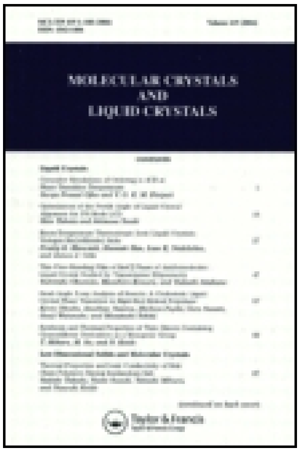

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Pecularities of Liquid Crystalline Order Formation in Polyesters with Irregular Chemical Composition

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PECULARITIES OF LIQUID CRYSTALLINE ORDER FORMATION IN POLYESTERS WITH IRREGULAR CHEMICAL COMPOSITION

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Abstract Formation of liquid crystalline (LC) order in thermotropic main-chain random copolymers (containing mesogens of one type and spacers of different lengths) were investigated by IR spectroscopy, DSC, X-ray and polarized microscopy methods. It was demonstrated that in such copolymers (CPLs) smectic liquid crystalline (LC) order can exist. Peculiarities in spacers behavior during transition to LC state are found. Conclusion about the dependence of the mechanism of smectic LC order formation on chemical structure of rigid components of CPLs is made.

INTRODUCTION

Earlier[1, 2] it was shown that aperiodic random CPLs in spite of their chemical heterogenity have the ability to form LC order in melt. Investigations of such systems are interesting on both applied and fundamental sides. On one hand they give the possibility of LC order characteristics variation in dependence on chemical composition of CPLs. On the other side studies of these systems are very useful for understanding general rules of LC order formation in complex polymer systems.

EXPERIMENTAL

Two sets of bicomponent aperiodic random CPLs were studied by polarized and unpolarized IR spectroscopy, DSC, X-ray and polarized microscopy methods.

In CPLs of the first set a rigid unit was constituted by fumaroyl-di-p-oxybenzoate (FOB) :

$$\text{-OOC-}C_6H_4\text{-OOC-CH=CH-COO-}C_6H_4\text{-COO-}$$

As a rigid unit in CPLs of the second set was terephtaloyl-di-p-oxybenzoate (TOB) :

$$\text{-OOC-}C_6H_4\text{-OOC-}C_6H_4\text{-COO-}C_6H_4\text{-COO-}$$

In both first and second sets of CPLs one of the constitutive components of spacer was always a methylene chain containing 10 CH_2 units. As alternative flexible component were used methylene chains containing either 6, 4 or 2 methylene units. And only in one sample of CPLs belonging to the second set a polyethyleneglycol (PEG) chain with 5 units was used as second flexible component. It should be noted that decamethylene chains in all CPLs were perdeuterated so we have the possibility to get information separately about the behavior of each component of the spacers in CPLs. The order parameters of both mesogen (S_m) and flexible (S_f) fragments were determined by equation (1)

$$S(m,f) = \frac{(R-1)}{(R+2)}\left(1 - \frac{3}{2}\,\mathrm{Sin}^2\vartheta\right) \qquad (1)$$

where R is the dichroism of the corresponding absorption band, ϑ is the angle between transition moment of this band and chain axes.

For S_m calculations band 1600 cm^{-1} was chosen with value ϑ equal 19°. Values of S_f were calculated using bands 2920 cm^{-1} (νCH_2), $\vartheta=75°$, and 2600 cm^{-1} (νCD_2), $\vartheta=90°$.[3]

As it was shown earlier S_f/S_m ratio can be considered as a criteria of intramolecular conformation and length of spacer [2]. Trans/gauche content in the spacers was estimated by ratio of optical densities of bands corresponding to bent vibrations of methylene groups in unpolarized IR spectra (1470 cm^{-1} - 1450 cm^{-1}).

First Set of Copolymers

The main peculiarity of CPLs of this row is the fact that the rigid fragment of the monomer unit (FOB) does not form LC state. As a result for homopolymers with such a rigid unit and methylene sequence as a spacer, the possibility of LC order formation is entirely due to link monomers in the chain .[4]

From comparison of isotropization temperatures for CPLs and corresponding homopolymers (Table 1) determined by DSC and polarized microscopy one can conclude that true mixed LC state was formed in melts of CPLs containing 10 and 6 methylene units in the spacer (FOB 10/6), when the ratio of constitutive components with 10 and 6 CH_2 groups in the flexible part were 1:1 - FOB 10/6-I, and 2:1, FOB 10/6-II. In the case of CPL with 10 and 4 CH_2 units in spacer, according to values of isotropization temperatures a complete mixed LC state doesn't form. And finally CPL with 10 and 2 methylene groups doesn't form LC order at all. It should be noted that according to X-ray data, observed LC order in all cited CPLs was smectic type.

TABLE 1 Characteristics of polymers studied (FOB)

Polymer	Spacer I	Spacer II	Comp	Cr-LC, °C	LC-Is, °C	spacing (exp.), A	spacing (theor.), A
FOB-10	$(CH_2)_{10}$			157	178	28,2-31	32
FOB-6	$(CH_2)_6$			200	230	24,5	27
FOB-4	$(CH_2)_4$			210	300	23,2	25
FOB 10/6-I	$(CD_2)_{10}$	$(CH_2)_6$	1:1	133	200	26,7	29,5
FOB 10/6-II	$(CD_2)_{10}$	$(CH_2)_6$	2:1	135	185	-	30,3
FOB 10/4	$(CD_2)_{10}$	$(CH_2)_4$	1:1	145	218	26,0	28,5

Determined from IR spectra the high absolute values of order parameters S_m (more than 0.9 in the bulk state and 0.75-0.8 in LC melt) for CPLs of this set with various compositions testify that heterogeneous structure of CPLs doesn't lead to a decrease of their orientational characteristics in comparison with the corresponding homopolymers [3,5]. Moreover, observed high values of S_m mean that spacers in CPLs have those conformations which ensure coaxiality of mesogen fragments along the chain and as a result straightening of CPL chains as a whole. Observed changes in S_f/S_m ratios (as cited above this ratio is dependent on intramolecular conformation) in LC state (Table 2)

TABLE 2 Ratios of S_f/S_m for FOB

Polymer	Semicrystalline			LC melt		
	S_{f10}/S_m	S_{f6}/S_m	S_{f4}/S_m	S_{f10}/S_m	S_{f6}/S_m	S_{f4}/S_m
FOB-10	~1	-	-	0,65	-	-
FOB-6	-	0,35	-	-	0,25	-
FOB-4	-	-	0,07	-	-	~0
FOB 10/6-I	0,84	0,64	-	0,60	0,43	-
FOB 10/6-II	0,84	0,5	-	0,60	0.32	-
FOB 10/4	0,84	-	0,2	0,60	-	0,07

For CPLs in comparison with corresponding homopolymers indicate that smectic type LC order in CPLs is accompanied by conformational changes in the spacers. These changes occur in such a way that lengths of flexible components draw together. Short spacers become more extended. This conclusion follows from the fact that S_f/S_m ratios for spacers containing 6 and 4 methylene units in CPLs are larger than corresponding ones for homolymers (see Table 2). From temperature dependence of S_m in studied CPLs it is seen that this parameter doesn't significantly change during semicrystalline to LC state transition. So observed changes in S_f/S_m ratios may be connected with conformational changes in spacers. Actually, direct estimation of the trans/gauche ratio for CPL FOB 10/6-I from optical densitie relations of bands corresponding to bent vibrations of CH_2 groups testify that hexamethylene spacer in this CPL is nearly completely extended: the fraction of trans-isomer in the bulk state is about 80% (compared with 60% for homopolymer FOB-6). Moreover, the calculated length of a fully extended monomer unit of FOB-6 is equal to 27 A, which is close to the experimentally determined value 26.7 A for FOB 10/6-I (Table 1). It should be noted that an increase of trans-isomer content in comparison with the homopolymer is observed also in the LC melt of CPL. This means that in LC state, the short spacer is more extended in comparison with homopolymers.

At the same time decamethylene chain according to IR data becomes shorter (the S_f/S_m ratio for it decreases in comparison with corresponding values for the homopolymer in LC state).

For studied CPLs of this type it was found that the increase in differences between lengths of flexible components leads to an increase of both width and asymmetry of DSC peaks. This phenomena can be explained by appearance of defects on the domain boundaries, content of which depends on spacer length differences.

It should be noted that studied random CPLs domains containing a significant value of monomer units are heterogeneous in content and have different temperatures of melt in various domain parts. In the first turn there occurs melting of parts with lower melting temperatures. In the case of CPLs FOB 10/6 these parts contain decamethylene chains. As a matter of fact, it was found that under transition to biphasic region the ratio of S_{f10}/S_m decreases whereas S_{f6}/S_m stays practically constant. So biphasic region in such CPLs consisting of domains with various degree of defects can be considered as a quasi-network. Obviously by this circumstance, the keeping of macroorientation of CPL samples at the beginning of transition into isotrop melt may be explained. Such behavior is a different feature of these random CPLs in comparison with homopolymers.

Second Set of Copolymers

In the opposite to CPLs of the first set, the rigid unit of this set of CPLs can form LC state. As a result, formation of LC order in this case occurs in quite a different way. From Table 3 one can see that the values of the S_f/S_m ratio for constitutive components of these CPLs are practically equal to those in the corresponding homopolymers. This means that conformations of the flexible components of CPLs and homopolymers are practically the same. According to X-ray data these CPLs also form smectic LC order. This is easily understandable only for CPL with 5 ethylene glycol units in the spacer, because lengths of this spacer and decamethylene one are very close.

TABLE 3 Characteristics of TOB

Polymer	Cr-LC, °C	LC-Is, °C	Semicrystalline				LC melt				spac. (exp.), A
			$\frac{S_{f10}}{S_m}$	$\frac{S_{f6}}{S_m}$	$\frac{S_{f4}}{S_m}$	$\frac{S_{fPEG}}{S_m}$	$\frac{S_{f10}}{S_m}$	$\frac{S_{f6}}{S_m}$	$\frac{S_{f4}}{S_m}$	$\frac{S_{fPEG}}{S_m}$	
TOB-10	230	290	0,74	-	-	-	0.4	-	-	-	30
TOB-6	260	320	-	0,25	-	-	-	0,18	-	-	26,5
TOB-4	300	>360	-	-	0,04	-	-	-	0	-	24
TOB-PEG	150	200	-	-	-	0,17	-	-	-	0,12	28
TOB 10/6 (1:1)	205	320	0,7	0,35	-	-	0,35	0,16	-		27
TOB 10/4 (1:1)	240	340	0,7	-	0,04	-	0,35	-	0	-	-
TOB 10/PEG (1:1)	190	270	0,5	-	-	0,60	0,3	-	-	0,12	29

For the other CPLs of the second set we suggested the following explanation of smectic LC order formation . It was already noted that the rigid fragment of the monomer unit of these CPLs is of mesogen type. Earlier[6] it was shown that similar mesogens units are already coaxial starting from dimer. So one can consider CPLs with this mesogen as a chemically heterogeneous chain consisting of rigid units.

Chains of this type can form smectic structure as a result of their sliding along each other so that mesogens of neighbouring chains overlap completely or in part. Variations in the overlap degree down to complete absence of overlapping in some parts of the chain are characteristic for this kind of CPLs structure. Such variations lead to certain differences in interlayer spacings and as a result to a "smoothing" of X-ray pattern. That is why one can consider the whole bulk CPL as a quasibiphasic system which consists of smectic layers distributed in a nematic matrix. A similar phenomenological description of aperiodic heterogeneous CPL behavior and LC order formation in it was suggested recently.[7]

To confirm the possibility of such mechanism of smectic order formation in the CPLs discussed, we conducted computer simulation behavior of two chains of model random CPL. The probability of AB contacts (contacts between two different constitutive components) was assumed equal to 0.5 and the extent of mesogens overlapping was set to 0.7. It was found that in a chain with degree of polymerization equal 50 about 0.5 units satisfy these conditions. This fact can be considered as a quite satisfactory confirmation of the proposed explanation of smectic LC order formation in discussed type of CPLs.

Thus our results demonstrate that the behavior of random main-chain CPLs is the quite opposite to the one of homopolymers blends with spacers of different lengths. If in the latter systems in the LC state segregation of components has occurred, CPLs have the ability to form mixed LC order. The mechanism of such LC order formation depends on chemical structure of the rigid unit of CPLs: in some cases LC order formation is accompanied by conformational changes in the spacer, in other ones conformational transformations of the spacer don't constitute the necessary condition for the existence of smectic LC order.

Conclusions about the active role of the spacer in LC state formation made earlier for thermotropic main-chain polymers with more simple chemical composition are also true for polymer systems with more complex chemical structure as the investigated random aperiodic CPLs. From conformational sets of spacer permitted for its isolated chain in the LC state only those are selected, which ensure coaxiality of mesogens along the chain and straightening the chain as a whole.

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