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Possible Chain Conformations in the Crystalline State of a Series of Mesogenic Polymers

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ABSTRACT: The chain repetition periods in the crystalline state for the series of polymers $[-1,4\text{-}C_6H_4C(CH_3){=}N{-}N{=}C(CH_3)\text{-}1,4\text{-}C_6H_4OOC(CH_2)_{n-2}COO-]_x$ with n = 8, 9, ..., 13 were determined. Through an analysis of the possible chain symmetries satisfying the equivalence principle and on the basis of simple energetic considerations, chain models of these polymers reproducing the experimental periods are outlined. The resulting conformations are such that the elongation axis of the rigid groups $-1,4\text{-}C_6H_4C(CH_3){=}N{-}N{=}C(CH_3)\text{-}1,4\text{-}C_6H_4-$ is significantly displaced from alignment with the chain axis. A proposal for the quantitative evaluation of the chain "waviness" of the polymers studied is presented.

Introduction

As has been shown in preceding papers,[1-3] mesophasic polymers can be obtained if rigid groups like $-1,4\text{-}C_6H_4C(CH_3){=}CH\text{-}1,4\text{-}C_6H_4-$ or $-1,4\text{-}C_6H_4C(CH_3){=}N{-}N{=}C(CH_3)\text{-}1,4\text{-}C_6H_4-$ are introduced with regularity within a flexible chain.

Thermodynamic studies have been performed on such polymers,[4,5] but only preliminary structural studies have been performed until now. In particular, the solid-state polymorphism of poly[oxydodecanedioyloxy-1,4-phenylene(2-methylvinylene)-1,4-phenylene] was investigated[6] and the structures of some low molecular weight model compounds were solved,[7,8] with the aim of obtaining indications useful for the establishment of the chain conformation in the crystalline state of homologous polymeric compounds. In this paper we are interested in studying the chain conformation in the crystalline state of polymers of the kind $[-1,4\text{-}C_6H_4C(CH_3){=}N{-}N{=}C(CH_3)\text{-}1,4\text{-}C_6H_4OOC(CH_2)_{n-2}COO-]_x$ with n = 8–13. The thermal behavior of the polymers has already been characterized;[4] they show nematic mesophases with strong odd–even effects.

In this paper we shall discuss the possible chain conformations that are compatible with the experimental chain repetition periods for the polymers of the series having both an odd number and an even number of carbon atoms in the aliphatic chain and that satisfy the minimum energy and equivalence principle.[9]

Experimental Section

The series of polymers considered, $[-1,4\text{-}C_6H_4C(CH_3){=}N{-}N{=}C(CH_3)\text{-}1,4\text{-}C_6H_4OOC(CH_2)_{n-2}COO-]_x$, comprises chains with n = 8–13. Hereafter, we shall indicate such polymers with the notation P_n, with n varying in the range indicated. The preparation of the polymers has been carried out according to a method already described.[1]

Fibers suitable for X-ray analysis were hot extruded.

Table I shows the chain identity periods (c) experimentally determined from fiber and tilted fiber spectra. The X-ray films showed good crystallinity but poor orientation so that the experimental periods are affected by the rather large errors indicated.

Scheme I

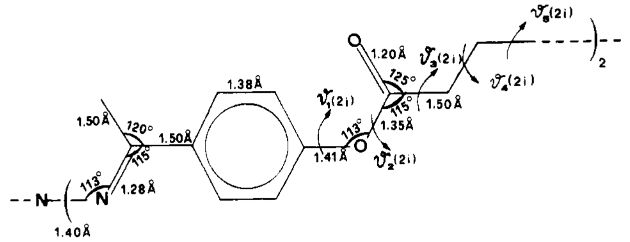


Table I
Experimental Identity Periods for the Polymers under Study

polymer	c/Å	polymer	c/Å
P_8	23.3 ± 0.8	P_{11}	46.7 ± 1.1
P_9	41.9 ± 1.3	P_{12}	28.4 ± 1.3
P_{10}	26.1 ± 0.7	P_{13}	53.4 ± 1.0

Geometrical and Energetic Considerations

The internal coordinates for the chain conformation of all the models studied have been chosen in conformity with the following geometrical and energetic considerations.

Bond Lengths and Valence Angles. Standard values of 1.54 Å and 112° have been used for the carbon atoms of the aliphatic chain. Values for the ester group have been chosen according to the results of structural studies on low molecular weight compounds[7,8] and according to literature data.[10] Values for the rigid group have been chosen according to ref 7 and 11.

Scheme I shows, in parentheses, half of the ith constitutional repeating unit, together with the values used for bond lengths and valence angles and the notation used for the torsion angles.

Torsion Angles. The rigid group has been assumed to be planar;[7] the torsion angles ϑ_2 (see Scheme I) were set equal to 180° on the basis of the structural indications of ref 7 and 8 and of the high torsional barrier owing to the partial double-bond character (see ref 12, p 183).

The torsion angles ϑ_1 have been assigned possible values of ±90° on the basis of the structure of model compounds studied in our laboratory[7,8] and of energetic considerations.[13] Indeed, for $\vartheta_2 = 180°$, the steric interactions between the carbonyl oxygen and the phenyl group hinder the trans-planar conformation about the phenyl–OCO bond. It may also be of interest to observe that the calculated identity periods will be almost invariant, whatever the value of ϑ_1, if a center of symmetry is assumed to be present at the middle of the N–N bond.

The ϑ_3 angles have been considered variable in the models because of the presumably low torsional barrier. The barrier is threefold and low (300 cal) for the CH_3–CO bond of methyl acetate.[14,15] The minima correspond to conformations in which the hydrogen atoms eclipse the carbonyl oxygen.

Calculations have been performed with the aliphatic chain in the all-trans conformation or containing one gauche bond in various positions. Acceptable values of the identity period are obtained only in the all-trans case or when the gauche bond is located at one of the odd positions, ϑ_{2n+1}. In this last case the energy of the isolated chain is higher, but the requirement for optimal *intermolecular* packing could stabilize the structure. Placing a gauche conformation at one of the ϑ_{2n} bonds results in identity periods shorter than the experimental ones. Notice that a gauche state of torsion angles near a trigonal carbon atom (as is the case for ϑ_4) may be as energetically favorable as a trans state (see ref 12, p 193).

Our reported calculations will refer to a constitutional unit like that of Scheme I, corresponding to half of the repeating unit. Without loss of generality, since we assume $|\vartheta_1| = 90°$, we shall set $\vartheta_1(2i) = +90°$. Once the values of the torsion angles are assigned for the constitutional unit $2i$, the chain conformation is unequivocally fixed, if suitable symmetry elements are assumed to be present in the chain.

Hereafter, we shall evaluate possible chain conformations under the above simplifying assumptions and we shall refer to $\vartheta_1(2i)$, $\vartheta_2(2i)$, $\vartheta_3(2i)$, $\vartheta_4(2i)$, etc. of the first half of a constitutional repeating unit simply as ϑ_1, ϑ_2, ϑ_3, ϑ_4, etc.

Possible Chain Symmetries and Calculations of the Chain Identity Periods

According to the equivalence principle,[9] the conformation of a polymer chain in the crystalline state is defined by a succession of equivalent structural units. The structural unit coincides in general (but not always) with the smallest unit (one or one-half monomeric unit) that can be repeated through symmetry operations (as allowed by the chemical symmetry; see ref 9, pg 11). The symmetry in the chemical constitution of the polymers under consideration does in fact allow the possibility that the structural unit coincides with one-half of a monomeric unit. As outlined at the end of the preceding paragraph, we took this possibility as an assumption, leading to a significant reduction of the parameters to be varied, in order to find a fit of the calculated results with the experimental data available for the identity periods. If such a fit is found, the corresponding calculated conformations have a significant probability of being a good representation of the real conformations in the crystalline state.

The possible symmetries that are in accordance with the above assumptions have been deduced in the following way. Symmetry elements that are compatible with the chemical structure of the polymers are as follows: (i) at the center of the N–N bond, a center of symmetry *i* or a twofold axis perpendicular to the chain axis; (ii) for *n* even, at the middle of the central CH_2–CH_2 bond, a center of symmetry *i* or a twofold axis perpendicular to the chain axis; (iii) for *n* odd, at the central (CH_2) carbon atom, a twofold axis or a plane of symmetry *m* perpendicular to the chain axis.

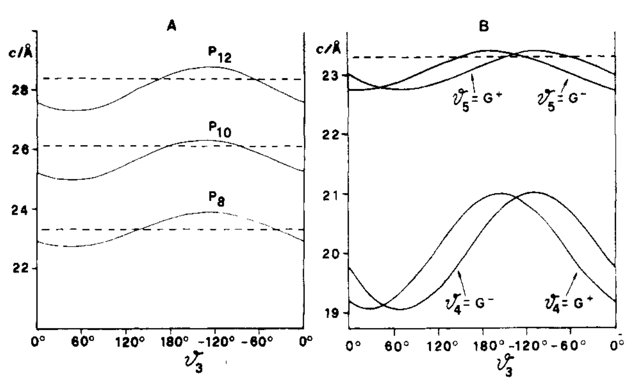


Figure 1. Calculated identity periods (*c*) vs. torsion angle ϑ_3 ($\vartheta_1 = +90°$, $\vartheta_2 = 180°$) for the polymers having *n* even (chain symmetry t*i*). Dashed lines correspond to the experimental periods. (A) All bonds of the aliphatic chains trans, *n* = 8, 10, 12. (B) For *n* = 8, aliphatic chain with ϑ_4 or ϑ_5 = ±60.

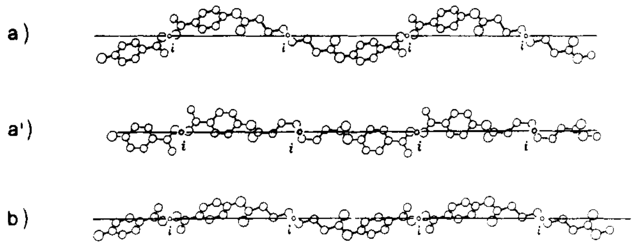


Figure 2. Projections of the P_8 chain models in the t*i* symmetry in a plane parallel to the chain axis ($\vartheta_1 = +90°$, $\vartheta_2 = 180°$). (a) and (a′) represent chain models reproducing the experimental period ($\vartheta_3 = +120°$, $\vartheta_5 = 180°$; $\vartheta_3 = -100°$, $\vartheta_5 = +60°$, respectively); (b) represents the all-trans chain model in the most extended conformation ($\vartheta_3 = -120°$).

In the case of polymers having an even number of carbon atoms in the aliphatic chain, the experimental periods correspond to the repetition of a single monomeric unit. Possible symmetries are then t*i* or t2.[16,17]

In Figure 1, the identity periods (*c*) vs. the torsion angle ϑ_3 as defined in Scheme I are reported for the series of polymers having *n* even in the t*i* symmetry. $\vartheta_1 = +90°$ has been assumed. All the curves reported in Figure 1A show a minimum at $\vartheta_3 = +60°$ and a maximum at $\vartheta_3 = -120°$. In this last case, the chain reaches its highest extension under the constraints of our energetic and geometrical assumptions. The calculated periods coincide with the experimental ones at around $\vartheta_3 = +120°$ (as shown by the dashed lines in the figure). In any event, the calculated periods for the t*i* symmetry may be considered to be in good agreement with the experimental data at any given ϑ_3 value, both for the all-trans planar aliphatic chain and for $\vartheta_5 = \pm 60°$ (as exemplified in Figure 1B for *n* = 8). In fact, the variation of the identity period with ϑ_3 is of the order of magnitude of the errors connected with the experimental measurements reported in Table I. In Figure 2, the projections of the chain of P_8 in a plane parallel to the chain axis in two conformations reproducing the experimental period ($\vartheta_3 = +120°$, $\vartheta_5 = 180°$ for a; $\vartheta_3 = -154°$, $\vartheta_5 = +60°$ for a′) are compared with the projection of the polymer chain in its highest extension (Figure 2b) compatible with our geometric and energetical assumptions ($\vartheta_3 = -120°$, the aliphatic chain all-trans planar, *c* = 23.9 Å).

The t2 symmetry is possible only for triplets ϑ_1, ϑ_2, ϑ_3 in which only one degree of freedom (instead of two) is available. For instance, when the aliphatic chain is all-

Table II
Possible Symmetries and Internal Rotation Angles (Deg) for the *n* Odd Terms of the Studied Polymers

	chain repetition groups		
	tic	s(2/1)*m*	s(2/1)2
$\vartheta_1(2i)$	+90	+90	+90
$\vartheta_2(2i)$	180	180	180
$\vartheta_n(2i)$	$+\vartheta_n$	$+\vartheta_m$	$+\vartheta_n$[a]
symmetry element	2	*m*	2
$\vartheta_n(2i+1)$	$+\vartheta_n$	$-\vartheta_n$	$+\vartheta_n$
$\vartheta_2(2i+1)$	180	180	180
$\vartheta_1(2i+1)$	+90	−90	+90
symmetry element	*i*	*i*	2
$\vartheta_1(2i+2)$	−90	+90	+90
$\vartheta_2(2i+2)$	180	180	180
$\vartheta_n(2i+2)$	$-\vartheta_n$	$+\vartheta_n$	$+\vartheta_n$
symmetry element	2	*m*	2
$\vartheta_n(2i+3)$	$-\vartheta_n$	$-\vartheta_n$	$+\vartheta_n$
$\vartheta_2(2i+3)$	180	180	180
$\vartheta_1(2i+3)$	−90	−90	+90

[a] For the s(2/1)2 symmetry a further condition related to the selected value of the unit twist binds the possible values of ϑ_n; i.e., if $\vartheta_4 = \vartheta_5 = ... = 180°$, then $\vartheta_3 = +92°$ or $-92°$ (not equivalent).

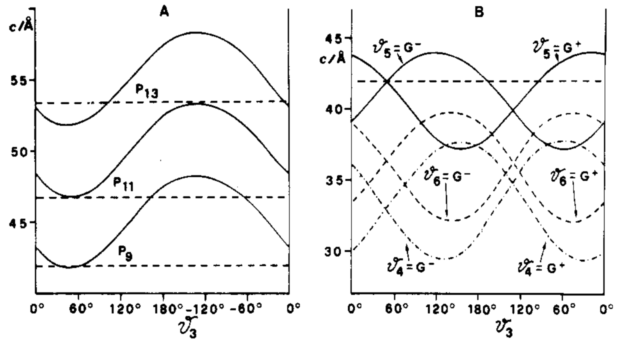


Figure 3. Calculated identity periods (*c*) vs. torsion angle ϑ_3 ($\vartheta_1 = +90°$, $\vartheta_2 = 180°$) for polymers having *n* odd (chain symmetry *tic*). Dashed lines correspond to the experimental periods. (A) All bonds of the aliphatic chains trans, *n* = 9, 11, and 13. (B) For *n* = 9, aliphatic chain with ϑ_4, ϑ_5, or $\vartheta_6 = \pm 60°$.

trans planar and $\vartheta_2 = 180°$, two possible solutions are $\vartheta_1 = 180°$, $\vartheta_3 = 0°$ and $\vartheta_1 = 0°$, $\vartheta_3 = 180°$. In the cases of the example the calculated periods for all the polymers of the even series are in agreement with the experimental values (as an example, for P_8 $c = 22.8$ Å at $\vartheta_1 = 180°$, $\vartheta_2 = 180°$, $\vartheta_3 = 0°$; $c = 23.0$ Å at $\vartheta_1 = 0°$, $\vartheta_2 = 180°$, $\vartheta_3 = 180°$). Since the t2 symmetry imposes more constraints on the chain conformation than the *ti* symmetry, it is less probable, in our opinion, that it represents the real chain conformation and the *ti* symmetry model (with the lower energy content) should be preferred.

As far as the odd terms of the series are concerned, the experimental identity periods require identical repetition every two monomeric units. The possible symmetries (see Table II) are *tic*, s(2/1)*m*, and s(2/1)2,[16,17] the first one being the most probable (vide infra).

Figure 3A shows the identity periods (*c*) vs. the torsion angle ϑ_3 calculated for the *tic* symmetry for the series of polymers with *n* odd when the aliphatic chain is assumed as all-trans planar. The experimental periods (dashed lines) are reproduced at around $\vartheta_3 = +60°$, when the chain is in the less extended conformation. The corresponding chain model for the P_9 polymer ($c = 41.8$ Å) is shown in Figure 4a, compared with the analogous model, Figure 4b, resulting at $\vartheta_3 = -120°$, when the chain is in the highest extension ($c = 48.4$ Å) compatible with our geometrical and energetic assumptions. The projection plane in the figure is perpendicular to the glide plane.

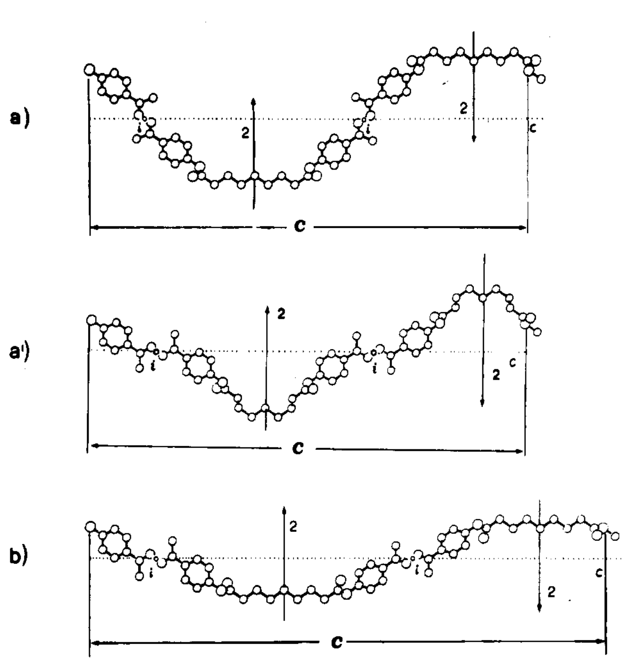


Figure 4. Projections of the P_9 chain models in the *tic* symmetry in a plane perpendicular to the glide plane ($\vartheta_1 = +90°$, $\vartheta_2 = 180°$). (a) and (a′) represent chain models reproducing the experimental period ($\vartheta_3 = +60°$, $\vartheta_5 = 180°$; $\vartheta_3 = +50°$, $\vartheta_5 = +60°$, respectively); (b) represents the all-trans chain model in the most extended conformation ($\vartheta_3 = -120°$).

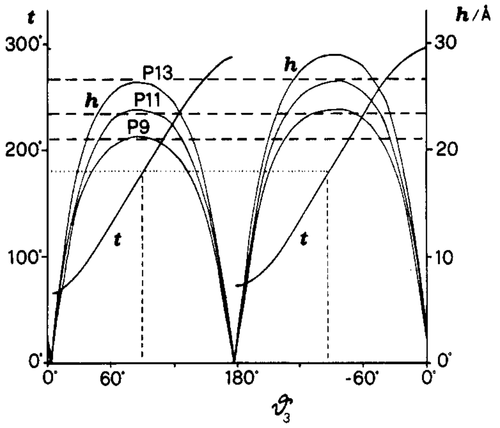


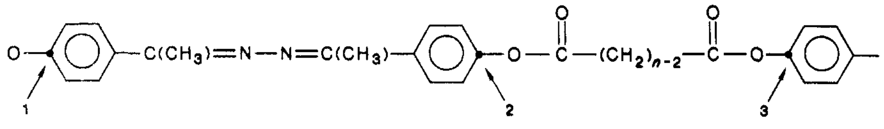
Figure 5. Calculated unit heights (*h*) and unit twists (*t*) vs. torsion angle ϑ_3 ($\vartheta_1 = +90°$, $\vartheta_2 = 180°$, aliphatic chain trans planar) for the series of polymers with *n* odd (chain symmetry s(*M*/*N*)2). Dashed and dotted lines correspond to the experimental unit heights and unit twists, respectively.

Corresponding data for the polymer with *n* = 9 when gauche bonds are included in the aliphatic chain are shown in Figures 3B and 4a′. The calculated periods, compared with the experimental ones, show that when *n* = 9, ϑ_5 but not ϑ_4 or ϑ_6 may be gauche; more generally, our calculations show that when *n* is odd, one of the ϑ_{2n+1}'s (but not one of the ϑ_{2n}'s) may be gauche.

Figure 5 shows the behavior of the unit height (*h*) and of the unit twist (*t*) for the s(*M*/*N*)2 symmetry vs. the torsion angle ϑ_3 in the series of odd polymers. The aliphatic chain is assumed to be trans planar. One ϑ_{2n+1} gauche bond could be included, but this would increase the energy of the isolated chain.

Only one case is compatible with the experimental data and corresponds to $M/N = 2/1$, and then to a unit twist of 180°. This unit twist value can be obtained for $\vartheta_3 = +92°$ ($\vartheta_1 = +90°$, $\vartheta_2 = 180°$) with good agreement between the calculated and the experimental periods ($c = 42.4$ Å

Scheme II



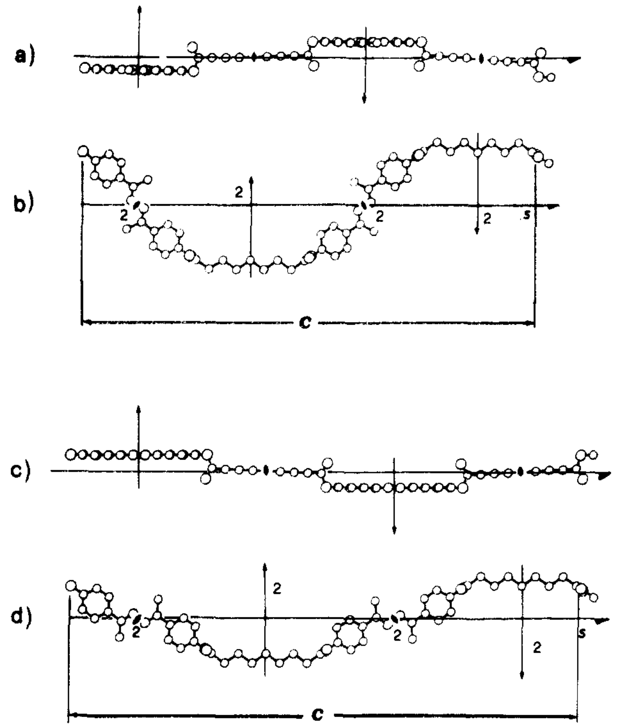


Figure 6. Projections of the P_9 chain models in s(2/1)2 symmetry in a plane parallel to the screw axis (ϑ_1 = +90°, ϑ_2 = 180°, aliphatic chain all-trans). (a) and (b) represent the chain model reproducing the experimental period (ϑ_3 = +92°), and (c) and (d) represent the chain model in the most extended conformation (ϑ_3 = -92°). For each conformation two different views are given: (a) and (c) are drawn in a plane parallel to the twofold axes associated with the rigid groups, and (b) and (d) are drawn in a plane parallel to the twofold axes associated with the aliphatic chains.

for P_9) and for $\vartheta_3 = -92°$ ($\vartheta_1 = +90°$, $\vartheta_2 = 180°$) with the calculated periods longer than the experimental values (c = 47.4 Å for P_9). The corresponding P_9 models in the s(2/1)2 symmetry calculated with these values of ϑ_3 are compared in Figure 6. Each conformation is presented in two different views rotated by 90° around the screw axis. The (a) and (c) projections are drawn in a plane parallel to the twofold axes associated with the rigid groups; the (b) and (d) projections are represented in a plane parallel to the twofold axes associated with the aliphatic groups.

In Figure 7 the unit height (h) is reported vs. ϑ_3 for a possible s(2/1)m symmetry of the P_9 polymer. Also in this case, the aliphatic chain is assumed to be trans planar. The calculated period is in agreement with the experimental value at around ϑ_3 = +60°, corresponding to the shortest extension in this symmetry. The model is compared in Figure 8 with the analogous model in the highest extended conformation (ϑ_3 = −120°, c = 48.4 Å). Both projections are represented in a plane perpendicular to the mirror plane m and then parallel to the screw axis.

All three chain symmetries discussed for the odd series of polymers are able to give chain models in agreement with our energetic assumptions. However, the s(2/1)2 symmetry (as well as the t2 symmetry for the even series) imposes more constraints than the *tic* symmetry on the chain conformation. The s(2/1)m symmetry contains

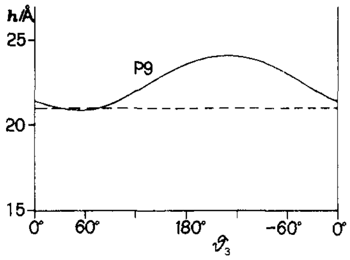


Figure 7. Calculated unit heights (h) vs. torsion angle ϑ_3 (ϑ_1 = +90°, ϑ_2 = 180°, aliphatic chain all-trans, chain symmetry s(2/1)m) for the P_9 polymer. The dashed line corresponds to the experimental unit height.

Table III
Parameters Characterizing the Molecular Alignment with the Chain Axis and Calculated Identity Periods for *Different Symmetries and Conformations of the* P_n Polymers[a]

polymer	sym	ϑ_3/deg	γ/deg	σ/deg	c/Å
Chain Conformations Corresponding to the Experimental Identity Periods					
P_8	*ti*	120	19.5	36.1	23.1
P_{10}	*ti*	120	21.9	37.4	25.5
P_{12}	*ti*	120	23.9	38.5	27.8
P_9	*tic*	60	44.0	46.1	41.8
P_{11}	*tic*	60	44.0	45.6	46.9
P_{13}	*tic*	60	43.9	45.3	52.0
P_9	s(2/1)m	60	43.7	43.7	41.8
P_9	s(2/1)2	92	45.8	46.9	42.4
Chain Conformations Corresponding to the Highest Extensions					
P_8	*ti*	-120	12.2	22.7	23.9
P_{10}	*ti*	-120	13.3	22.8	26.4
P_{12}	*ti*	-120	14.2	23.0	28.8
P_9	*tic*	-120	26.3	29.3	48.4
P_{11}	*tic*	-120	26.3	28.7	53.5
P_{13}	*tic*	-120	26.2	28.2	58.3
P_9	s(2/1)m	-120	25.9	25.9	48.4
P_9	s(2/1)2	-92	22.4	25.4	47.4

[a] γ and σ angles are defined in the text (see Scheme II). The aliphatic chain has been assumed to be all-trans planar.

mirror planes, and mirror planes are of rare occurrence as molecular symmetry elements. All in all, in our opinion it is likely that the chains have a *tic* symmetry in the crystalline state.

Analysis of the Alignment of Rigid Groups to the Chain Axis

The projections of the polymers reported in this paper show for all the series significant displacements of the rigid groups as well as of the zigzag chain from alignment with the chain axis. That is true also for the calculated conformations with the highest extension, though in this case the chains are less "wavy". Moreover, the P_n chains with n even (see Figure 2 for the P_8 chain) are less wavy than the P_n chains with n odd (see Figures 4, 6, and 8 for the P_9 chain); the inclusion of gauche bonds in the aliphatic chain, though not energetically favorable for the isolated chain, gives rise often to a lower waviness of the polymer chain.

The waviness of the chains can be correlated to the inclination of the rigid groups and of the aliphatic chains

Table IV
Parameters Characterizing the Molecular Alignment with the Chain Axis in the Most Probable Symmetries for the P_8 and P_9 Polymers[a]

polymer	sym	ϑ_3/deg	ϑ_4/deg	ϑ_5/deg	ϑ_6/deg	γ/deg	σ/deg	c/Å
		Chain Conformations Corresponding to the Experimental Identity Periods						
P_8	*ti*	+120	180	180	180	19.5	36.1	23.1
P_8	*ti*	−100	180	+60	180	10.8	20.4	23.4
P_8	*ti*	−160	180	−60	180	10.8	20.4	23.4
P_9	*tic*	+60	180	180	180	44.0	46.1	41.8
P_9	*tic*	+50	180	+60	180	22.4	22.6	41.9
P_9	*tic*	−98	180	+60	180	42.5	42.8	41.9
P_9	*tic*	+48	180	−60	180	39.6	43.2	41.9
P_9	*tic*	−164	180	−60	180	25.3	28.0	41.9

[a] γ and σ angles are defined in the text (see Scheme II). The possible presence of gauche bonds along the flexible chain has been taken into account.

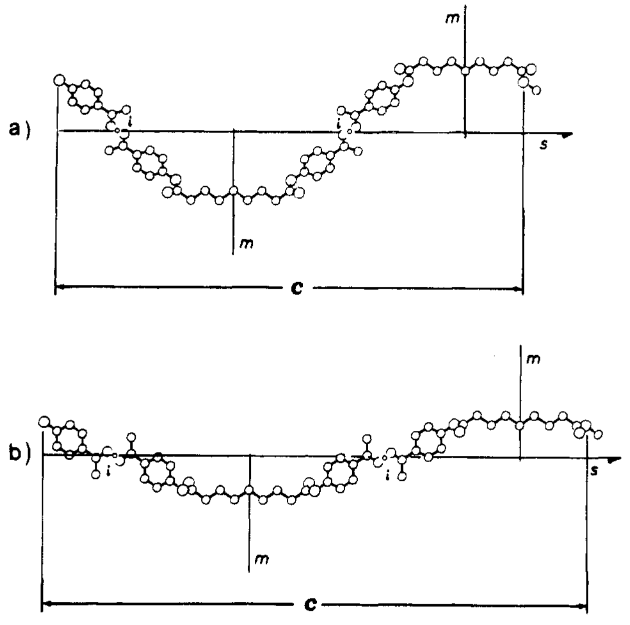


Figure 8. Projections of the P_9 chain models in s(2/1)*m* symmetry in a plane perpendicular to the mirror planes *m* (hence parallel to the screw axis) ($\vartheta_1 = +90°$, $\vartheta_2 = 180°$, aliphatic chain all-trans). (a) represents the chain model reproducing the experimental period ($\vartheta_3 = +60°$), and (b) represents the chain model in the most extended conformation ($\vartheta_3 = -120°$).

with respect to the chain axis. To this end, we may introduce the following parameters (see Scheme II): γ is the angle between the line passing through atom 1 and atom 2 and the chain axis, and $180° - \sigma$ is the angle between the lines 1–2 and 2–3. γ is a measure of the inclination of the rigid groups with respect to the chain axis, while σ may be taken as a possible measure of the waviness of the chain.

In Table III we report the values of the angles γ and σ for some different symmetries of the polymer chains, both for the conformation that reproduces the experimental period and for the most extended conformation in the case that the aliphatic chain is all-trans planar. In the even series, an increase in n corresponds to an increase in σ and hence in the waviness; the opposite occurs in the odd series. Moreover, in the conformations reproducing the experimental periods, γ as well as σ values are always higher than the corresponding values characterizing the more extended conformations. The rigid groups are less inclined relative to the chain axis in the polymers of the even series than in the polymers of the odd series. We expect a higher chain waviness to be associated with lower elastic moduli of the oriented fibers.

The values of γ and σ obtained for the P_8 and P_9 polymers in the *ti* and *tic* symmetries when the aliphatic chain is all-trans are compared in Table IV with those obtained when gauche bonds are introduced along the aliphatic chain. The data are presented for the conformations reproducing the experimental periods. The inclusion of a gauche bond along the aliphatic chain may give rise to a better alignment of the rigid group with the chain axis; though the conformational energy of the isolated chain would be higher, the increase could be compensated by a better packing.

Conclusions

Through the analysis of all possible chain symmetries for the polymers studied it has been shown how chain models reproducing the experimental periods can be constructed. The experimental periods may be reproduced if the aliphatic chain is assumed to be all-trans planar or if gauche bonds are introduced in an odd (ϑ_{2n+1}) position. In this last case, the conformational energy of the isolated chain is higher with respect to the all-trans-planar situation.

The chain models found for the even series in the two possible symmetries *ti* and t2 are all equally good; the *ti* symmetry (see, for example, Figure 2 for P_8) is to be preferred because of the lower number of geometrical constraints that it imposes on the chain.

As far as the odd series is concerned, at least three different chain models for three different symmetries have been calculated for each polymer; the models with the *tic* symmetry are preferable (see, for example, Figure 4 for P_9).

All the proposed models present wavy polymer chains, the waviness being more pronounced in the odd than in the even series.

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Registry No. P_8 (SRU), 57085-49-1; P_8 (copolymer), 57086-47-2; P_9 (SRU), 81772-00-1; P_9 (copolymer), 81772-26-1; P_{10} (SRU), 57085-48-0; P_{10} (copolymer), 57086-48-3; P_{11} (SRU), 81772-01-2; P_{11} (copolymer), 81772-27-2; P_{12} (SRU), 57085-47-9; P_{12} (copolymer), 57086-46-1; P_{13} (SRU), 81772-02-3; P_{13} (copolymer), 81772-28-3.

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Thermotropic Polypeptides. 3. Investigation of Cholesteric Mesophase Properties of Poly(γ-benzyl L-glutamate-*co*-γ-dodecyl L-glutamates) by Circular Dichroic Measurements

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ABSTRACT: A series of poly(γ-benzyl L-glutamate-*co*-γ-dodecyl L-glutamates) were synthesized with various dodecyl contents, and the thermotropic mesophase properties of the cholesterics were investigated. The mesophase arose in copolymers with dodecyl content >30%. Its temperature region ranged above a definite temperature, T_2, which decreased from 115 to 50 °C with increasing dodecyl content. The cholesteric pitches corresponding to the visible wavelength, as determined from the CD spectrum, were observed for mesophases in copolymers with dodecyl content of 30–60% and in the temperature region 100–160 °C. In this limited observation of pitches, the pitch increased with temperature for a given copolymer or with dodecyl content at a given temperature. Each dependence appeared to be independent of the degree of polymerization. The present liquid crystal was characterized by having a high viscosity. The formation of a cholesteric twisted configuration or the transformation of one configuration to another, hence, proceeded with a fairly long response time, and some structural characteristics of the cholesterics were able to be extracted from the observation of CD spectra through these slowly proceeding events. The high viscosity also enabled the perfect solidification of the cholesteric structure or its related optical properties by chilling the cholesteric mesophase below T_2.

Introduction

Paper 1 of this series[1] reported the first observation of thermotropic liquid crystals on α-helical poly(γ-methyl D-glutamate-*co*-γ-hexyl D-glutamates). In that paper, it was deduced that the thermotropic liquid crystalline nature can be induced for copolymers with intermediate hexyl contents of 30–70% and that an appreciable difference in the length of the side chains, probably a difference of five or more methylene units, is necessary for producing the thermotropic nature in copolymers. Paper 2[2] also indicated that even in homopolymers of L-glutamates, the thermotropic nature appears if *n*-alkyl groups longer than decyl are attached to the side chain. In both cases, the long flexible side chains are responsible for the occurrence of thermotropic liquid crystals such that they may play the role of solvent in familiar lyotropic liquid crystals. These novel liquid crystalline (LC) polymers, having a mesogenic α-helical rod surrounded by flexible side chains, should be differentiated from two familiar kinds of thermotropic LC polymers—the so-called main-chain LC polymers[3,4] and the side-chain LC polymers[5,6]—and classified into a third kind of LC polymer together with cellulose and isocyanate derivatives,[7-10] as illustrated in Figure 1.

The type of liquid crystal formed in a polypeptide system is cholesteric because of the chilarity of the main chain. Cholesteric liquid crystals are especially interesting and promising. Among their most important properties are their extremely strong rotatory power and their selective reflection of circularly polarized light in a narrow band of wavelength.[11] The latter leads to spectacular color effects, the wavelength, λ_m, of the color being related to the pitch, P, of the cholesteric helix and the refractive index, n, according to the relation

$$\lambda_m = nP \sin \theta \tag{1}$$

This equation also represents the dependence of λ_m on the angle θ between the plane of the cholesteric layer and the direction of the incident light. For light perpendicular to the plane of a thin sample and with molecules lying parallel to a planar surface, the relation is $\lambda_m = nP$. Tilting the plane of the sample to the incident light causes a blue shift of λ_m.[12] In general, the pitch is sensitive to changes in temperature or pressure for both lyotropic and thermotropic cholesteric liquid crystals. Such a sensitivity has been extensively examined by experimental and theoretical analyses to establish what essential physical force causes the twisted configuration of the cholesteric structure.[13-15] With respect to application, the sensitivity has also promised the use of cholesteric liquid crystals in electrooptical displays and temperature indicators.[15,16]

Apart from their optical properties, cholesteric LC polymers are of special interest in the search for materials having superior mechanical properties. The uniaxial alignment characteristic of the nematic phase is useful for the production of high-modulus fibers,[17] since the resulting distribution of molecules about the fiber axis can be very narrow. On the other hand, a biaxial orientation characteristic of the cholesteric phase is ideal for polymeric films.[18] A thin cholesteric layer exhibiting a Grandjean texture (or a planar texture) would have all of the molecular axes uniformly distributed in the plane of the film. If this structure can be retained during solidification, the resulting film, similar to an "angle-ply" laminate, would have optimum mechanical properties when tested along any arbitrarily selected direction in the film plane. This

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