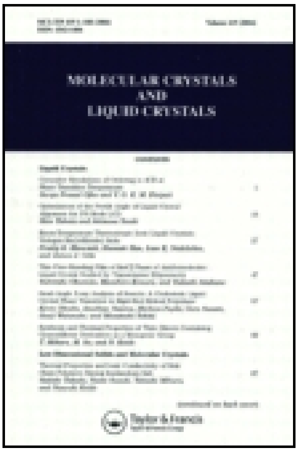

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LIQUID CRYSTALLINE ORDERING IN MELTS OF THERMOTROPIC POLYMERS WITH MALONIC ACID FRAGMENT IN SPACER.

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Abstract With object to evaluate the effect of spacer chemical composition on chain conformation of thermotropic polymers in liquid crystalline (LC) state, linear and combined (main chain/side chain) polymers, containing fragment of malonic acid (FMA) in methylene spacer were studied. It is shown that owing to presence of FMA chain conformations of the studied polymers differ substantially from those of RF-polymers with simple methylene spacer. In lc melt the main chain of polymers investigated has "hairpin"- like conformation with parallel allignment of neighbouring mesogens. In the case of combined polymers the side chain is located inside the hairpin, and mesogens of both main and side chains are found to be mutually parallel Described polymer structure in LC melt provides the explanation for experimentally observed similarities between properties of LC melts of studied polymers and those of low molecular weight liquid crystalls.

INTRODUCTION

A large volume of experimental data has been obtained demonstrating that polymers in liquid crystalline (LC) state significantly differ from their low molecular weight analogs in such main characteristics as order parameters and thermodynamic characteristics (enthalpy and entropy) during the transition from isotropic to LC melt.[1-4] Theoretical treatments[4,5] explain the observed differences by stiffening of macromolecules resulting from changes molecular fragments structure or molecular structure as a whole which accompany this transition.

The extent of stiffening depends on the mechanism ensuring chain flexibility, in other words, on chemical structure of macromolecules. For a specific class of so called RF-polymers (polymers with rigid mesogen and flexible spacer in the backbone) conformational changes can be determined both by asymmetry of repeating unit and by energy difference of rotational isomers of spacer.[5,6]

To establish the effect of chemical structure of macromolecules on mechanism of LC state formation and peculiarities of LC ordering main-chain and combined (main- chain/side chain) thermotropic polymers with fragment of malonic acid (FMA) in spacer were investigated. The general formula of that polymers is:

$-(OC-CHR-COO(CH_2)_6O(C_6H_4)_2O(CH_2)_6O)$, where

$R = H$ is polymer I

and $R = (CH_2)_6O(CH_3)C_6H_4-N=N-C_6H_4CN$ is polymer II

It is well known that conformation of FMA depends on dipole-dipole interactions between C=O groups.[7] So one can suggest that during the phase transitions changes in FMA conformation are possible and as a result changes in conformation of chain as a whole. In the case of combined polymers (polymer II) presence of side chain may effect on both conformation of FMA and asymmetry of repeating unit.

EXPERIMENTAL

Polymers I and II were synthesized using the known methodics.[8,9]

Polymer I

Table I lists the temperatures of transition to LC state and to isotropic melt determined by DSC and polarized microscopy, and polarized IR spectroscopy; values of layer spacings determined by X-ray diffraction technique. According to data of polarized microscopy at 120°C polymer is in smectic A phase, but combined shape of DSC curve proves existence of another smectic phases (unknown). Several types of smectic phases were observed in polymers with similar chemical structure.[10]

TABLE I Phase transitions temperatures (T, °C) and values of layer spacings (L, A).

Method of determination	Temp. of phase transitions, °C – .			L, A	
DSC	K 98 S_1	120 S_2	130is	cryst.	26.1
Polariz. microsc.	K 105 S_1	122 S_A	136is	LC(124°)	26.5
				length of fully	32
IR spectr.	K 102	LC	138is	ext.chain	

Conformational and orientational characteristics of studied polymers were determined by IR spectroscopy. Orientation of samples was effected by two methods. The first one corresponds to spontaneous homeotropic orientation which occurs at melting of polymer film on KBr surface. The second method consists in smoothing of LC melt on KBr surface with subsequent cooling of sample. The order parameters of mesogen (Sm) and flexible (Sf) fragments of polymer chain were calculated from the equations (1),(for the first method of orientation) and (2), (for the second one) using values of dichroism of corresponding IR bands.

$$D_{orA}/D_{orB}\ [1.5\ \mathrm{Sin}^2\vartheta_B + (1-S)]/[1.5\ \mathrm{Sin}^2\vartheta_A + (1-S)] = D_{unorA}/D_{unorB} \qquad (1)$$

where $D_{orA(B)}$ is valus of optical density of chosen band in spectrum of homeotropic oriented sample, $D_{unorA(B)}$ is the density of the same band in spectrum of isotopic sample, S is order parameter value, $\vartheta_{A(B)}$ is value of angle between transition moment of IR band chosen and corresponding bond.

$$Sm(f) = R-1/(R+2)(1-1.5Sin^2\vartheta) \qquad (2)$$

where R is dichroism value of corresponding band. For Sm calculation bands at 1600 cm^{-1} (ν C–C of benzene ring, ϑ is equal 19^0 with axes of ring) and 820 cm^{-1} (δ C–H vibrations of ring, ϑ is equal 80^0 with plane of ring) were used. For Sf calculation band at 2930 cm^{-1} (ν as CH_2 groups, ϑ is equal 75^0 with axes of all-trans sequence of CH_2 groups in methylene chain) was applied.[11] Note that calculated values of order parameters are found to be practically the same. So this values can be considered as equilibrium ones.

At the assumption of domain orientation and including of both mesogen and flexible fragments in domain, experimental order parameters Sm and Sf may be presented by the equation (3).[6]

$$Sx = \langle Sxl\rangle\, S'S'' , \qquad (3)$$

where $\langle Sxl\rangle$ is the average intramolecular value of the local parameter for mesogen (x=m) or spacers (x=f) with respect to the axes chosen for each mesogen pair along the chain; S' is the order parameter of these axes with respect to common director in LC domain; S'' is the order parameter characterizing the macroscopic domain orientation relatively to the direction of orientation. It is important that the observed values of Sm and Sf are related to the corresponding intramolecular $\langle Sml\rangle$ and $\langle Sfl\rangle$ parameters by common coefficient $S'S'' < 1$ which does not depend on x=m or x=f . Since experimental Sf/Sm ratio is determined only by those conformations of monomer units which exist in studied state.

RESULTS AND DISCUSSION

Fig.1 shows plots of Sm , Sf and Sf/Sm vs temperature. As can be seen the order parameters are reversible during the heating-cooling cycle when heated to 124^{0}. So one can conclude that macroorientation of sample in this temperature range is unchanged and observed variations of Sm, Sf and Sf/Sm values during transition from LC to crystalline state are connect with intradomain and intramolecular reorganizations (see eq.3). Strong decreasing of Sm values with decreasing temperature may be due transitions between different smectic phases. Similar behavior was observed[10] for layer spacing values for

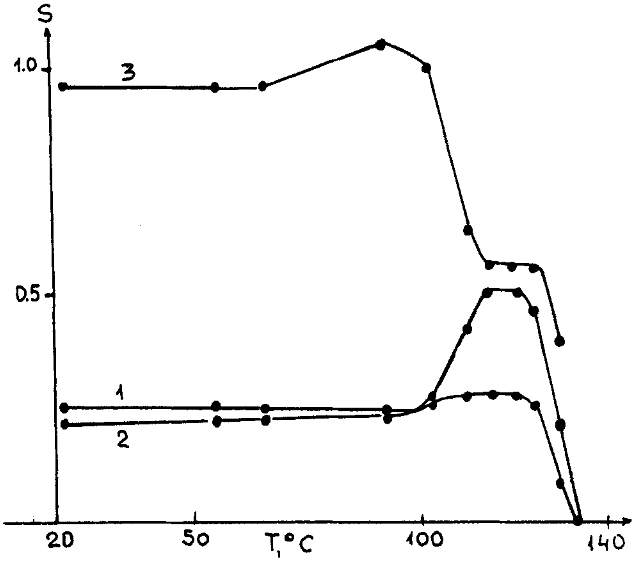

FIGURE 1 Temperature dependences of order parameters of mesogen Sm - 1 and flexible Sf - 2 fragments and ratio of Sf/Sm - 3.

polymer with similar chemical structure of the main chain and was explained by authors due to transition from smectic A to smectic C phase.

Variations of Sf/Sm values during transition from LC to crystalline state are correspond to changes in itramolecular orientation and conformation (value of product S'S'' for Sm and Sf are equal). This ratio decreases from 0.95 (at 22^{0}) to 0.56 (at 124^{0}). At the same time variations in Sf values constitute only 11% at this conditions and then large decrease in Sf/Sm ratio is in the great part due to change in orientation of mesogen. Because in our case the mesogens are rigid changes in their orientation can be connect with conformational transformations in spacer without large effect on Sf values (e.g. due to changes only in conformation of the end groups).

Information about conformational set of methylene sequences of spacer one can obtain from IR spectra in the region of δ CH vibrations of CH_2 groups of methylene chain (1480–1440 cm^{-1}): bands at 1480 and 1440 cm^{-1} are attributed to *trans* and *gauche* isomers of these sequences, correspondingly.[11] According to our qualitative estimations fraction of *gauche* isomer in crystalline state of polymer I is larger than in the case of RF polymers studied by us earlier.[6] In LC and isotropic melts ratios of *trans/gauche* isomers are practically the same and close to those for isolated methylene chain at the same temperature. But presence of order in spacer in LC state testifies to the different distribution of rotational isomers along the methylene chain in LC state from that in isotropic melt. The large fraction of *gauche* isomers in crystalline state of polymer I is probably the main reason decreased values of repeating unit length in comparison with that for its fully extended chain (see Table 1).

It can be assumed that the chain of polymer I consists of two branches, mutual arrangement of which depends on conformation of FMA. Let us consider possible conformations of such branches. In IR spectra of polymer investigated in all phase states one can see two bands corresponding to νs and νas vibrations of C=O groups of FMA (1747 and 1733 cm^{-1}). This means that plane *cis*-conformation of FMA is exluded from possible conformational set of FMA, because only one band C=O must be present in spectrum of such conformation..

With the aid of computer program PCMODEL we can confirm that FMA should not be really in plane *cis* conformation and several local energy minima correspond to structures of FMA in which esters groups planes turned relative to each other Specific conformation of FMA depends on chemical structure of chain in which it is included.

As can be seen from table 2 the preferred conformation for systems 2-4 is so called "hairpin" conformation with parallel arrangment of neighbouring (along the chain) mesogens (Figure 2).

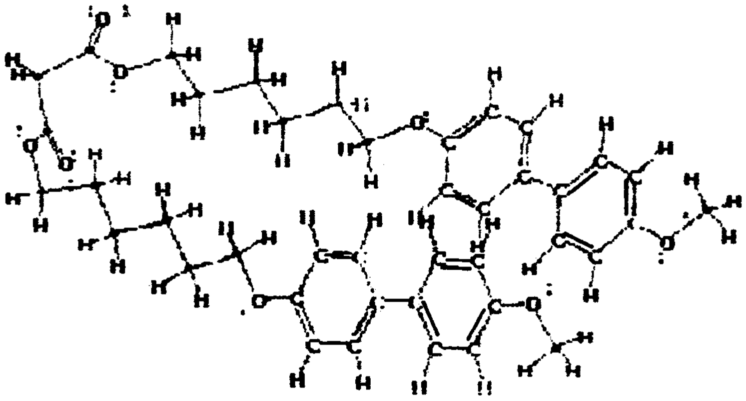

FIGURE 2 Representation of model "hairpin" conformation with minimal energy, calculated by PCMODEL program

TABLE 2 Values of energy difference (ΔE) between "hairpin" end "extended chain" conformations, calculated angle (ϑs) between bisektor of C=O bonds of FMA and axes of chain of model system ROOC-CH_2-COOR and experimental values of ϑs.

N	R	ΔE (kJ)	ϑs, ^{0*} calc. hairpin	extend	exp
1	CH_3	2.3			
2	$(CH_2)_6OCH_3$	10.0	29	80.5	49-54
3	$(CH_2)_6OC_6H_4OCH_3$	16.7	32.2	81.2	
4	$(CH_2)_6O(C_6H_4)_2OCH_3$	29.3	32.6	85.9	

* experimental values of ϑs were obtained from dichroism measurements of νs of C=O groupsin polarized IR of oriented sample taking into account that transition moment of this vibration is directed along bisector of the angle between C=O bonds.

One can suppose that for bulk state of polymer under consideration energy advantage for hairpin conformation can be compensated by intermolecular interactions. So we studied also alternative model structure, more extended and as a result less advantageous from energy consideration.

For obtaining more detailed information about of FMA structure in both crystalline and LC states we compare calculated and experimental values of ϑs. As is seen experimental values of ϑs are in the gap between ϑs corresponding to hairpin and extended conformations. Variation of torsion angles of FMA relatively of their minimal values in model system 4 (see Table 2) which is more closest to real structure of polymer I shown that hairpin conformation is conserved at least till ϑs = 65^0

(Figure 3). These conformations surpass those with minimal energy less than 7 kJ (for the case when all C-C bonds of methylene chain are in *trans*-conformation). This fact means that experimental values of ϑs correspond to hairpin conformation. It worth to note that mentioned increase of energy of hairpin conformation at large values of ϑs in real polymer chain can be partly compensated by strengthening of interactions between benzene rings, with decreasing distance between them due to appearence of *gauche* isomers in spacer.

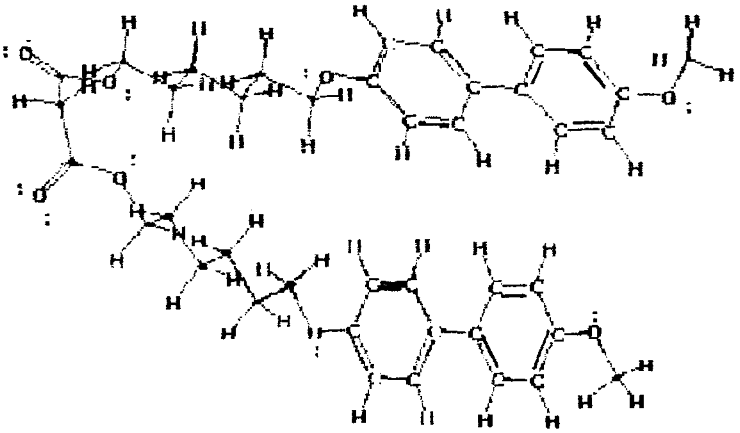

FIGURE 3 Representation of model "hairpin" conformation, calculated with variation of torsion angles in FMA.

Including FMA in the spacer of polymer I with 12 CH_2 groups, on the one hand increases distance between mesogens (according to,[12] in RF-polymers with biphenyl as a mesogen and methylene spacer LC state was not observed if spacer length was longer than 12 CH_2 groups) *and on the other precludes from* coaxiality of mesogens in the extended chain structure. As a result such extended chain is not advantageous for LC state formation. On the contrary hairpin conformation satisfies to conditions of

LC order organization: 1) it corresponds to minimal energy for isolated chain, 2) mesogen fragments in each branch of this structure are coaxial with spacer and at the same time are parallel to each other.

Our conclusion about hairpin conformation of chain in polymer I is confirmed also by the facts that observed Sm values (are equal 0.55 - 0.60 at temperature of transition from isotropic to LC melt) are less than those for extended chain (Sm = 0.7-0.8)[6,13] and close to Sm values for low molecular weight compounds. Change of enthalpy during LC state - isotrop transition are also close for those in low molecular weight compounds.[14]

Polymer II

Table 3 lists of temperatures of phase transitions, determined by different techniques, layer spacings from X-ray diffraction data and value of enthalpy during from LC to isotrop transition.

TABLE 3 Temperatures of phase transition (T), values of layer spacing (L) and ΔH for polymer II

Method of determination	Temp. of phase transition, ^0C	L, A^a Cr	LC	ΔH, kJ LC-isotr
DSC	K 96 S_1 126 S_2 138is	21.5	23.8	
Polar. microsc.	K 90-92 S_i 122 S_A 140is			3.2
IR spectr.	K 92 LC 136is			

a- For comparison: length of fully extended chains are 32 A, for main chain and 24 A - for the side chain.

Orientation of samples of polymer II was effected only by second method of orientation. In this case it is possible to calculate of mesogens order parameters separately for backbone and side chains, using IR spectroscopy technique. We used for backbone the band at 820 cm^{-1}; for side chain band at 2227 cm^{-1} (ν CN, with transition moment directed along the CN bond) and 860 cm^{-1} (δ C-H of azobenzene ring; transition moment is normal to the plane of ring).

Figure 4 shows the temperature plots of dichroism and

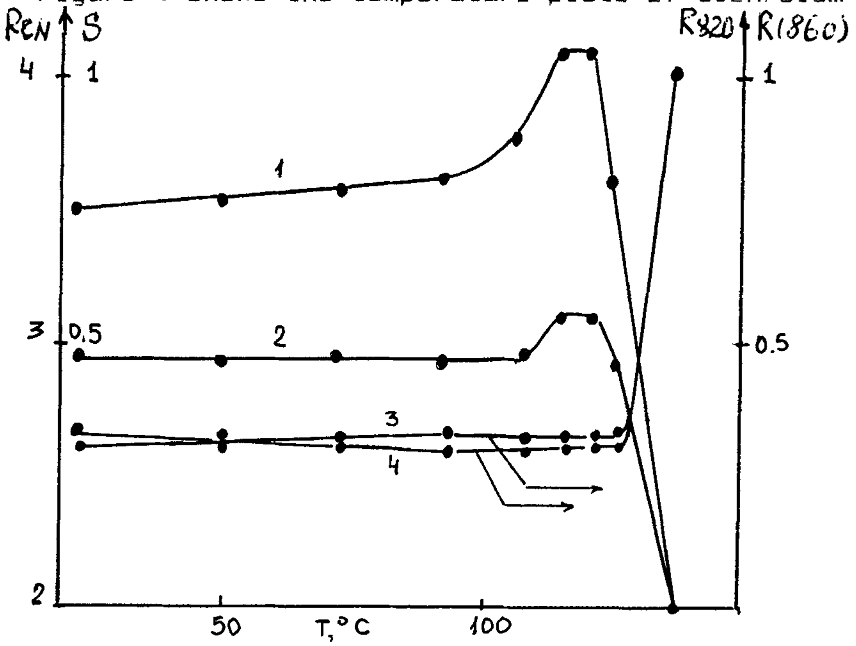

FIGURE 4 Temperature dependences of dichroism of νCN band (R_{CN}) - 1, value of order parameter of side chain, calculated from dichroism of νCN -2, dichroism of bands at 820 - 3 and at 860 cm^{-1} - 4

Sm values for side chain. Note that Sm value of polymer II in LC state is equal to 0.5 and so is very close to that of polymer I. Moreover dichroism values of bands at 820 cm^{-1} and 860 cm^{-1} (corresponding to main and side chains) practically coincide in the investigated temperature range. This leads to the conclusion about parallel arrangment of mesogens of both main and side chains at least in LC melt. The same conclusion has been reached in [15,16] for combined polymers with similar chemical structure, studied by electron microscopy and X-ray diffraction.[10]

Similar to the polymer I, conformation and conformational changes during phase transitions in polymer II are determined by presence of FMA in its backbone Table 4 lists values of ϑ C=O groups of FMA in both crystalline and LC states calculated from polarized IR spectra.

TABLE 4 Experimental values of ϑs of C=O groups of FMA in different phase states

T, °C	ϑs, ° exper.	ϑs, ° calc.
22	40.4	
92	53.8	32.2(hairpin)
124	54.4	
138		85.3(extend)

It is seen that experimental values of ϑs are close to those for polymer I and in LC state correspond to ϑs calculated for model system in hairpin conformation.

However, the range of ϑs changes during the transition of polymer II from crystalline to LC state is broader than the one for polymer I. This means that differences between conformations of FMA as well as differences between conformations of backbone in considered states of polymer II are larger than those in polymer I.

This conclusion is also confirmed by changes of optical densities ratios of νs and νas bands of C=O groups of FMA during crystalline - LC state transition. According to our results this ratio connect with conformational changes in FMA. It was found that changes of this ratio is larger for polymer II in comparison with polymer I. At the same time values of $\Delta\nu_{1/2}$ (width of f IR band at the half of its maximal density), which can be as a measure of conformational uniformity, for νs and νas of C=O groups bands in spectra of polymer II are low compare with those for polymer I. This indicates that conformational set of FMA in former case is narrower due to necessity of correlation in arrangment of mesogens of both main and side chains. It worth noticing that according to DSC data temperature range of isotrop - LC state transition is also narrower for polymer II.

Confirmation of the conclusion about "hairpin" conformation of polymer investigatedis provided by analysis of characteristics of flexible fragments of both chains in polymer II. We made an estimation of dichroism (R_m) and order parameter of main chain spacer in LC state from observed dichroism (Robs) of νas of CH_2 groups band, using an equation (4)

$$\text{Robs} = \frac{(R_s + 2)R_m C + (R_m + 2)(1-C)R_s}{(R_s+2)C + (1-C)(R_m+2)} \qquad (4),$$

where R_s is the value of dichroism of νas vibrations, corresponding to CH_2 groups of the side chain, C is the fraction of methylene groups of main chain spacer in common value of methylene groups of both chains.

For this analysis Sf value of side chain was supposed to be practically equal to Sm value of the side chain on the reach, that according to X-ray data side chain of polymer II in LC state is fully extended and axis of mesogen and spacer coincide (angle between them is 175^0). It was found with such assumption the Sf value of main chain in LC state is 0.2 and ratio Sf/Sm is 0.4.

Both of these values are less than those for polymer I (0.3 and 0.5) at the same conditions. This demonstrates substantial disordering of polymer II backbone.

It is probably that reason of such disordering is high content of *gauche* isomers in this chain, which is in agreement with X-ray data about significant shortening (by 8A) of backbone compared with the length of fully extended chain (32 A). Such shortening is necessary for parallel arrangment of mesogens of main and side chains in hairpin structure.

With the aid of PCMODEL program we made an attempt to determine the preferable conformation of combined polymer. However, due to limited possibilities of this computer programme in searching of "good" energy minimums for such complete system. structures obtained by the use of PCMODEL can not to form LC order, because they do not provide necessary arrangement of mesogen

Nevertheless the following experimental results indicate that in polymer II (as well as polymer I) the backbone has the hairpin conformation, inside of which a side chain is located because: 1) experimental values of ϑs of FMA C=O groups are close to those calculated for hairpin conformation of polymer I; 2) the mesogens of both main and side chains are mutually parallel and 3) coincidence in the LC state layer spacing, determined by X-ray diffraction with length calculated for fully extended side chain (this coincidence was also observed in a number of other combined polymers with similar chemical structure).

Taken as a whole, our experimental data together with results of model calculations permit to conclude that presence of FMA in RF-polymers (linear as well as combined) promote folding of their backbone chains and formation of hairpin- like configurations. In combined polymer side chain is located inside of hairpin structure. Data obtained on structural organization of polymers I and II confirm earlier conclusion[17] that those chain conformations can be realized in LC state which are permitted for isolated chain. For the first time effect of chemical structure of spacer on extent of LC ordering in RF-polymers was considered in[5].

Note, that in its turn, such changes of backbone chain conformation of polymers with FMA (its transition from extended form observed for polymers with simple methylene spacer to the hairpin one) determine macrocharacteristics of LC state:values of order parameters at the clearing temperature, their dependence on mol. weight, thermodynamic characteristics of transition from LC to isotropic melt.

So, according to [18] value of order parameter at clearing temperature for combined polymer with similar chemical structure reaches to its limited value at degree of polymerization about 2-3, when for RF-polymers with methylene chain as a spacer these limited values were attained for chain with 8-10 units.[19]

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