})
$N\equiv C^1-C^2H$	acetonitrile (AN)	2255[21]
	benzonitrile (BN)	2231[22]
	methylbenzonitrile (methyl-BN)	2217[22]
	cyanobiphenyl (CNBP)	2237[22]
	ethylcyanobiphenyl (ethyl-CNBP)	2222[18]
	ethoxycyanobiphenyl (ethoxy-CNBP)	2228

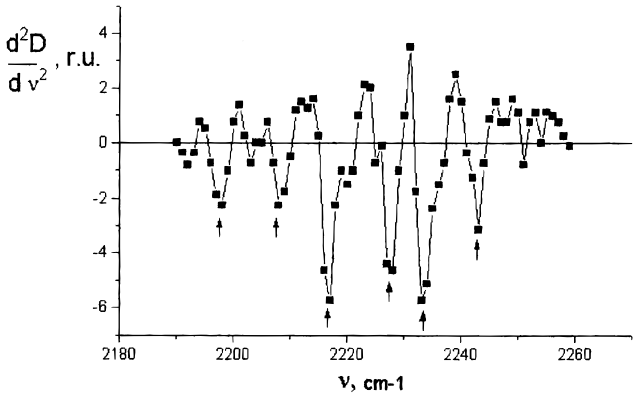


Figure 3. Second derivative of the IR spectra for γ-cross-linked ($M_w/M_c = 11.6$) copolymer.

to a high signal/noise ratio (600−1000 for the initial spectra), it is well seen that the band consists of six components including the main band at 2228 cm^{-1} and five satellites of different intensities (Table 1). Note that the position of every satellite found is the same for all the polymer systems studied and coincides with that for spectral bands in the differential spectrum of solutions. At the same time the contribution of various components into the total band intensity differs from system to system (Table 1). The high quality of the deconvolution is proven by the fact that the intensities of components significantly exceed the accuracy of synthetic spectra (correlation coefficient is equal to 0.998) calculated by a standard program.

The complex structure of the $\nu_{C\equiv N}$ mode may be caused by several reasons. It is known that the interaction with the participation of the free electron couple belonging to the nitrogen atom in the nitrile group (H-bonding, complexes formation, and coordination) leads to the growth of the $\nu_{C\equiv N}$ frequency while the dipole−dipole interaction is accompanied by its decrease.[12]

As seen from Table 1, the structure of the $\nu_{C\equiv N}$ band (the total number of the satellites and their frequencies) does not change after the introduction of foreign (hydroxyethyl acrylate) units or cross-links into the macromolecule. This means that the interaction of proton donors such as OH− or NH (in −HNCOO−) groups with the free electron couple in the C≡N group does not influence the band shape. On the other hand, the existence of satellites at both sides of the main C≡N band cannot be explained by dipole−dipole interaction only. In our opinion, all these facts reflect conformational inhomogeneity of the aromatic core of mesogenic fragments (alkoxycyanobiphenyls). We suppose that the most important factor which determines the shape of the $\nu_{C\equiv N}$ band results from the effective interaction of the $C^1\equiv N$ bond with the neighboring bonds and, in particular, with the conjugation changing force constant of the C^1-C^2 bond in the $N\equiv C^1-C^2-$ structure.[11,13]

Analysis of the data published[14−17] on the conformation of molecules containing biphenyl moieties shows that there is a certain relationship between the aromatic core conformation and the phase state of a particular system. For instance, crystalline biphenyl has a plane conformation, while the dihedral angle between benzene rings (φ_{min}) is equal to 44° in the gas phase[14] and 33° in a diluted solution.[15] The reason for this change is the difference in the strength of intermolecular interactions in the gas phase (almost free molecules) and in the solid state (strong interaction between neighboring molecules).

As for substituted biphenyls such as 4-*n*-alkyl-4′-cyanobiphenyl (alkyl-CNBP) and 4-*n*-alkoxy-4′-cyanobiphenyl (alkoxy-CNBP), which are able to form an LC phase, the alkyl radical length or its replacement for the alkoxyl radical only slightly affects the φ_{min} value. It is equal to 40−43° for crystalline samples and 36−38° for samples in the nematic phase.[15−17] A more significant change in the φ_{min} value (a drop of ∼10°) was observed in the FTIR study of the phase transition isotropic−nematic for alkyl-CNBP.[18]

Contrary to the change of the φ_{min} angle due to the phase transition, one has never observed any change in its magnitude within the one and the same phase. For example, the φ_{min} in methoxy-CNBP remains constant in the whole temperature range of the nematic liquid crystal.[17]

Nevertheless, as was mentioned above, we believe that the set of biphenyl-containing fragments having different conformations in polymer systems under investigation contributes to the spectral features observed. To find out a possible origin of these structures, one has to point out the existence of dimer associates with partial overlapping of aromatic cores and antiparallel dipoles together with single molecules (monomers) in both low molecular weight and polymer liquid crystals containing polar mesogenic groups such as cyanobiphenyl derivatives.[19−21]

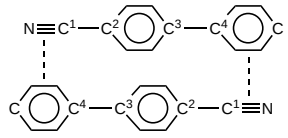
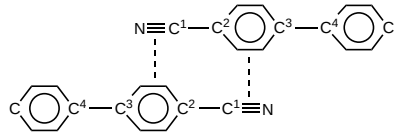
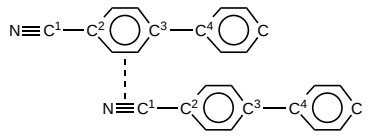
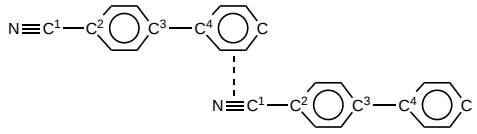
Two questions arise: whether biphenyl-containing molecules within the aggregates of different kinds can have a conformation different from that of a single molecule and how it can be displayed in IR spectra.

Table 3. Geometrical and Electronic Parameters Calculated for Model Molecules

	acetonitrile (AN)	benzonitrile (BN)	methylbenzonitrile (methyl-BN)	CNBP	ethyl-CNBP	ethoxy-CNBP
			Bond Length, A			
$N\equiv C^1$	1.1634	1.1635	1.1636	1.1635	1.1636	1.1636
C^1-C^2	1.4392	1.4214	1.4210	1.4211	1.4210	1.4211
C^3-C^4			1.4807	1.4626[a]	1.4611	1.4609
			Dihedral Angle, φ_{min} (deg)			
				41.3	39.9	40.3
			Bond Order			
$N\equiv C^1$	2.9012	2.8868	2.8857	2.8860	2.8858	2.8856
C^1-C^2	0.9931	1.0016	1.0024	1.0023	1.0025	1.0025
C^3-C^4			0.9997	1.0046	1.0066	1.0076
			Dipole Moment, D			
	2.894	3.337	3.729	3.718	4.186	4.519

[a] The C^3-C^4 bond length for biphenyl is equal to 1.507 Å.[23]

Table 4. Possible Dimeric Associates of CNBP[a]

dimer	structure	molecule
D_1		
D_2		
D_3		1 2
D_4		1 2

[a] Electronic overlapping resulting from nonvalent interaction is denoted by dotted lines.

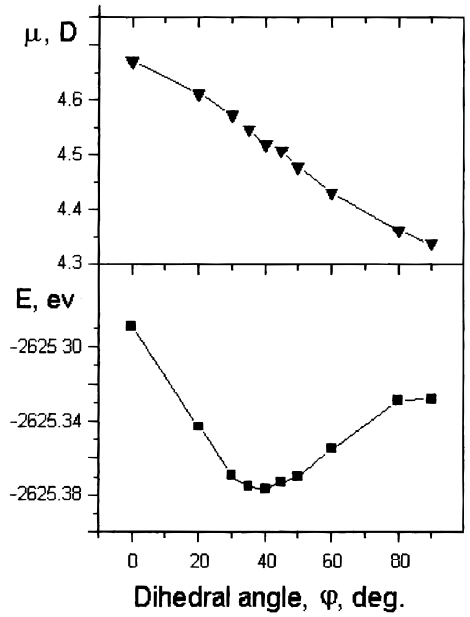


Figure 4. Calculated full energy and dipole moment of cyanobiphenyl with respect to the dihedral angle between phenylene rings.

To clear up the influence of the aromatic core conformation of the cyanobiphenyl mesogenic fragment on the geometry and electronic properties of the $C^1\equiv N$ and C^1-C^2 bonds which in turn determine the $\nu_{C\equiv N}$ frequency, we carried out a comparative analysis of a series of model molecules with increasing conjugation length using quantum chemistry calculations.

Model molecules and their C≡N stretch frequencies are presented in Table 2. This table shows that the frequency decreases with the appearance of a conjugation but it changes nonmonotonically with the growth of the conjugation length. Calculated geometrical and electronic parameters for model molecules are presented in Table 3. It is seen that the φ_{min} values calculated for isolated molecules of CNBP and its derivatives practically coincide with those obtained for the molecular ensemble in the solid state.[24−26] Parameters of the $C^1\equiv N$ and C^1-C^2 bonds calculated for these molecules change in a complex way but insignificantly. More pronounced changes proving the growth of the conjugation were obtained only in the region between benzene rings; namely, the C^3-C^4 bond length monotonically decreases, while the bond order (electronic bonding and Mullikenian population) monotonically increases. As far as the φ_{min} is concerned, it changes nonmonotonically but in correlation with the change of the C≡N stretch frequencies.

For this reason one could expect that the variation of the φ value for a chosen molecule would have a considerable affect on the other parameters. Figures 4 and 5 show that the variation of the φ value for ethoxy-CNBP from 0 to 90° essentially affects the dipole value and bond orders while the bond lengths change far less, with the parameters of the $C^1\equiv N$ and C^1-C^2 bonds changing complexly especially near the φ_{min}.

The potential energy for ethoxy-CNBP with φ equal to 0 and 90° increases up to 8.46 and 4.73 kJ/mol, correspondingly. These values are compatible with those obtained for biphenyl (6.0 and 6.5 kJ/mol[23]), but in contrast to biphenyl, the perpendicular conformation of the ethoxy-CNBP aromatic core is much more favorable than the plane one.

Thus, even a small deviation of the angle from φ_{min} is able to change the electronic parameters of a molecule, affecting the $\nu_{C\equiv N}$ frequency.

Going further from isolated molecules to dimers, it is necessary to consider a possible structure of dimers under investigation. There are two known antiparallel dimeric associates of CNBP (denoted as D_1 and D_2 in Figure 6 and Table 4). Together with these dimers

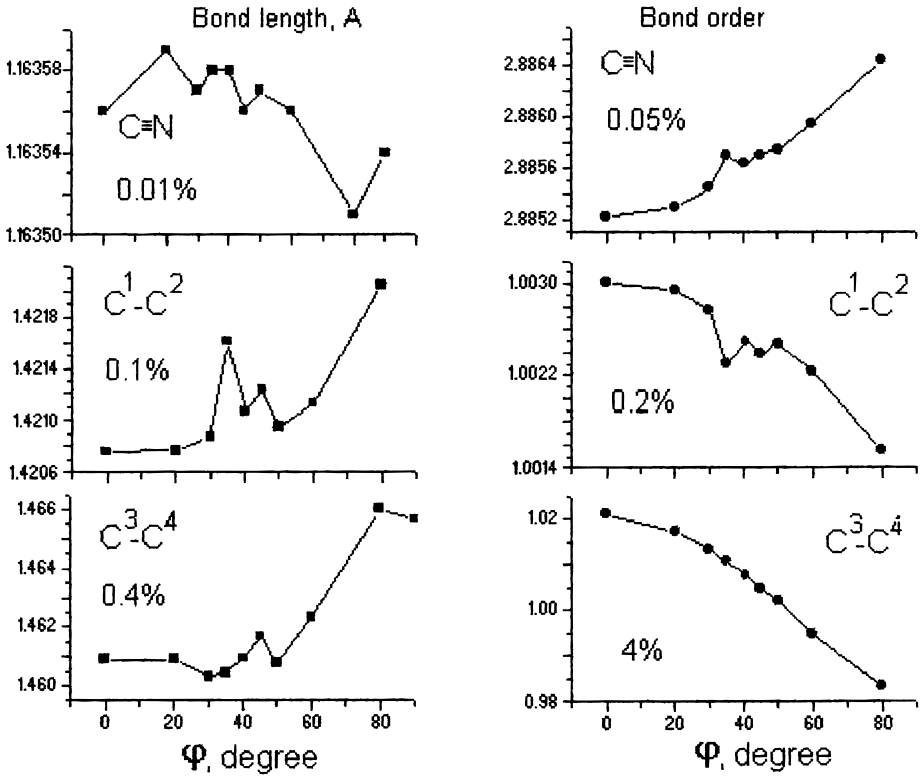


Figure 5. Geometrical and electronic parameters of cyanobiphenyl calculated with respect to the dihedral angle between phenylene rings. Maximal deviation limits for each parameter (in percent) are given in corresponding plots.

Table 5. Energetic Parameters Calculated for CNBP and Its Dimers

system	E, eV	ΔH, kJ/mol	dimerization energy, kJ/mol
CNBP	−1993.719	331.15	
dimers			
D_1	−3987.446	661.58	−0.72
D_2	−3987.453	660.81	−1.49
D_3[a]	−3987.435	662.62	0.32
D_4[a]	−3987.437	662.35	0.05

[a] Barrier processes with barrier heights of 1.46 and 0.94 kJ/mol for the D_3 and D_4 dimers, respectively.

which can be formed only by mesogenic fragments belonging to different low molecular weight molecules or polymer chain segments, we suggest considering stable parallel dimers (denoted as D_3 and D_4 in Figure 6 and Table 4) formed by neighboring mesogenic groups belonging to the same segment within the same polymer chain but shifted in respect to each other. The formation of such dimers should essentially be considered as caused by the polymeric nature of the side-chain cyanobiphenyl-containing systems which differentiates them from low molecular weight substances.

Data from Table 5 show that the formation of the antiparallel dimers (D_1 and D_2) is energetically favorable, with the D_2 formation being twice as preferable. At the same time, as one could expect, the formation of the D_3 and D_4 dimers needs additional energy. Nevertheless, the values of the dimerization energy are so small (0.32 and 0.05 kJ/mol) that these low barriers could be overcome in polymer systems. The reason for this is the cooperative effect of the macromolecular chain which makes the neighboring dipoles align parallel to each other along the chain. Therefore, one can expect that the four dimers could be formed within the same phase state of side-chain polymer.

Table 6 shows that in all cases dimerization leads to a change of the aromatic core conformation and conjugation strength. The C≡N bond orders for antiparallel dimers where both molecules are positioned equivalently to each other (D_1 and D_2) diminish, whereas φ_{min} increases for D_1 and decreases for D_2. For parallel dimers (D_3 and D_4) in which molecular positions are nonequivalent, the C≡N bond orders either remain unchanged or grow. The φ_{min} value decreases for second members of both dimers and either grows (for D_3) or remains the same for the first molecules.

Data comparison from Tables 1 and 6 allows one to assume that the complex structure of the $\nu_{C\equiv N}$ band in FTIR spectra of LC polymers with CNBP mesogenic fragments could be connected with the conformational inhomogeneity of the aromatic core of mesogen fragments, forming a mesophase. We should stress that although our calculations have been performed for the low molecular weight model there has been no report so far on the observation of such conformational structures in vibrational spectra for low molecular weight compounds neither in the isotropic nor in the nematic phase. This proves once more that the reason for this is the polymeric nature of the systems studied when the IR analysis was for LC polymers below glass transition temperature.[27] At these conditions lifetimes of different structures may be comparable to each other and high enough to visualize the whole set of conformers forming both "single" mesogens and dimeric associates with the help of IR spectroscopy. It is necessary also to point out that the coexistence of monomers and dimers of different structural types in low molecular weight liquid crystals was calculated and proven in ref 28.

As far as the assignment of the individual component of the $\nu_{C\equiv N}$ band to a certain chemical structure is concerned, one should consider the correlation between

Table 6. Geometrical and Electronic Parameters Calculated for Cyanobiphenyl and Its Possible Dimeric Structures

				D_3		D_4	
	CNBP	D_1	D_2	1	2	1	2
			Bond Length, Å				
$N\equiv C^1$	1.1635	1.1636	1.1635	1.1635	1.1636	1.1635	1.1634
C^1-C^2	1.4211	1.4213	1.4214	1.4215	1.4211	1.4211	1.4213
C^3-C^4	1.4626	1.4624	1.4625	1.4626	1.4625	1.4626	1.4623
			Dihedral Angle, φ_{min} (deg)				
	41.3	41.9	41.0	42.3	40.6	41.3	40.3
			Minimal Intermolecular Distance, Å				
		4.98	4.51	5.32		4.72	
			Bond order				
$N\equiv C^1$	2.8860	2.8857	2.8853	2.8860	2.8864	2.8861	2.8856
C^1-C^2	1.0023	1.0022	1.0023	1.0024	1.0022	1.0022	1.0022
C^3-C^4	1.0046	1.0047	1.0045	1.0045	1.0048	1.0045	1.0046
			Dipole Moment, D				
	3.718	0.466	0.154	7.198		8.169	

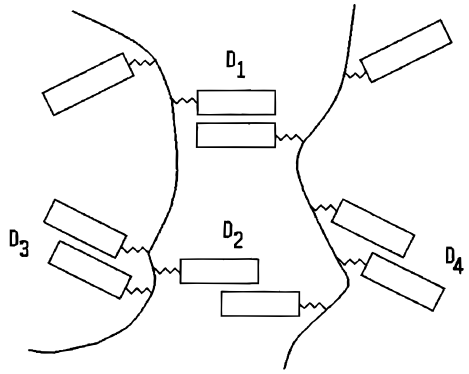


Figure 6. Schematic representation of possible dimeric associates for cyanobiphenyl.

Table 7. Tentative Assignment of Individual Components of the $\nu_{C\equiv N}$ Band

frequency of the component, cm^{-1}	dihedral angle, φ_{min} (deg)	assignment
2243	42.3	fragment 1 in D_3
2233	41.9	D_1
2228	41.3	solitary mesogenic fragment or fragment 1 in D_4
2217	41.0	D_2
2208	40.6	fragment 2 in D_3
2198	40.3	fragment 2 in D_4

the $\nu_{C\equiv N}$ frequency and φ_{min} value given in Table 7. Arguments in favor of this assignment are as follows:

(1) Since the formation of the D_2 dimer releases twice as much energy as the formation of the D_1 dimer (Table 5), the total amount of the D_2 dimers should exceed that of D_1 by 2 times. This is exactly what has been observed for linear polymers (Table 1).

(2) Introduction of rather extended fragments of cross-links belonging to the cross-linking agent homogeneously distributed over the polymer matrix[26] should stabilize "interchain" dimers (D_1 and D_2). Indeed, Table 1 shows that the total amount of such dimers in chemically cross-linked elastomers is higher than that in the linear copolymer (50.4%).

On the other hand, since every cross-link is a defect of the structure, the total amount of such dimers should decrease with the growth of the cross-linking density. It is seen from Table 1 that for the cross-linking density equal to 0.5 (branched system), 2.3, and 11.2 the total relative part of "interchain" dimers is equal to 54.9, 53.2, and 1.9%, correspondingly, and decreases with the growth of the cross-linking density.

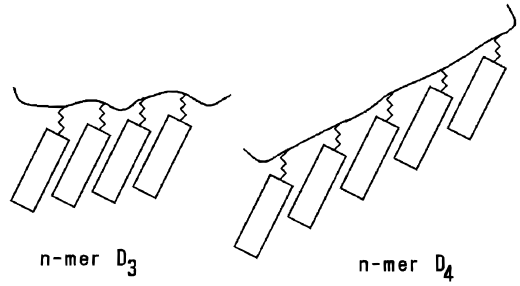


Figure 7. Schematic representation of possible *n*-meric associates for cyanobiphenyl.

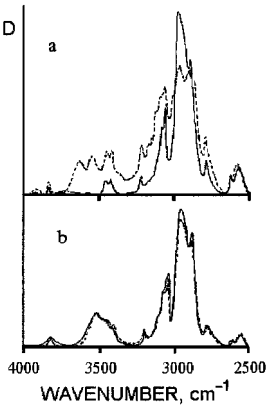


Figure 8. FTIR spectra of homo- (a) and copolymer (b) before (solid line) and after (dashed line) γ-cross-linking (M_w/M_c = 11.6).

(3) In contrast to chemically treated elastomers, cross-links in γ-irradiated polymers are shorter and are distributed inhomogeneously.[27] FTIR spectra show (Figure 8) that under γ-irradiation cross-links are created mainly at the expense of the CH and CH_2 groups (the FTIR intensity in the range of 2800−3000 cm^{-1} decreases). In this case an intramolecular process with participation of nonmesogenic and mesogenic units is possible together with the intermolecular cross-linking. Short cross-links arising here should destabilize the "interchain" dimers (D_1 and D_2) and could stabilize the parallel dimers D_3 and D_4. Indeed, Table 1 shows that the total part of the "interchain" dimers in γ-ray cross-linked elastomers considerably decreases in comparison with linear polymers (from 47.2 to 42.6% in homopolymer and from 50.4 to 44.2% in copolymer). This decrease occurs mainly at the expense of "long" dimers (D_2), while the amount of "short" (D_1) dimers even

slightly increases. At the same time a relative part of parallel dimers (D_3 and D_4) substantially grows.

Note that the number of the first and second members in parallel dimers (Figure 6 and Table 4) should be equal, but on the other hand they could join neighboring mesogenic fragments, forming correspondent *n*-mers (Figure 7). In such *n*-mers there are several fragments of the second kind (2) per one fragment of the first kind (1). On γ-induced cross-linking not only the relative amount of parallel dimers but also the length of their *n*-mers may increase.

To summarize, one may conclude that the high sensitivity of the C≡N stretch mode allows one to find the presence of mesogenic fragments with a different electronic state of the C≡N group in nematic side-chain polymers (linear and cross-linked) visualized by FTIR spectroscopy. The set of satellites is supposed to reflect the variety of structure fragments which form the LC phase in the side-chain LC polymer. The coexistence of various structures based on mesogenic fragments which are either elements or defects of the LC phase is connected with the macrostructure of the polymeric matrix and related to the change (broadening and distortion) of the $\nu_{C\equiv N}$ band profile.

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References and Notes

(1) Dong, R. J.; Tomchuk, E.; Waid, C. G.; Visitainer, J. J.; Bock, E. *J. Chem. Phys.* **1977**, *66*, 4121.
(2) Dianoux, A. J.; Volino, P. *J. Phys.* **1980**, *41*, 1147.
(3) Aver'janov, E. M.; Zhuikov, V. A.; Adomenas, P. V. *Pis'ma Zh. Eksp. Teor. Fiz.* **1981**, *33*, 262; *Zh. Eksp. Teor. Fiz.* **1981**, *81*, 210.
(4) Volino, P.; Martins, A. F.; Dianoux, A. J. *Mol. Cryst. Liq. Cryst.* **1981**, *66*, 37.
(5) Aver'janov E. M.; Zyrjanov, V. Ja.; Zhuikov, V. A.; Ruolene, Ju. I. *Zh. Strukt. Khim.* **1983**, *24*, 101.
(6) Platé, N. A.; Shibaev, V. P. *Comb-shaped Polymers and Liquid Crystals*; Plenum Press: New York, 1987.
(7) Shibaev, V. P.; Kostromin, S. G.; Platé, N. A. *Eur. Polym. J.* **1982**, *18*, 651.
(8) Zoubarev, E. R.; Talroze, R. V.; Platé, N. A. *Polym. Sci.* **1997**, in press.
(9) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
(10) Bellamy, I. J. *The Infrared Spectra of Complex Molecules*; Methuen & Co. Ltd.: London, 1954.
(11) Kirov, N.; Simova, P. *Vibrational Spectroscopy of Liquid Crystals*; House of Bulgarian Academy of Science: Sofia, Bulgary, 1984.
(12) Denisov, G. S.; Ryltsev, E. V.; Suglobov, D. N. *Opt. Spektrosk.* **1967**, *23*, 628.
(13) Bellamy, L. J. *Advances in Infrared Group Frequencies*; Methuen: Bungay, Soffolk, 1968.
(14) Almenningen, A.; Bastiansen, O.; Fernholt, L. *J. Mol. Struct.* **1985**, *128*, 59.
(15) Celebre, G.; Longeri, M.; Sicilia, E.; Emsley, J. W. *Liq. Cryst.* **1990**, *7*, 731.
(16) Sinton, S. W.; Zax, D. B.; Murdoch, J. B.; Pines, A. *Mol. Phys.* **1984**, *53*, 333.
(17) Emsley, J. W.; Horne, T. J.; Zimmermann, H.; Celebre, G.; Longeri, M. *Liq. Cryst.* **1990**, *7*, 1.
(18) Zhuikov, V. A. Ph.D. Thesis, L. V. Kirenskii Physical Insitute, SO RAS, Krasnojarsk, 1986.
(19) Coates, D. *Liq. Cryst.* **1987**, *2*, 423.
(20) Shibaev, V. P. Side Chain Liquid Crystal Polymers. In *Liquid Crystal Polymers*; Platé, N. A., Ed.; Khimia: Moscow, 1988; p 240.
(21) Noirez, L. Ph.D. Thesis, Orsey, University Paris XI, 1989.
(22) Nakanishi, K. *Infrared Absorption Spectroscopy*; Holden-Day: San Francisco, 1962.
(23) Trotter, J. *Acta Crystallogr.* **1961**, *14*, 1135.
(24) Haase, W.; Paulus, H.; Pendzialek, R. *Mol. Cryst. Liq. Cryst.* **1983**, *100*, 211.
(25) Vani, G. V. *Mol. Cryst. Liq. Cryst.* **1983**, *99*, 21.
(26) Walz, L.; Paulus, H.; Haase, W. *Z. Kristallogr.* **1987**, *180*, 97.
(27) Zoubarev, E. R. Ph.D. Thesis, A. V. Topchiev Petrochemical Institute RAS, Moscow, 1996.
(28) Toriyama, K.; Dunmur, D. A. *Mol. Cryst. Liq. Cryst.* **1986**, *139*, 123.

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