Structural changes through phase transitions in liquid-crystal polymers: 1. A spectroscopic study of polyesters

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Previous work on lattice dynamics and vibrational spectra of disordered chain molecules has allowed the identification of spectroscopic signals characteristic of the molecular microstructure. These data are used for the identification from the infra-red spectrum of the structural changes with temperature of a 'symmetric' liquid-crystal polyester and of a few model compounds. The K–S phase transition is prepared by the introduction of *GTG'* defects in the flexible spacers in a temperature range well inside the K phase. The S phase is characterized by the generation of a larger concentration of *GTG'* conformational kinks while no *GG* defects are observed. Thus the flexible chain does not coil in a 'liquid-like structure'. The same structural situation is observed for the I phase. These results have interesting implications for the description of the structural changes of this polymer molecule through phase transitions. A mechanism for the transition is proposed.

(Keywords: structure; phase transition; liquid crystal polymers; spectroscopy; polyesters)

INTRODUCTION

In the past few years theoretical and experimental studies on molecular and lattice vibrational dynamics of simple chain molecules have shown that their infra-red and Raman spectra exhibit absorption or scattering bands specifically associated either with ordered one-dimensional (1D) or three-dimensional (3D) structures or with intramolecular or intermolecular disordered microdomains[1–3]. With these spectroscopic signals one can tackle the problem of order–disorder in macromolecular systems whose solution is required for the understanding of their macroscopic physical properties.

In this paper we specifically refer to the vibrational properties of ordered and disordered polymethylene molecules, which have been widely studied in recent years. The set of spectroscopic signals found for these systems is a very powerful diagnostic tool for the understanding of the structures of more complex polymeric systems containing long polymethylene sequences[3–6].

With these methods we have previously studied structural evolution as a function of temperature through the various phase transitions of two of the simplest systems in the class of liquid crystals, namely dodecylcyanobiphenyl (12-CB)[7] and dodecyloxycyanobiphenyl (12-OCB)[8]. From these studies it was clearly shown that the K–S transition is characterized by the fact that the alkyl chain originally in *trans* conformation collapses into a 'liquid-like' structure, which remains mostly unperturbed through the S–I transition. The problem of the interplay between the length and structure of the polymethylene chain and the nature of the mesogenic group in liquid-crystal polymers is a matter of active study at present. This paper reports on the results of our studies of a prototype liquid-crystal polyester. In particular we deal with a prototype 'main-chain' centrosymmetric liquid-crystal polymer whose peculiar properties seem uniquely associated with the structure and behaviour of the molecular chain backbone.

The polymer studied is

$$-[(CH_2)_{10}-OOC-C_6H_4-OOC-C_6H_4-COO-C_6H_4-COO]_n-$$

hereafter referred to as HTH-10. For a more complete understanding of the problem we have also studied the spectra of two model compounds, namely the monomer M,

$$CH_3(CH_2)_9-OOC-C_6H_4-OOC-C_6H_4-COO-C_6H_4-COO-(CH_2)_9CH_3$$

and the model X,

$$C_6H_5-OOC-C_6H_4-COO-C_6H_5$$

The chemical structures of the molecules studied are sketched in *Figure 1*.

EXPERIMENTAL

HTH-10 has been synthesized and its liquid-crystal properties have been described by Chiellini *et al.*[9], according to the procedure previously reported[10]. Not

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much is yet known on its detailed structure; some X-ray diffraction data are reported by Frosini *et al.*[11] and its infra-red spectrum has been studied by Benedetti *et al.*[12,13]. We have remeasured the transition temperatures by d.s.c. and they agree with those already reported in the literature within a few degrees Celsius. The transition temperatures of the polymer and of the model compounds studied are reported in *Table 1*.

Temperature-dependent infra-red spectra have been recorded with a Nicolet 7199 interferometer. The temperature of the heating cell was measured with a thermocouple with an accuracy of ±1°C. The as-received samples were melted on KBr windows and recrystallized. The reversibility of the heating process as studied from the vibrational spectra was checked.

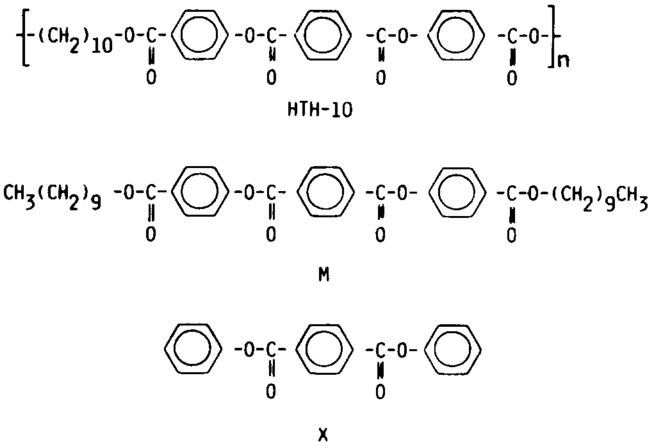


Figure 1 Chemical structures of the polymer (HTH-10) and model compounds (M and X) studied in this work

Table 1 Phase transition temperatures (°C) for HTH-10 and model compounds X and M

	K_1–K_2	K–S	S–I (K–I)
HTH-10		221	260
		216[a]	265[a]
X			191
M	93	139	147

[a]Transition temperatures determined by d.s.c.

INTERPRETATION OF THE I.R. SPECTRA AT ROOM TEMPERATURE

Before proceeding to the detailed analysis of the temperature-dependent spectra (which describe the phase transitions in molecular terms), we outline an overall analysis of the spectra in terms of the chemical structure of the materials studied.

The room-temperature spectrum of HTH-10 (*Figure 2*) shows spectral patterns that can be easily observed in the two model compounds X and M. X represents the mesogenic part of HTH-10 while M represents the repeat unit of the polymer. In *Figure 2* we sketch the overall vibrational assignment qualitatively derived from the spectra of the model compounds (*Figures 3* and *4*).

The vibrational analysis of the polymer must consider first the selection rules for the polymer as a one-dimensional crystal along which phonons propagate without any intermolecular perturbation[14]. The polymer is centrosymmetric, and thus the symmetric, *gerade* (g) Raman-active normal frequencies should not coincide with the antisymmetric, *ungerade* (u) infra-red-active modes. The splitting between g and u modes can occur only if the intramolecular coupling is sizable; if the vibrational motions are uncoupled, accidental degeneracy may occur and some of the i.r.- and Raman-active modes may coincide. It is common knowledge that for such very large molecules intramolecular coupling takes place only between oscillators topologically located so as to favour kinetic coupling (through the inertial terms) or coupling due to the vibrational potential (through locally cooperative changes of the electronic structure during vibration). A typical case will be discussed later in this paper for the vibrations of the C=O groups.

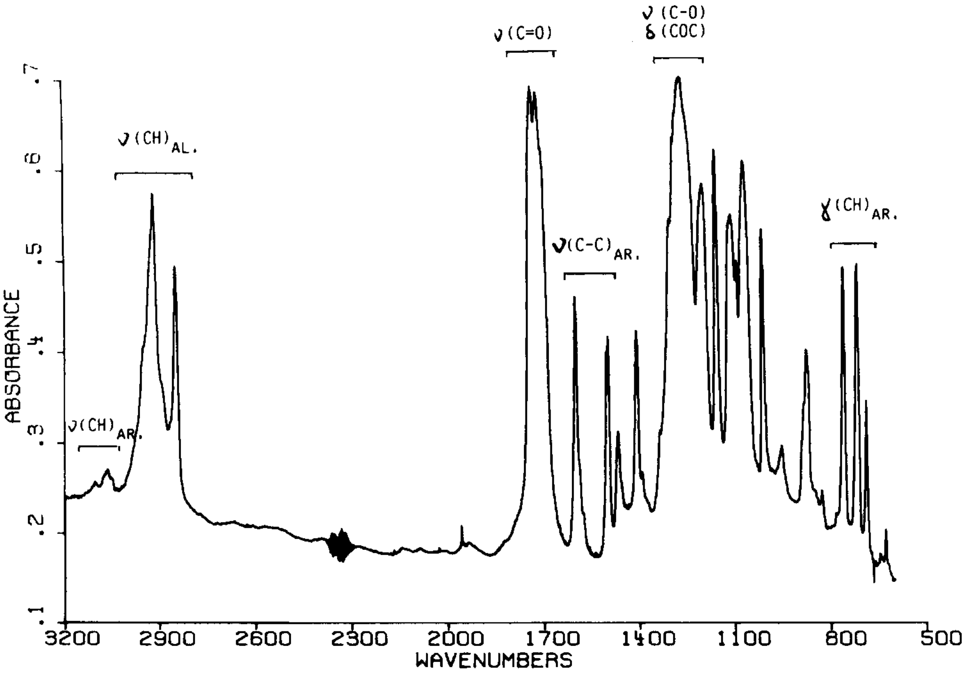


Figure 2 Infra-red spectrum at room temperature of HTH-10

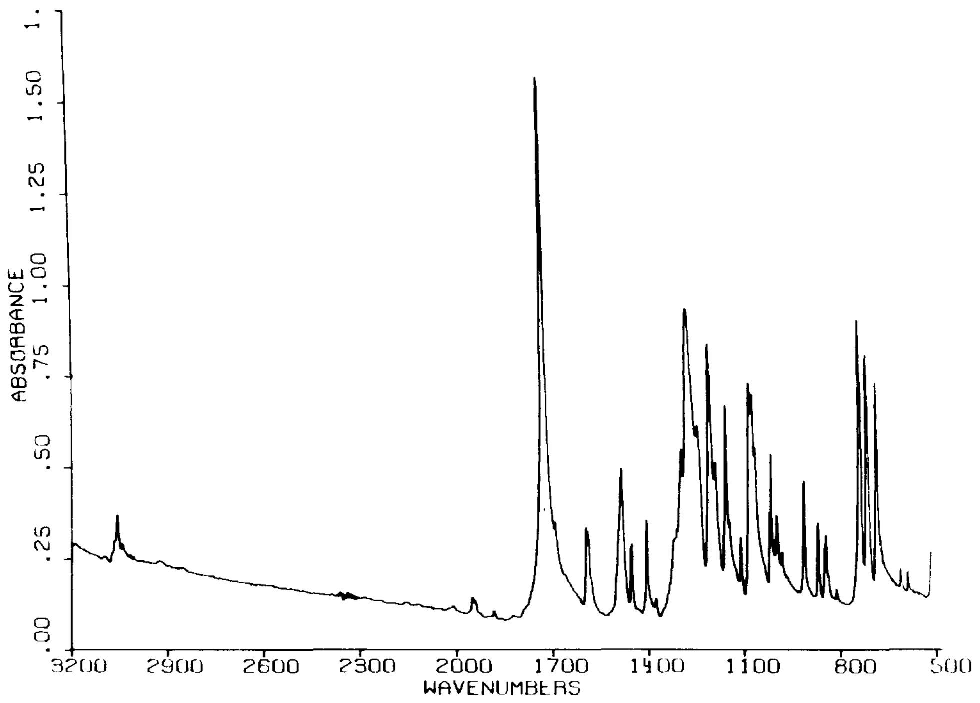


Figure 3 Infra-red spectrum at room temperature of model compound X (see text)

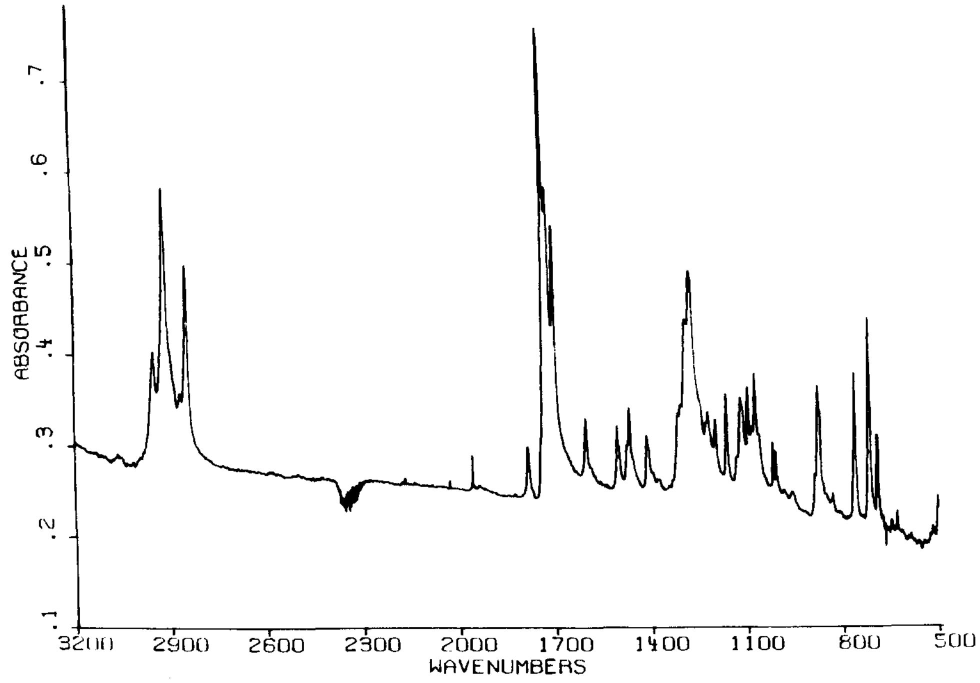


Figure 4 Infra-red spectrum at room temperature of model compound M (monomer) of HTH-10

C–H stretchings

The C–H groups located in positions 2, 3, 5 and 6 in the aromatic rings result in the weak absorptions near 3100 cm^{-1}. The vibrations are highly localized and decoupled. For the aliphatic CH_2 groups we consider, in a first approach to the problem, the group modes d^- and d^+ described as antisymmetric and symmetric C–H stretching, respectively, for the CH_2 groups. They give rise to the infra-red bands at 2918 and 2850 cm^{-1}, respectively[15,16]. No distinction is made between the symmetrically non-equivalent CH_2 groups.

C=O stretchings

The very strong multiplet absorption near 1730 cm^{-1} is not easily accounted for. The use of model molecules is particularly useful for the understanding of the rather complex multiplet structure shown by HTH-10 in the carbonyl stretching range. In order to resolve experimentally the complex multiplet, we have adopted the known method of band deconvolution. This procedure has been attempted several times, with great caution in order to ensure reliability and reproducibility. The temperature-dependent spectra of HTH-10 in the 1800–

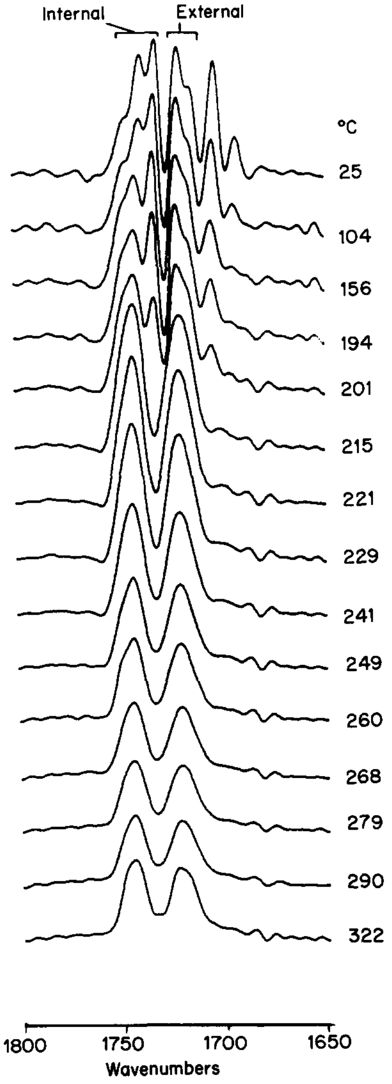


Figure 5 Temperature dependence of the deconvoluted infra-red spectrum of HTH-10 in the C=O stretching region

1600 cm^{-1} range after deconvolution (*Figure 5*) show at least seven peaks, which reduce to two (1743 and 1720 cm^{-1}) at the K–S transition. In *Figure 6* we report the spectrum without deconvolution.

The interpretation of the spectrum in the C=O stretching range may be attempted in various ways once a few basic structural features of these systems are accepted.

First is the coplanarity and conformational rigidity of the benzene 1–4 diester in the centre of the molecule; such a structure has been the matter of some discussion in the literature[17–20]. We have recently performed *ab initio* quantum-chemical calculations with large basis sets on model molecules such as C_6H_5–$COOCH_3$. After full geometry optimization with STO-3G (Slater-type orbitals, three Gaussian) basis set, the molecule turns out to be coplanar because the p_z electrons of the C=O group are conjugated with those of the benzene ring. The barrier height at $\phi = 90°$ is calculated[21] to be 4.9 kcal mol^{-1}. Coplanarity favours conjugation, lengthens the C=O bond length and shortens the ring–COOR bond length. These geometrical changes have been described by the calculation of ref. 21. Since the calculated barrier height is reasonably high, in this paper we keep the OOC–C_6H_4–COO unit rigidly coplanar at all temperatures. The coplanarity of the ester group with the benzene ring was previously indicated by semiempirical potential energy calculations on dimethyl terephthalate[17,18] in agreement with X-ray diffraction studies (for a comprehensive discussion and references, see refs. 19 and 20).

The next step is the search for evidence of *cis* or *trans* geometries of the C=O groups about the central benzene ring. The semiempirical calculations of refs. 17–20 cannot distinguish between these two 'configurations' since no term in the potential couples the C=O groups separated by the benzene ring. For this reason the results presented in refs. 17 and 18 report identical energies for the two geometries. The mutual exclusion between infra-red- and Raman-active modes observed in the spectra of the model compounds (as discussed later in this paper) and the results of X-ray diffraction studies, again on model molecules, indicate the centrosymmetric *trans* configuration as the most likely.

The existence of intramolecular coupling between the C=O groups via the benzene ring is an important issue in this field and some evidence should be sought from vibrational spectroscopy. This problem will be dealt with in this paper along with the discussion of the vibrational assignment, which follows below.

The vibrational assignment and the justification of the complex multiplet structure observed in the C=O stretching region can be tackled in two possible ways. We think it is necessary to discuss these for a more general understanding of the phenomenon, which has already been observed in the spectra of many similar systems, but has not yet been explained.

Conformational multiplicity from spectroscopic correlations. Let R and Ar indicate the saturated and aromatic (or unsaturated) residues that may be attached to the ester group and let L_i and l_i ($i = 1, 2$) label the internal coordinates of stretching of the internal and external C=O bonds, respectively, in the mesogenic group of the systems studied in this work. We first use the spectroscopic correlations among the ester molecules proposed by Jones[22]. According to Jones, molecules of the type R–CO–O–R′ (no conjugation) absorb near 1735 cm^{-1}; molecules of the type Ar–CO–O–R (with conjugation) absorb near 1720 cm^{-1}; the downward shift is ascribed to the decrease in bond order (hence increase in the bond length and decrease in stretching force constant) because the C=O is conjugated with the aromatic ring. More important is the fact (so far not explained) that molecules of the type Ar–CO–O–Ar′ absorb near 1745 cm^{-1}. This fact clearly shows that the existence of a network of p_z electrons adjacent to the –O– group does affect the electronic distribution, and hence the dynamic properties of such systems, seemingly making the C=O bond stiffer than in any other case. Rotation about either side of the –O– group may change such perturbations.

In the polymer and model molecules studied in this work we find both structures Ar–CO–O–Ar′ and Ar–CO–O–R. Following Jones we must then assign the absorptions near 1735 cm^{-1} and near 1720 cm^{-1} to L and l type vibrations, respectively. Let us assume that the assignment by Jones of the C=O stretching mode of the Ar–CO–O–Ar′ molecule at 1745 cm^{-1} corresponds to a structure that contains the largest perturbation, so far unidentified, of the C=O group by the Ar′ residue. The fact that in our molecules we observe a band near 1735 cm^{-1} (see also *Figure 3*) indicates that the conformation about the –O–Ar′ bond is different so as to reduce the perturbation. Upon melting, in the I phase, the L modes vibrate near 1745 cm^{-1}, indicating a change in the conformation in the –O–Ar′ bond approaching the limiting conformation of the models studied by Jones.

Following the viewpoints taken in this subsection, the multiplet structure observed in the spectrum of HTH-10 should be ascribed to the existence in the sample, at room temperature, of more than one structure characterized by different preferential rotational states about the –O–Ar′ bond. The existence of discrete preferential conformational isomers would imply the existence of specific interactions, which generate several sharp minima in the conformational energy function.

In this case the origin of the multiplicity of conformations should be sought in the role played by the lone pair of the oxygen atom in the $-O-C_6H_4-$ group, which may show conformationally dependent coupling with the p_z orbitals of the benzene ring. This fact requires further theoretical study. So far in the literature dealing with liquid crystals the torsion about the –O–Ar′ bond has been taken as +65°[23] based on previously reported data from X-ray diffraction studies on model molecules[20].

One can also postulate that, because of strong intermolecular interactions, different intermolecular arrangements may affect L and l modes. This would imply that, qualitatively, more than one different crystalline structure exists in the sample, their structures being very similar if spectroscopic selection rules are to be kept similar. The existence of two different kinds of unit cells has already been postulated by Frosini *et al.*[11].

If more than one crystalline phase exists in the solid sample, as prepared (or after melting and solidification), the evolution of the spectrum with temperature should show several discontinuities at specific transition temperatures. This is not the case for the observed spectrum, which shows a continuous evolution through K–S and S–I phase transitions. The d.s.c. data we have recorded do not give unambiguous indications of the existence of several crystalline phases.

Intramolecular and crystal-field splitting. The second possible approach to the vibrational assignment of the C=O stretching bands is to consider the possible existence of intra- and intermolecular coupling and to apply the selection rules determined by the symmetry of the system as discussed earlier in this section. This issue has never been addressed specifically before.

If the molecules are centrosymmetric (at least in the mesogenic part), the C=O stretching modes can be described by the following linear combinations of the internal coordinates: $L^+ = L_1 + L_2$, $L^- = L_1 - L_2$ and $l^+ = l_1 + l_2$, $l^- = l_1 - l_2$. Because of symmetry for centrosymmetric systems L^- and l^- modes are infra-red-active while L^+ and l^+ modes are only Raman-active.

If the oligomers are considered as isolated systems and the polymer as a 1D crystal, the extent of splitting of these modes depends on the extent of intramolecular coupling between C=O groups. While it is certain that l^+ and l^- modes are accidentally degenerate since their distance is large, the L^+ and L^- modes may show splitting due to intramolecular coupling, if it exists.

The existence of intramolecular coupling between L type C=O groups cannot be inferred theoretically since any conclusion depends strongly on the theoretical model adopted. We have thus considered the experimental spectroscopic data from model molecules such as dimethyl terephthalate (DMT) and diphenyl terephthalate (DPT). We have taken data reported in the literature and compared them with those recently recorded by us (*Table 2*). The experimental data on DMT seem to show a small but real g/u splitting, with the g modes higher than the u mode, thus implying a positive intramolecular interaction force constant between the two C=O bonds.

Table 2 Experimental splitting (cm^{-1}) of *gerade* (g, Raman) and *ungerade* (u, infra-red) modes due to intramolecular coupling in benzene 1-4 diester molecules

	ν			
	g	u	$\Delta\nu$	Ref.
Dimethyl terephthalate	1728	1716	12	24
Diethyl terephthalate	1724	1719	5	24
Dimethyl terephthalate	1728	1724	4	25
Dimethyl terephthalate	1725	1722	3	26
Diphenyl terephthalate	1735	1730	5	26

In the S phase of our polymer, strong and directional forces due to 3D packing are removed and the i.r. lines at 1740 and 1721 cm^{-1} must be assigned to L^- and l^- modes, respectively (see *Figure 5*). The L^+ and l^+ levels should occur (even if not observable because of symmetry) slightly above and on top of the corresponding L^- and l^- levels, respectively. With the onset of 3D order in the K phase, crystal-field splitting may occur, generating a multiplicity of vibrational levels; the number of levels and their symmetry properties depend on the number of molecules per unit cell and on the symmetry of the lattice. The assignment of each band in the observed multiplet would be arbitrary. What is important is to look at the observed pattern as the possible result of crystal-field splitting. Its existence can be accounted for by the fact that the C=O groups (and their vibrational frequencies) are extremely sensitive to the environment, as observed and predicted in many other cases[27–30].

C–O stretching and COC deformations. These modes generally occur in the 1350–900 cm^{-1} range as strong absorptions surrounded by and overlapped with many other medium–strong bands to be ascribed qualitatively to C–C bond stretchings. The large electrostatic bond dipole moment on the C–O bonds (and the large dipole moment changes during vibration) induce a strong polarization of the nearby C–C bonds, thus giving rise to other strong absorptions as observed. Moreover, large dynamic couplings take place in these modes. In other words the intrinsically weak transitions in this frequency range borrow intensity from the very strong C–O and COC modes. With the help of the spectra of X and M we identify reliably only the absorption of the 'internal' C–O groups at 1275 cm^{-1}. The vibrations of the external C–O groups are inextricably hidden in the observed very strong and complex spectral pattern in this frequency range.

Out-of-plane C–H deformations. The choice of the out-of-plane deformation modes of the aromatic C–H groups cannot be made on the basis of the existing classical correlations, since these modes are strongly perturbed when the ester (or ether) groups are attached to the ring. From a survey of the spectroscopic data in the literature we make the following assignments: the medium–strong line at 690–700 cm^{-1} is due to the out-of-plane deformation mode of the C=O group, the line near 720 cm^{-1} is associated with the out-of-plane mode of the C–H groups adjacent to the C=O group, while the line near 750 cm^{-1} is due to the out-of-plane mode of the C–H adjacent to the –O– of the ester group.

THE STRUCTURE OF THE FLEXIBLE SPACERS AT ROOM TEMPERATURE

A question that must soon be answered is the conformation at room temperature of the flexible spacers connecting the mesogenic aromatic group.

The fact that d^- and d^+ modes (C–H stretchings) occur near 2920 and 2850 cm^{-1}, respectively, indicate that most of the chains are *trans* planar. This is also supported by the observation of the CH_2 bending at 1470 cm^{-1}. It is known that when localized *G* or *G'* rotational isomers are formed, bands arise on the higher-frequency side of d^- and d^+ modes[15,16] and on the lower-frequency side of the CH_2 deformation[31]. These spectral changes are observed upon heating the sample, as will be discussed below.

It may be thought that an alkyl chain made up by only ten CH_2 groups is too short for the existence of a *trans* planar structure, and slightly or strongly twisted chains may occur. Theories and experiments on short polymethylene spacers, e.g.

$$-O\overset{\varphi_1}{-}CH_2\overset{\varphi_2}{-}CH_2\overset{\varphi_3}{-}CH_2\overset{\varphi_4}{-}O-$$

show that almost invariably $\phi_1 = \phi_4 = 180°$, while $\phi_2 = \phi_3 + 60°$[20]. The case of long flexible chains is not yet much studied. While some data are available on the conformation of long alkyl chains in monomeric liquid crystals in the K and S phases[7,8], knowledge on the conformation of long flexible spacers in polymer liquid crystals is very limited. Sigaud *et al.*[23] have treated theoretically the problem of order in the nematic phase of semiflexible polyesters and reached the conclusion that the whole *trans* planar conformation should be preferred. Recent X-ray diffraction studies on low-molecular-weight liquid crystals with alkyl chains of seven or eight CH_2 groups capped with cyanobiphenyl molecules have shown that the chains are strictly coplanar[32].

The existence of slightly twisted chains may be envisaged by assuming a conformationally dependent effect by the lone pair of the oxygen in the –O– group on the CH_2 groups in α and β positions, etc. In spite of several efforts theoretical spectroscopic predictions for the existence of such twisted chains (conformational solitons or conformons)[33] have not yet found unquestionable experimental evidence.

On the other hand, the existence of *gauche* defects in an otherwise all-*trans* lattice gives rise to clear and well understood markers in the infra-red spectra[1–3]. In the case of the HTH-10 polymer, the onset of *gauche* defects is clearly observed only when the sample is heated above 150°C, as will be discussed below.

We conclude that enough evidence is found to consider the conformation of the flexible spacers at room temperature as planar zig-zag.

TEMPERATURE-DEPENDENT SPECTRA

Mesogenic groups

We focus first on the evolution with temperature of the spectrum of the vibrations associated with the mesogenic groups (*Figure 6* for HTH-10, *Figure 7* for X and *Figure 8* for M). In the discussion that follows, we aim mainly at the interpretation of the spectra of HTH-10, using the spectra of model compounds as a source of independent data for correlations.

Starting with the region of the C=O group stretchings, we recall the vibrational assignment discussed above. For HTH-10 the splittings due to intermolecular or intramolecular interactions disappear at the K–S transition near 215°C. What is structurally meaningful is that the spectrum (for HTH-10, M and X) after the transition has occurred corresponds to the state in which the intramolecular forces (i.e. 1D crystal) are more dominant than in the K phase. Under the assumption of keeping the internal diester unit strictly coplanar, the fact that the L^- mode shows a sizable shift towards higher frequencies (from K to S) indicates that the diagonal stretching force constant, i.e. the nature of the C=O, has changed because of conformational changes about the –O–Ar′ group or because of changes in the intermolecular

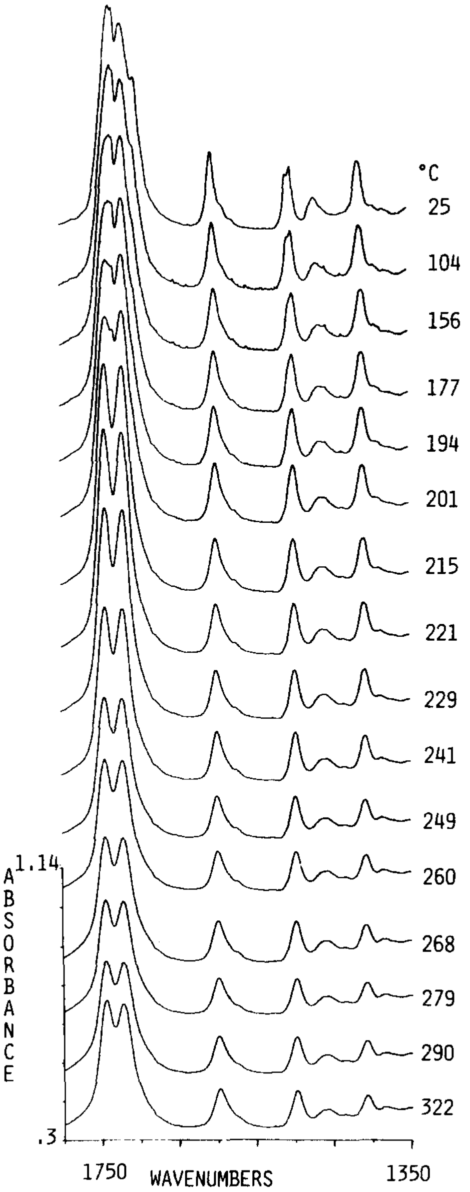


Figure 6 Temperature dependence of the infra-red spectrum of HTH-10 (1800–1350 cm^{-1})

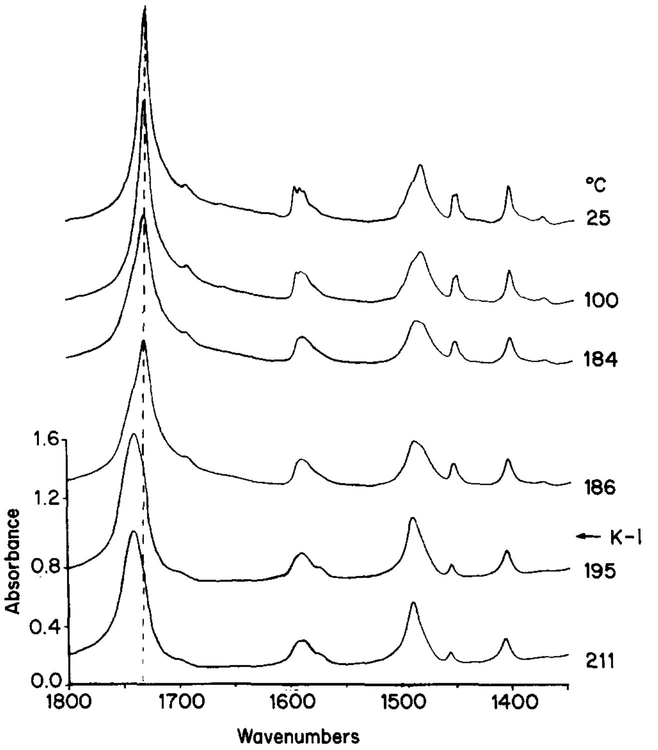


Figure 7 Temperature dependence of the infra-red spectrum of model compound X (1800–1350 cm^{-1})

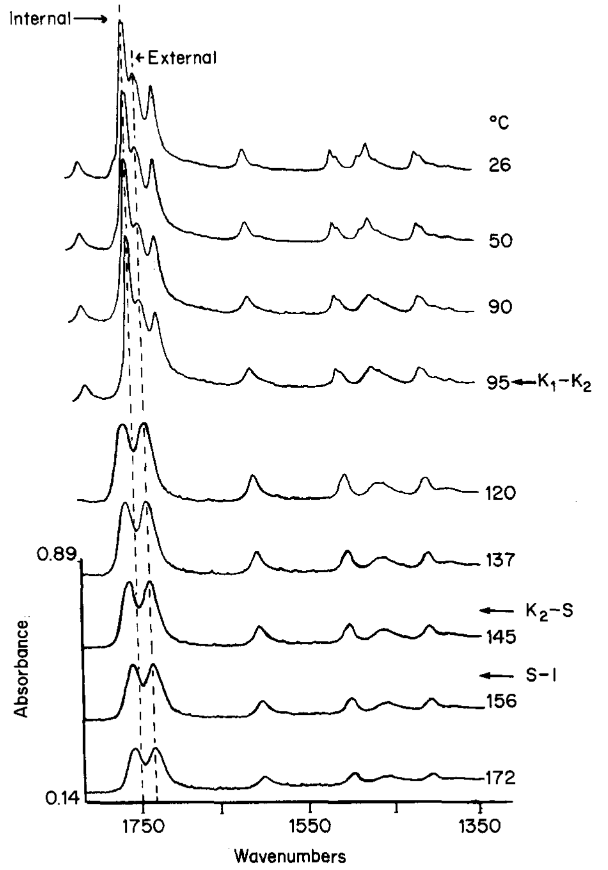


Figure 8 Temperature dependence of the infra-red spectrum of model compound M (1800–1350 cm^{-1})

coupling. So far there is no evidence that the rotation about the R(1)–O(2) bond in the R(1)–O(2)–CO–Ar group changes the C=O stretching frequency, while the frequency may reasonably shift because of intermolecular interactions. Since *l* does not shift, no conclusion can be drawn on the conformational changes about the R(1)–O(2) bond; on the other hand, the lack of shift shows that intermolecular interactions are not changed. It is thus suggested that intermolecular forces affect the centre more than the outer sections of the mesogenic groups. We are in the process of studying the vibrational spectra of suitable model compounds to collect more experimental evidence of these conformational problems relevant for these kinds of materials.

We now move to the spectral range 1350–900 cm^{-1} (*Figures 9, 10* and *11*) where the C–O stretchings and C–O–C deformations occur. According to Jones[22] when the C=O stretching mode at 1700 cm^{-1} shifts upward the corresponding C–O mode shifts downward. This is consistent with our experiments. Indeed, as discussed above, at the K–S transition the L^- mode moves upward while the external C–O mode moves from 1275 to 1255 cm^{-1}.

A very relevant observation needs to be pointed out, namely that for HTH-10 the spectra of the mesogenic part in the S and I phases are practically identical; this happens also for M in the K$_2$, S and I phases. This fact indicates that the structure and intermolecular interactions between mesogenic groups which generate the

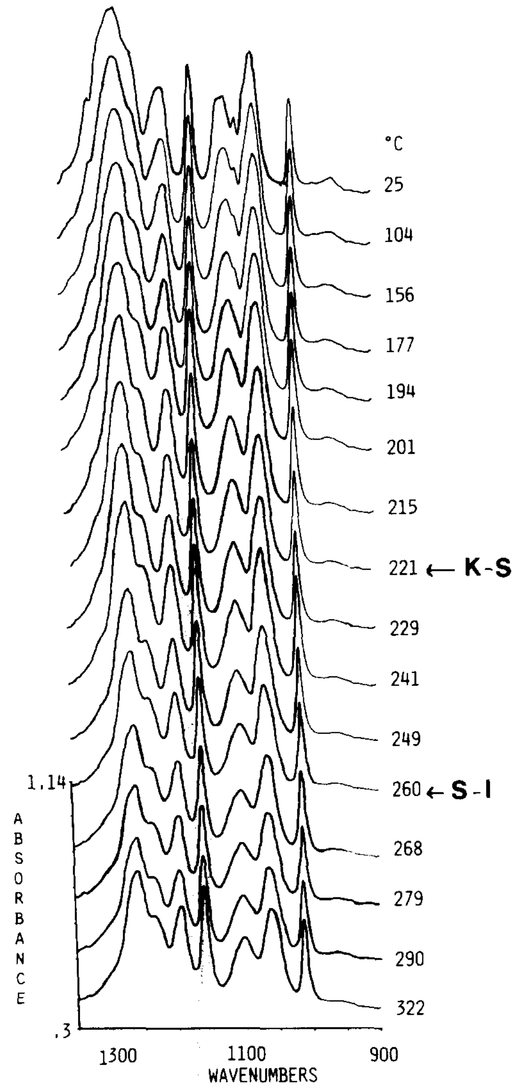


Figure 9 Temperature dependence of the infra-red spectrum of HTH-10 (1350–900 cm^{-1})

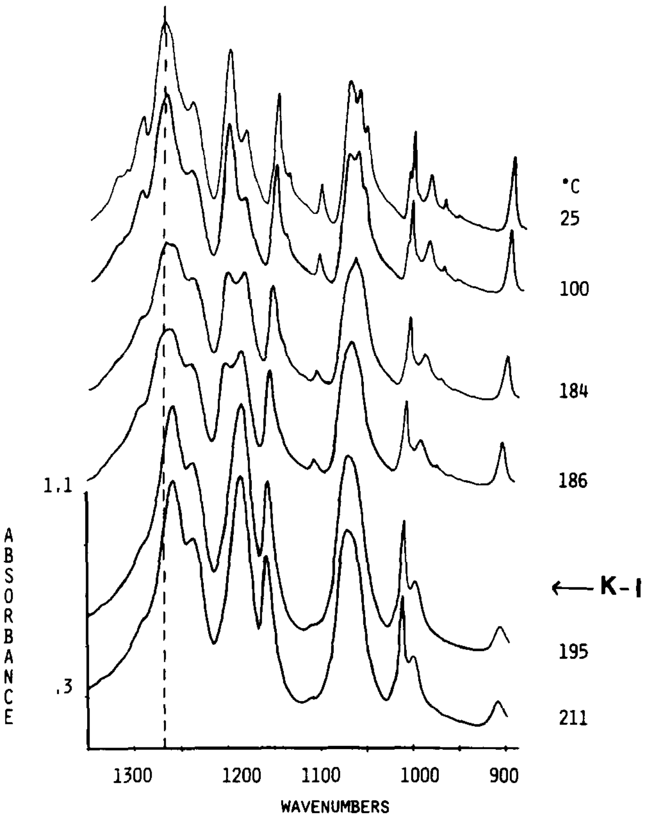


Figure 10 Temperature dependence of the infra-red spectrum of model compound X (1350–900 cm^{-1})

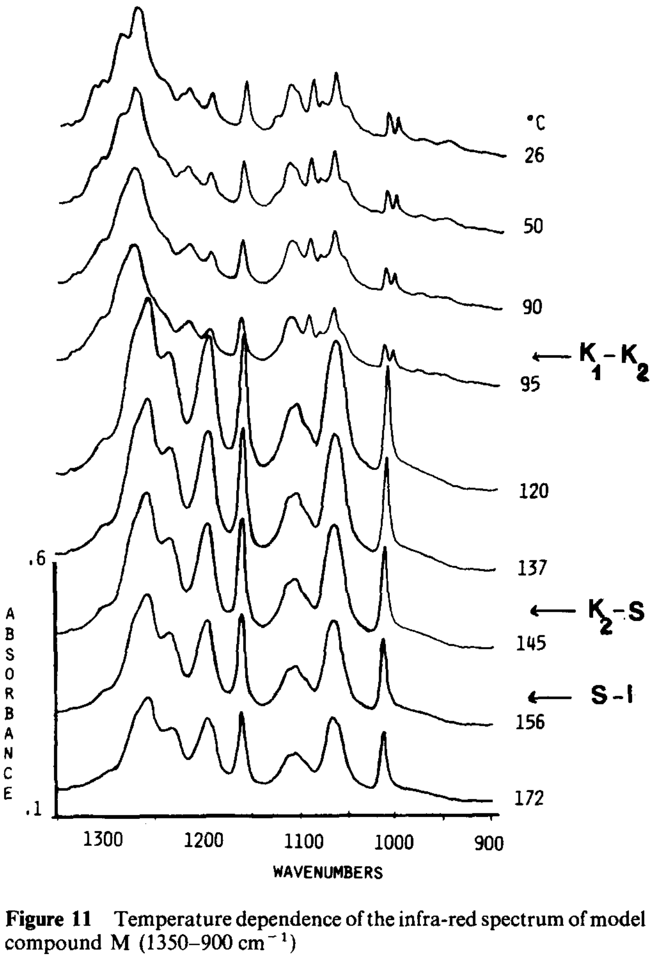


Figure 11 Temperature dependence of the infra-red spectrum of model compound M (1350–900 cm^{-1})

mesomorphic phase remain locally the same also in the I phase.

The physics of such local properties represents the important problem of short- *versus* long-range interactions in such systems. In our experience[3] the vibrational spectra reveal the existence of long-range forces only when networks of delocalized π electrons can be found within the molecule and the normal modes involved are largely collective. In most of the other cases the normal modes are topologically more localized around specific sites of the molecule as a result of the dynamics determined by short-range forces and short-range coupling[28]. This seems to be the case for the materials studied in this work.

Flexible spacers

The results of lattice dynamics and spectroscopic analysis of conformationally disordered n-alkanes[1–6] are used here for the interpretation of the spectroscopic changes with temperature of bands associated with vibrations of polymethylene chains acting as flexible spacers. The spectroscopic infra-red markers for conformational distortions in polymethylene chains are the following:

(i) The characteristic defect bands in the CH_2 wagging range are *GTG'* 1365 and 1306 cm^{-1}, *GG* 1353 cm^{-1}, end-*G* 1343 cm^{-1}, and *GTG'* and *GTG* 1306 cm^{-1} (refs. 1–6).

(ii) When *G* structures are inserted in a host lattice of a *trans*-polymethylene chain, the antisymmetric CH_2 stretching mode in the defect $d^-(G)$ occurs at frequencies slightly higher than the corresponding *trans* mode $d^-(T)$ near 2920 cm^{-1}. This generates an asymmetry on the higher-frequency side of $d^-(T)$ at 2935 cm^{-1}, which coalesces into a broader band near 2930 cm^{-1} when the concentration of *G* defect becomes significant[15,16]. An analogous upper shift of the symmetric CH_2 $d^+(T)$ mode ($2850 \rightarrow 2855$ cm^{-1}) is observed when *G* defects are introduced[7,8]. This behaviour is clearly noticeable in the Raman spectra[15,16].

(iii) A broad band due to the scissoring modes of *gauche* CH_2, $CH_2(G)$, occurs near 1455 cm^{-1} on the lower-frequency side of $CH_2(T)$ near 1470 cm^{-1} (ref. 31).

(iv) For an all-*trans* 1D lattice, C–C stretching modes give rise to two strong lines in the Raman spectrum near 1150 and 1050 cm^{-1}. C–C stretching of *G* defects gives rise to a strong and broad Raman line near 1095 cm^{-1}. For a perfect centrosymmetric all-*trans* chain, these modes do not occur in the infra-red. When the local or overall symmetry of the system is lowered because of disorder, these modes gain infra-red intensity[15,31] because of a slight polarization of the C–C bond[34]. The more conformational disorder that exists, the stronger the C–C(*G*) band becomes.

Let us analyse the spectrum of HTH-10 with the spectroscopic tools listed above. Observation (ii) is verified in the spectrum of *Figure 12*. Thus at room temperature the flexible spacers are mostly *trans* planar (band at 2920 cm^{-1}), but a sizable concentration of conformationally distorted structures already exists (shoulder near 2935 cm^{-1}). The same information is obtained from observation (iii) in *Figure 13*: $CH_2(T)$ 1470 cm^{-1}, $CH_2(G)$ 1445 cm^{-1}. Observation (iv) cannot be verified (*Figure 9*) because the spectrum is crowded

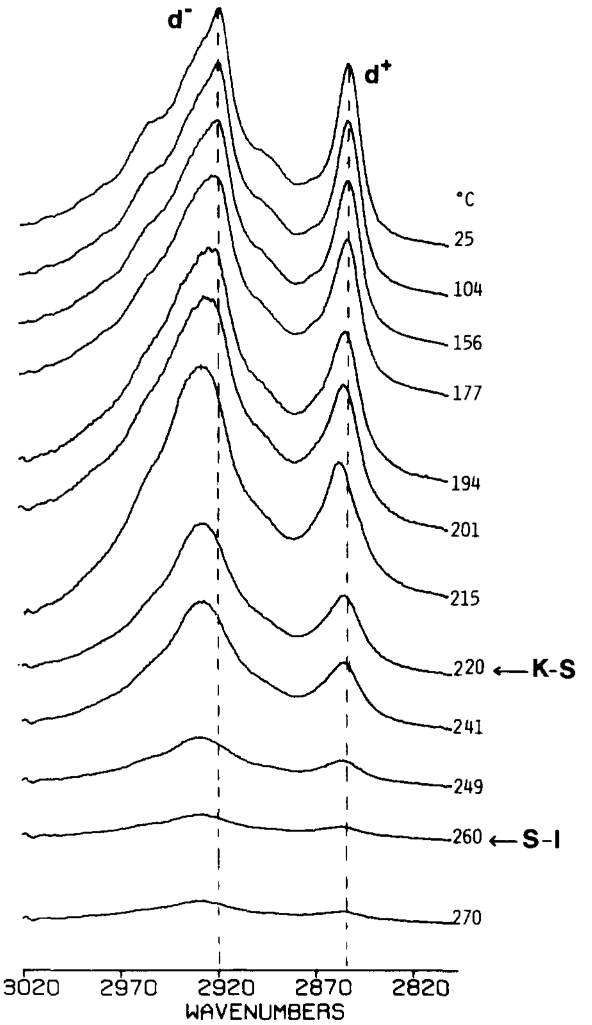


Figure 12 Temperature-dependent infra-red spectra of HTH-10 in the C–H stretching region

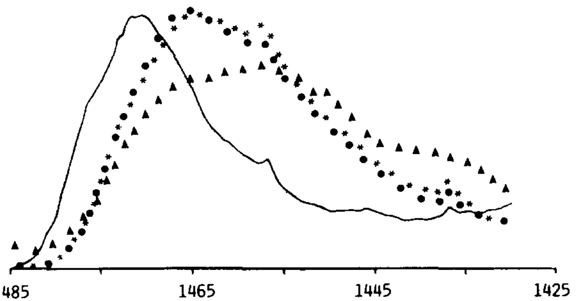


Figure 13 Infra-red absorption of CH_2 scissoring modes of HTH-10 at various temperatures. ———, 30°C; ●, 200°C; *, 215°C; ▲, 255, 260, 270°C

by many overlapping and as-yet unidentified vibrations in this frequency range. The conformation of the spacers becomes increasingly disordered while still in the crystalline phase ($\sim 150°C$) already 65°C below the K–S phase transition. The largest increase in concentration of *G* defects occurs, however, within the temperature range of existence of the S phase.

While observations (ii) through (iv) indicate the formation of *G* structures, in general, they are not able to distinguish between specific kinds of conformational defects that may occur. Observation (i) is of great help in this case. Of the defect modes listed in case (i) in *Figure 14* we only see that the *trans* planar structure (no defect modes in this frequency range) evolves with temperature with the generation of only the defect mode near 1365 cm^{-1} characteristic of *GTG'* defects (*Figure 14*). No absorption due to *GG* defects (band at 1353 cm^{-1}) is observed. The intensity of the *GTG'* defect mode increases sharply at the K–S transition, remains in a smooth plateau until the S–I transition occurs and increases steeply in the I phase. It has to be noted that even in the I phase the *GG* defect mode is still practically not observable. We think that the fact that no *GG* defects are observed in all phases is very relevant in the field of this class of liquid-crystal polymers.

CONCLUSIONS: A MOLECULAR DESCRIPTION OF THE PHASE TRANSITIONS

The present spectroscopic study provides experimental data for proposing a model for the description of the evolution of the molecular structure of HTH-10 with temperature. At room temperature the sample contains a sizable concentration of crystalline material. In this phase the polymethylene spacers are predominantly in the *trans* planar structure even if a certain amount of

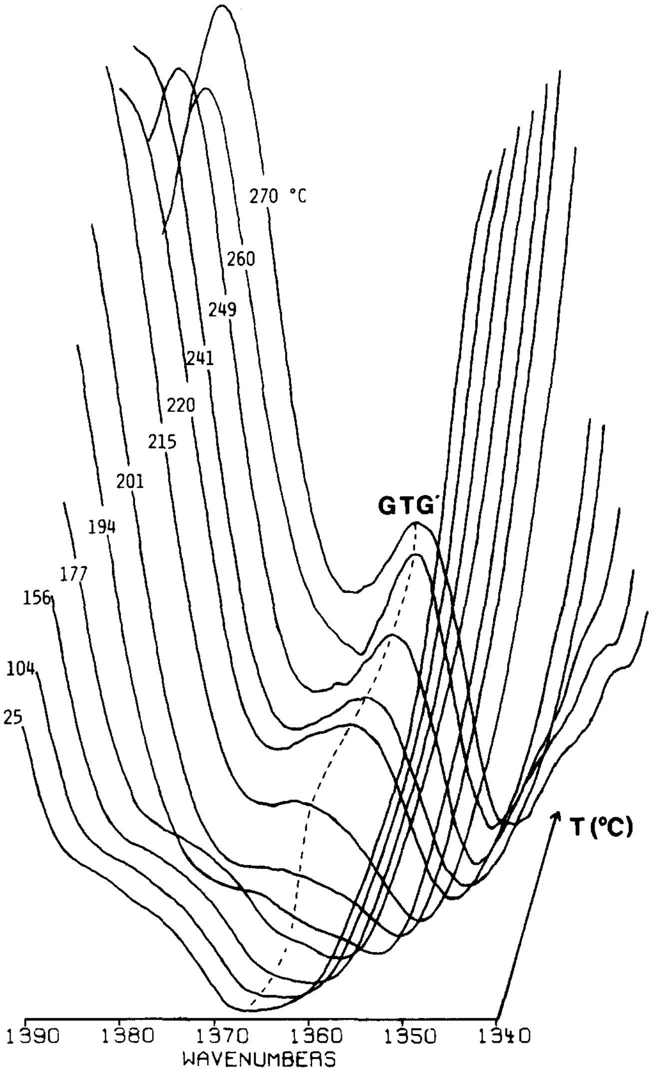


Figure 14 Temperature-dependent infra-red spectra of CH_2 wagging defect modes of HTH-10 showing the development of *GTG'* defect

conformationally irregular structure (thus amorphous) exists.

Already in the K phase we observe the onset of molecular structural changes with increasing temperature. At 150°C a sizable concentration of *G* defects is already seen in the spectrum. This means that in the pretransitional state, in preparation for the K–S transition, the flexible spacers start being conformationally distorted, with the consequent shrinking of their length. The shrinking may be a collective phenomenon, which forces almost identical or correlated conformational changes of the flexible unit, thus forcing identical and simultaneous shortening of the distances between mesogenic groups. Alternatively, if the collectivity is limited only to short distances, a shearing motion between chains (or bundles of chains) should necessarily occur driven by a conformational 'kinking' of the flexible units.

Indeed, small perturbations of the mesogenic groups are observed in the C=O stretching range. Qualitatively we notice a parallel evolution with temperature within the K phase of C=O stretchings and defect modes.

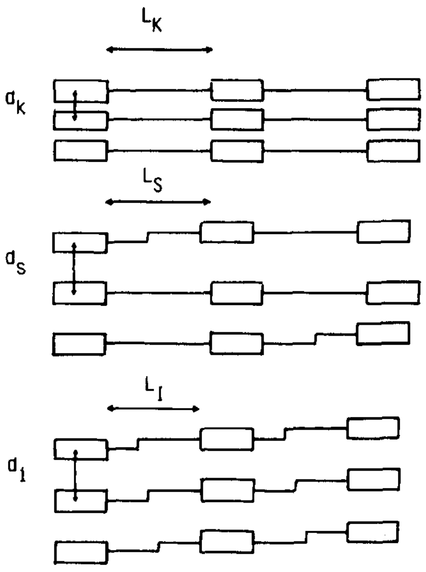
A more drastic change is observed in the C=O stretching range at the K–S transition; the ordered 3D lattice is destroyed and the population of *GTG'* defects increases suddenly (*Figure 14*).

The important information obtained in this work is that the observed conformational distortion of the spacers does not describe the formation of 'liquid-like' domains since no *GG* but only *GTG'* defects are observed. The molecular model for the spacers consistent with the spectrum is that of an alkyl chain containing mostly 'kinks' of the *GTG'* type. *GTG'* defects do not change the trajectory in space of the alkyl chain, but keep both arms at either side of the defect still parallel.

Thus, within the S phase the spacers increase their longitudinal shrinking with no further perturbation of the mesogenic groups, which at the K–S transition have already lost all indications of 'crystallinity', i.e. the intermolecular forces between mesogenic groups have weakened. In this state no strong forces oppose the conformational shrinking of the alkyl chain. It reasonably follows that further sliding of the mesogenic groups may occur even if we do not have any spectroscopic evidence.

The lack of any sizable concentration of *GG* structures even in the I phase leads to the interesting conclusion that the molecular structure in the I phase is not substantially different from that in the S phase. Indeed, the alkyl chains do not seem to have coiled in the 'liquid-like' structure observed for other polymethylenic molecules. One way to reconcile the existence of a macroscopically isotropic phase with the spectroscopic observations on the molecular level is to propose that the isotropic phase consists of a collection of microdomains whose directors are randomly oriented. However, inside the microdomains the polymer molecules are organized as they are in the S phase.

The scenario on a molecular level for the phase transitions of this material consistent with the spectroscopic observations discussed in this paper is sketched in *Figure 15*. This figure shows that the most important phenomenon that occurs in the flexible spacers through phase transitions is the onset of a cooperative or collective clustering of *GTG'* kinks between adjacent chains. Alkyl chains still remain bundled together but allow for the onset of a collective kinking, which does not, however, perturb dramatically the transverse dimensions of the bundles. Similar cases of collective kinking have been observed in bilayered organic perovskites[35] or bilayered structures of organic zirconates[36].



$L_K > L_S \geq L_I$
$d_k < d_s \leqslant d_i$

Figure 15 Sketch of the structural changes of HTH-10 accompanying the various phase transitions consistent with the analysis of the infra-red spectra

Our model revives the concept of the 'meander model' early proposed by Pechold, who has influenced for many years the field of polymer physics[37]. More work needs to be done along this direction.

The observation of the splitting of C=O, *L* and *l* modes discussed at the beginning of this paper reveals again the known fact that vibrational frequencies are mostly sensitive to short-range intramolecular interactions. This is even more true when intermolecular interactions are considered, since interatomic forces do not extend to large distances for non-ionic molecules. Thus, also in the case of liquid-crystal polymers, the vibrational spectrum provides information on the microstructure of the polymer, i.e. on local order/disorder at short range.

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