Generalized Van der Waals Analysis of Thermodynamic Properties of Side Chain Liquid Crystalline Polymers

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Generalized Van der Waals Analysis of Thermodynamic Properties of Side Chain Liquid Crystalline Polymers

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Dilatometric studies were performed on the nematic and isotropic phases of a low molar mass and two polymeric liquid crystals, containing identical mesogenic groups. The polymers were found to display higher transition temperatures, increased densities and lower expansion coefficients relative to the corresponding values of the low molar mass model system.

The thermodynamic properties of the low molar mass and polymeric liquid crystals were analyzed on the basis of a generalized Van der Waals approach, incorporating geometric parameters characteristic of the mesogenic groups as well as anisotropic and isotropic interaction parameters. The results indicate that the increase of the density characteristic of the transition from a low molar mass to a polymer system is an important factor in controlling the shift of the transition temperature as well as of the thermal expansion coefficient. In addition, however, we found that, within the framework of the theory, the effective molecular volume of the mesogenic units within the polymers are increased and the effective axial ratios of the mesogenic units are decreased relative to the corresponding values of the low molar mass system. These variations are obviously caused by the coupling of the mesogenic units to the non-mesogenic chain backbone.

Keywords: liquid crystalline polymer, density variations, phase transition, Van der Waals analysis

I. INTRODUCTION

Thermodynamical quantities of liquid crystalline side chain polymers, such as the location of liquid crystalline transition temperatures, the range of thermal stability of a given mesophase or the densities of the liquid crystalline and of the isotropic fluid state were observed

to differ consistently from those found for low molar mass liquid crystals containing exactly the same mesogenic units.[1,2] This holds to a lesser extent also for the magnitudes of the enthalpy and volume changes at liquid crystalline transitions and for pretransitional properties.

The transition temperatures are shifted to higher values and the width of the phases on the temperature scale increases as we go from a low to a high molecular weight system. Furthermore, it was often observed that the polymers are able to display additional liquid crystalline phases which were not exhibited by the corresponding low molar mass system.[1]

These differences between the thermodynamical properties of low molar mass and polymer system have been envisioned, in an intriguingly simple picture, as being caused by the density changes induced by the polymerization process. Pressure induced density increases are known to give also rise to shifts of the transition temperatures to higher values, to an increase of the range of stability of a given mesophase and to the formation of additional mesophases.[3] The basic assumption is that there is an analogy between the effect of density variations induced by pressure and of density variations induced by the polymerization process.

There exists, of course, a set of indications that this picture may be oversimplified. NMR-studies as well as Neutron scattering studies have revealed that the conformation of the flexible main chain is influenced by the anisotropic structure within the mesophases and that a weak orientation correlation exists between the mesogenic group and neighboring units of the backbone of the flexible chain.[4,5,6]

It is for this reason that we have decided to investigate the role of the density variation induced in liquid crystalline side chain polymers systems by the polymerization process on the basis of an appropriate theoretical approach. We were particularly interested in the role of the spacer groups and of the flexible main chain in controlling thermodynamic properties. The experimental part of our studies involved the determination of the densities within the isotropic and nematic phases as well as of the transition temperatures for a low molecular weight liquid crystal and for two liquid crystalline side chain polymers, containing an identical mesogenic group. These data were analyzed in a first step with respect to the role of the density increase, originating from the transition from a low molar mass to a polymeric system. Secondly we related the thermodynamic properties to molecular geometric properties and molecular attractive interactions using a generalized Van der Waals approach, both for the low molar

mass as well as for the polymer systems. We decided to compare the thermodynamic properties of a low molar mass systems, composed of a rigid core and a flexible tail with those of two liquid crystalline side chain polymers carrying the corresponding structural units as a side chain. It will become apparent below that this is—within the framework of the theory—a more appropriate comparison than the one between the monomer systems and the corresponding polymer systems.

II. THEORETICAL CONSIDERATION

It has generally been accepted that both the long ranged isotropic and anisotropic intermolecular attractive interactions as well as short ranged anisotropic repulsive interactions are of about equal importance for the formation of mesophases as well as for their thermal stability.[7] It is therefore evident that geometric parameters, characteristic of the mesogenic groups, control the anisotropic repulsive forces and influence thermodynamic properties appreciably.[8,9] In order to simplify the theoretical treatment most theories of liquid crystalline phases make, however, assumptions with respect to the relative importance of the attractive and repulsive interactions. Furthermore, they usually do not relate geometric parameters to macroscopic properties.[10,11]

It is the advantage of the generalized Van der Waals treatment that it incorporates both the attractive and the repulsive interactions, that it relates molecular properties to macroscopical properties and that it renders an equation of state.[9,12–17]

The geometries of the mesogenic groups are modelled, as shown in Figure 1, by those of spherocylinders, i.e. by hemispherically capped cylinders of length l and diameter $2a$. Characteristic parameters are thus the molecular volume v_0 and the ratio x of the length to the width, given by:

$$x = l + \frac{l}{2a}$$

The starting point is the following expression for the isotropic and anisotropic part of the pairwise attractive interactions between two molecules i and j having a cylindric symmetry whose long axes form an angle $\gamma(\Omega_i, \Omega_j)$ (Figure 1)[13,14]:

$$U(r_{ij}, \Omega_i, \Omega_j) = -\frac{C_{iso}}{r_{ij}^6} - \frac{C_{aniso}}{r_{ij}^6} \cos^2\gamma(\Omega_i, \Omega_j) + \ldots$$
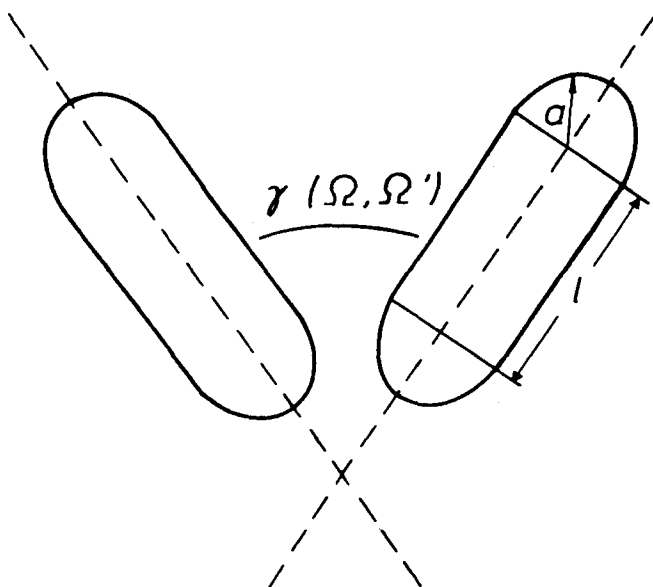
FIGURE 1 Configuration of mesogenic molecules.

where the parameters C_{iso} and C_{aniso} are controlled by the average value and the difference of the molecular polarizibility tensor. The average value of the pair attraction is calculated from this expression according to:

$$a(\Omega_i, \Omega_j) = \int_{\substack{excl. \\ volume}} U(\vec{r}_{ij}, \Omega_i, \Omega_j) d\vec{r}_{ij}$$

where the average has to be taken only over those separations r_{ij} which do not violate the excluded volume conditions for a pair of molecules (Figure 1). The mean field $\psi(\Omega)$ felt by a single molecule with the orientation Ω relative to macroscopic frame of reference is found to be given by:

$$\psi(\Omega) = s_N \int f(\Omega_j) a(\Omega, \Omega_j) d\Omega_j$$

where $f(\Omega_j)$ is the single particle orientation distribution function. It

has been shown that the potential due to the attractive forces can be expressed to an excellent approximation by[12,15]:

$$\psi(\Omega) = -\lambda_0 s_N v_0 - \lambda_2 s_N v_0 S P_2(\cos \Omega)$$

where S denotes the orientational order parameter, defined as:

$$S = \langle P_2(\cos \Omega) \rangle$$

and where the potential parameters λ_0 and λ_2, which are independent of the temperature and the density, are controlled by the isotropic and anisotropic polarizibility of the mesogenic groups through the parameters C_{iso} and C_{aniso}.[15]

It is an interesting feature of this treatment that the anisotropic potential parameter is mainly governed by the isotropic part of the attractive interaction because of excluded volume effects. Based on a scaled particle approach, the particular thermodynamical potential, which is controlled by the repulsive interactions, is expressed—as a function of the orientational distribution function $f(\Omega)$—in terms of the geometric parameters of the mesogenic groups introduced above:

$$F_{\text{Hard Rod}} = F(v_0, X, s_N, f(\Omega))$$

The minimalization of the total thermodynamical potential with respect to the orientation distribution function leads to the following expressions for the orientation distribution function

$$f(\Omega) = (4\pi Z)^{-1} \cdot \exp[\Lambda \cdot S \cdot P_2(\cos \Omega)]$$

where the quantity Λ is defined as:

$$\Lambda = 5\pi r v_0 s_N [1 - (1 - q) \frac{v_0 s_N}{3} \{8(1 - v_0 s_N)^2\}^{-1} + \frac{\lambda_2 v_0 s_N}{kT}$$

and

$$q = \frac{4\pi}{3 v_0 a^2} \quad V = \frac{al^2}{v_0}$$

It thus contains the anisotropic potential parameter, the density as

well as geometric parameters. The Van der Waals model gives rise to a self consistent equation for the nematic order parameter S:

$$S = Z^{-1} \int_0^\pi P_2(\cos \Omega) \exp[\Lambda \cdot S \cdot P_2(\cos \Omega)] \sin \Omega d\Omega$$

as well as to the following equation of state:

$$\frac{P \cdot v_0}{kT} = \Pi - \frac{1}{2} (\lambda_0 + \lambda_2 S^2) \frac{(v_0 s_N)^2}{kT}$$

where the quantity π is given by:

$$\Pi = \frac{v_0 s N}{(1 - v_0 s N)^3} \left\{ \Lambda + v_0 s_N + \frac{2(3x^2 - 1)}{(3x - 1)^2} (v_0 s_N)^2 \right.$$

$$\left. + \frac{3(x - 1)^2}{3x - 1} \left[\Lambda + \frac{x + 1}{3x - 1} v_0 s_N \right] \left(1 - \frac{5}{8} S^2 \right) v_0 s_N \right\}$$

These equations are used to gain information on the interrelation between thermodynamical properties of low molecular and high molecular liquid crystalline systems, the geometry of the mesogenic groups as well as the density of the isotropic and anisotropic fluid state. It has to be pointed out that in the derivation of the equation of state an approximation is used which leads to a reduction of the predicted value of the order parameter relative to the one expected for a rigorous treatment. The magnitude of this deviation amounts approximately to 0.15.[16] Therefore, in order to compare the predicted and the experimental values for the order parameter one has to adjust the predicted values.

III. EXPERIMENTAL

The experiments and the analysis of the data in terms of the generalized Van der Waals theory were performed for a low molecular weight liquid crystal as well as for two side chain liquid crystalline polymers, all of which carry the same mesogenic unit. This is shown in Figure 2. It is obvious that we do not consider the monomer systems but rather a low molar mass model system, since we wanted to study the influence of the coupling of this unit to two polymer backbones
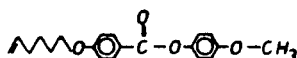
PMe $C_6 OCH_3$

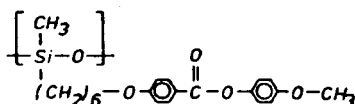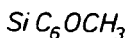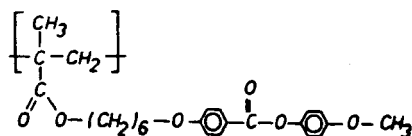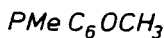Si $C_6 OCH_3$

$C_6 OCH_3$

FIGURE 2 Chemical structures of the low molar mass and polymer systems studied.

which differ with respect to their flexibility. The difference in the flexibility is obvious from the values of the glass transition temperatures, which amount to 280 K for the SiC_6OCH_3 polymer and to 316 K for the $PMeC_6OCH_3$ polymer. All samples exhibit a nematic phase at elevated temperature and a nematic isotropic transition within a range of temperatures which is easily accessible to dilatometric techniques.

The transition temperatures as well as the nature of the liquid crystalline phases were determined by using an polarizing microscope, equipped with a Mettler hot stage, by differential scanning calorimetry, by X-ray analysis as well as by dilatometry.

The density of the isotropic and nematic phase were determined experimentally by means of standard dilatometry, using glass dilatometers equipped with glass capillaries having an inner diameter of 0.5 mm. The dilatometer was filled with the sample, evacuated and then filled with mercury. The height of the mercury level was determined to within 10 μm by means of a cathetometer. The temperature was controlled within 0.1 K.

The experimental data were then analyzed in terms of the equations given above which relate eight variables, namely the particle density

s_N, the pressure p, the temperature T, the molar volume of the mesogenic group v_0, the axial ratio x, the order parameter S as well as the potential parameters λ_0 and λ_2.

In principal, one should define the two potential pararmeters (the parameter λ_0 should be related to the heat of evaporation), take the values of the molecular volume and of the length to width ratio x, as estimated from Van der Waals radii and molecular models, and calculate the densities of the nematic and isotropic phase, the transition temperature as well as the temperature dependence of the order parameter.

However, due to the lack of data on the potential parameters, we have taken the reversed way. It consisted in specifying the experimentally obtained densities of the isotropic and anisotropic phases, the transition temperature as well as the molecular parameters x and v_0.

Considering just the isotropic phase, the potential parameter λ_0 can be calculated:

$$\lambda_0 = \frac{2kT}{(v_0 s_N)^2}\left[\Pi(S = 0) - \frac{Pv_0}{kT}\right]$$

The requirement is that this parameter is positive and nonzero. This may impose in certain cases restrictions on the allowed values for the length to width ratio x and the molecular volume v_0. Once this value has been established, we proceed to determine the potential parameter λ_2:

$$\lambda_2 = \frac{1}{S^2}\left\{\frac{2kT}{(v_0 s_N)^2}\left[\Pi(S \neq 0) - \frac{Pv_0}{kT}\right] - \lambda_0\right\}$$

It is obvious that the potential parameter λ_2 and the order parameter S are related by a nonlinear equation containing two unknown quantities. Numerical methods are required in order to solve the equation.

Again the requirement is that the potential parameter has to be positive and that the order parameter S is a well behaved function of the temperature. A readjustment of the values of the geometric parameters x and v_0 is necessary if this is not the case.[16,17] This adjustment is physically sound, since the properties of molecules possessing partially flexible tails and exhibiting deviations from the shape of spherocylinders have to be projected on the properties of spherocylinders. The allowed (effective) values obtained in this way

for the potential parameters and the geometric parameters are the quantities which will be discussed in the following. We will look for variations induced by the transition from a low molar mass to a polymer liquid crystal and we will evaluate the role of chain backbone in controlling thermodynamical properties.

IV. RESULTS OF DILATOMETRIC STUDIES

a. Low molar mass liquid crystal C_6OCH_3

The low molar mass liquid crystal displays a crystal I to crystal II transition at a temperature of 335.3 K and a crystal to isotropic melt transition at a temperature of 338.5 K on heating. On the other hand, an isotropic to nematic phase transition is observed on cooling. A monotropic nematic phase exists thus which has a clearing temperature of 331.4 K.

Figure 3 displays the temperature dependence of the specific volume in the neighborhood of the nematic isotropic transition temperature. The specific volume is found to be about 0.9125 cm³/g at the transition temperature (Table I). The specific volume is found to vary nearly continuously within the transition range. The data obtained are indicative of the presence of strong low temperature pretransitional effects and the absence of high temperature pretransitional
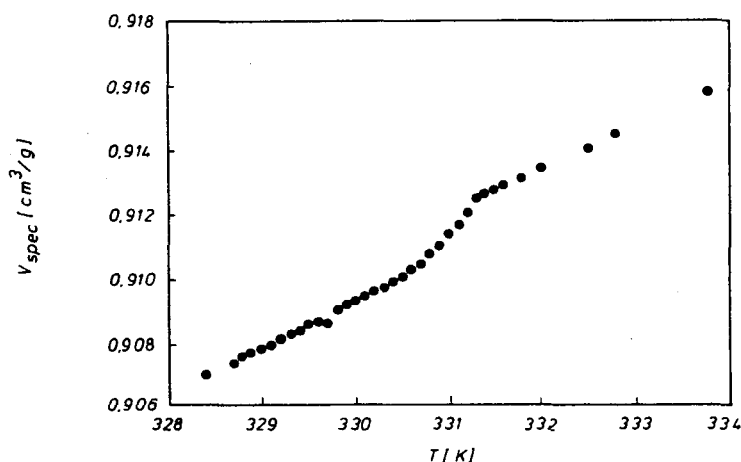

FIGURE 3   Temperature dependence of the specific volume in the neighborhood of the nematic isotropic phase transition temperature (Low molar mass system C_6OCH_3).

TABLE I

Substances	T_{NI} K	$V^+_{Spec.,N}$ $cm^{-3}g^{-1}$	$\Delta V_{NI}/V_N$ %	α_N K^{-1}	α_I K^{-1}
C_6OCH_3	331.4*	0.912	0.18	15.20	13.96
$PMeC_6OCH_3$	385.7	0.869	0.39	5.31	6.16
SiC_6OCH_3	381.4	0.886	0.38	6.29	6.60

$^+: T = T_{NI}$
$*:$ Monotrop

effects. Such a behaviour has been found to be fairly characteristic of the nematic to isotropic phase transition in general.[19,20,21,22]

The relative increase of the specific volume at the transition from the nematic to isotropic phase amounts to 0.18%. This value is certainly influenced by the presence of pretransitional effects. The lower temperature range is inaccessible because of the onset of the crystallization. The expansion coefficient was found to be $1.41 \ 10^{-3} \ K^{-1}$ within the isotropic phase and about $1.52 \ 10^{-3} \ K^{-1}$ within the accessible temperature range in the nematic phase. This value is again influenced by pretransitional effects.

b. Liquid crystalline side chain polymer $PMeC_6OCH_3$

The polymer exhibits a glass transition temperature of 316 K and a nematic to isotropic phase transition at 385.7 K. The clearing temperature is thus shifted by about 54 K relative to the corresponding transition in the low molar mass system. The specific volume at the transition temperature amounts to 0.8693 cm^3/g (Table I). The specific volume is thus lower by 4.7% relative to the values observed for the low molar mass system at the transition temperature. Figure 4 displays the variation of the specific volume with the temperature in the neighborhood of the nematic isotropic transition temperature. Again one finds a rather smooth variation of the specific volume within the transition range, characteristic of pretransitional effects.

This is also obvious from the variation of the expansion coefficient in the nematic and in the isotropic phase, displayed in Figure 5. The expansion coefficient is found to diverge at the low temperature side and to stay constant at the high temperature side of the transition, as the transition temperature is approached from below and above. The expansion coefficient approaches an approximately constant value of about $5.31 \ 10^{-4} \ K^{-1}$ at low temperatures within the nematic phase. It amounts to $6.16 \ 10^{-4} \ K^{-1}$ for the isotropic phase (Table I). It is

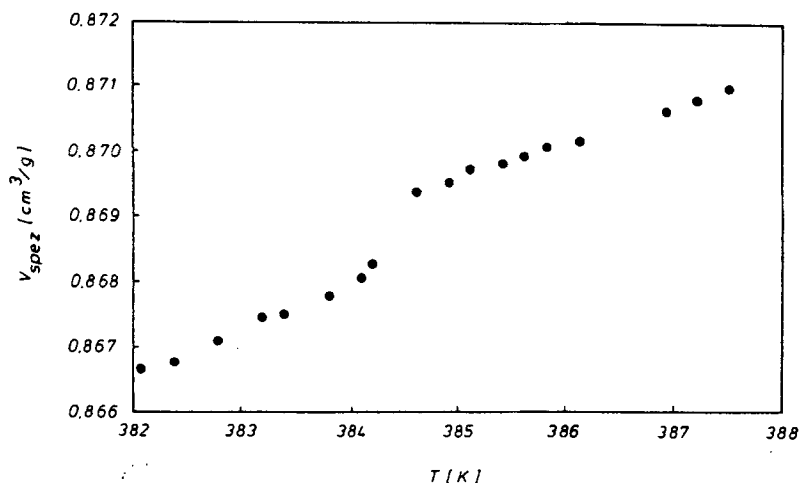FIGURE 4   Temperature dependence of the specific volume in the neighborhood of the nematic isotropic phase transition temperature (PMeC$_6$OCH$_3$).

apparent that the expansion coefficients found for the polymer liquid crystal are much lower than the corresponding values of the low molar mass liquid crystal. The relative increase of the specific volume is found to be $\Delta V/V_{nem} = 0.39\%$ if the density of the nematic phase is extrapolated from temperatures outside of the pretransitional range and about 0.16% if the actual data are taken. The last value agrees rather closely with the one observed for the low molar mass liquid crystal.
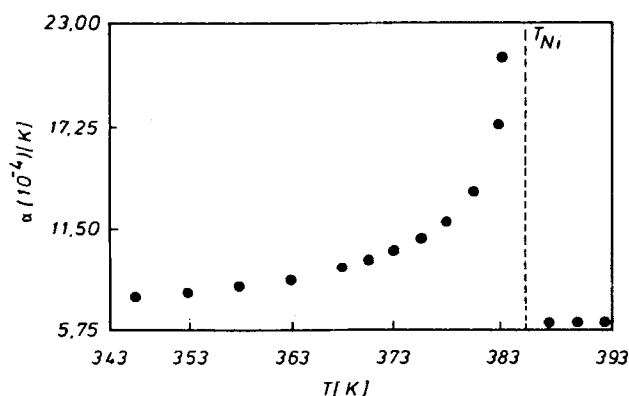

FIGURE 5   Variation of the thermal expansion coefficient in the neighborhood of the nematic isotropic phase transition temperature (PMeC$_6$OCH$_3$).
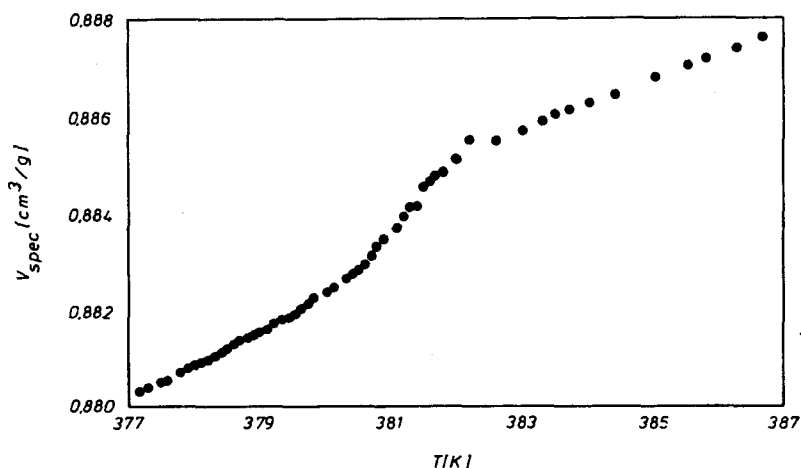
FIGURE 6   Temperature dependence of the specific volume in the neighborhood of the nematic isotropic phase transition temperature (Siloxane polymer).

c. Liquid crystalline side chain polymer SiC_6OCH_3

The siloxane polymer displays a glass transition at about 280 K, a smectic to nematic transition at 317 K and a nematic to isotropic phase transition at 381.2 K. The specific volume at the clearing temperature amounts to 0.8855 cm³/g and is thus similar to the value found for the polymer $PMeC_6OCH_3$ (Table I). Figure 6 displays the now familiar smooth variation of the specific volume within the nematic-isotropic transition range.

The thermal expansion coefficient is found to diverge on the low temperature side of the transition and to be constant at the high temperature side of the transition, in agreement with the behavior of the low molar mass and polymer system discussed above. The values amount to $6.29 \ 10^{-4} \ K^{-1}$ which is characteristic of the nematic phase outside the pretransitional range and to $6.60 \ 10^{-4} \ K^{-1}$ for the isotropic phase (table). These values are similar to the ones found for the polymer $PMeC_6OCH_3$. They differ strongly from those found for the low molar mass system. The relative increase of the specific volume at the nematic isotropic transition is found to amount to $\Delta V/V_{nem} = 0.38\%$,[22] if determined from density values obtained by extrapolation from temperatures outside the pretransitional range. These values are thus similar to those found for the polymer $PMeC_6OCH_3$.

The experimental results discussed above have revealed that the

nematic to isotropic phase transitions in low molar mass and in polymeric systems have some basic features in common, at least on a qualitative basis. The variation of the specific volume within the transition range is found to be smooth, due to the presence of low temperature pretransitional effects. The transition from a low molar mass to a polymer liquid crystal system results, however, for a constant structure of the mesogenic group, in a shift of the nematic isotropic transition temperature of 50–54 K, in a decrease of the specific volume of about 3–5% and finally in an appreciable decrease of the thermal expansion coefficients both in the nematic and in the isotropic phase.

V. ANALYSIS OF THE EXPERIMENTAL DATA

Analysis based on the effect of the density increase

At first, we will discuss the question whether one is able to account for.the differences between the thermodynamic properties of the low molar mass system and the polymer systems purely in terms of the decrease of the volume induced by the polymerization. It is obvious from the data reported above, that the density increase is of about equal magnitude for the two polymers, possessing different backbones and that both their transition temperatures T_{NI} as well as their thermal expansion coefficients are similar. Based on published results on the pressure induced volume changes and on the pressure induced increase of the transition temperatures,[21,22] we have calculated the variations of the transition temperatures and of the thermal expansion coefficient which would result just from an increase of the density.

The results are displayed in Table II. The surprising finding is that the predictions agree quite well with the data obtained experimentally, as far as the polymer $PMeC_6OCH_3$ is concerned. The agreement is less well for the siloxane polymer. So the tentative conclusion is that the density increase certainly makes a major contribution to the

TABLE II

	$PMeC_6OCH_3$	SiC_6OCH_3
V/V_{mon} $(T_{NI})/\%$	4.82	3.29
T_{NI} pred/K	380	363
T_{NI} obs/K	385.7	381.2
α_I pred/$10^{-4}K^{-1}$	8.18	9.63
α_I obs/$10^{-4}K^{-1}$	6.16	6.60

variations of the thermodynamic properties observed as we go from a low molar mass to a polymeric liquid crystal. The anisotropic phase becomes more stable as the packing density of the anisotropic particles is increased.

It is, however, evident that this approach corresponds just to a first approximation, since deviations between experimental values and predicted values exist, particularly in the case of the siloxane polymer. The approximation discussed so far neglects the variations induced in the repulsive and attractive interactions resulting from the coupling of the mesogenic units to the chain backbone. It is for this reason that we decided to use a more refined approach, namely the generalized Van der Waals approach, to analyze the thermodynamic data. This approach has certainly many disadvantages which become apparent in a quantitative analysis.[16,17] It has, however, the advantage that the density enters the expression for the attractive mean field directly and that it leads to an equation of state. One expects that the characteristic parameters of the theory will not be changed, as we go from the low molar mass to the polymer system, once we have taken the density variations into account. Variations of the potential parameters or of geometric parameters will indicate the short comings of the simple approach described above.

Analysis based on the generalized Van der Waals theory

It was already pointed out by Pineda[16] that the predictions of the generalized Van der Waals theory depend critically on the choice of the geometric parameters v_0 and x. It was found that the magnitude of these parameters are usually not identical to the corresponding values of the real molecule considered. The reason is that it is the effective volume v_0 and effective axial ratio x of a spherocylinder, which enters into the basic expressions of the theory. The presence of nonmesogenic tails on the molecules and the deviations from the uniaxial symmetry about the long axis of the molecules will influence the effective values appreciably.

It is for this reason that the analysis of individual low molar mass systems on the basis of the generalized Van der Waals theory yields only qualitative information. More quantitative conclusions can certainly be drawn when the analysis is done for a series of low molar mass systems with identical mesogenic group or for systems in which the mesogenic group are either free or attached to a polymer backbone.

In agreement with data published in the literature[16,17] and in agree-

ment with the restrictions of the theory discussed above we found that one cannot use the true geometry, i.e. the mesogenic core and the tails of the molecule in order to calculate the effective molecular volume and axial ratio. The observation is that these values give rise to a negative value of the anisotropic potential parameter and thus to unreasonable variations of the order parameter with the temperature.

On the other hand one is able to obtain positive values for this parameter, if the molecular volume and the axial ratio x of the mesogenic group are reduced to $v_0 = 290$ A^3 and $x = 2.5$. These values are slightly smaller than the ones calculated for the pure mesogenic group within the molecule. These amount to approximately $v_0 = 303$ A^3 and $x = 2.65$. Similar values were found for other low molar mass liquid crystals such as PAA (p-azoxyanisole),[23] see Table III. It thus seems that it is predominantly the rigid mesogenic part of the total molecule which controls the formation of anisotropic phases, at least within the framework of the Van der Waals theory.

The absolute magnitudes of the isotropic and anisotropic potential parameters are compared in Table III with data obtained on other low molar mass systems[23] for the particular case of the respective nematic isotropic transition temperatures. The result is that the results obtained for the different low molar mass systems are similar. These values will be discussed below in more detail.

It is observed that, in contrast to the assumptions implicit in the theory, these parameters still depend on the temperature. The isotropic potential parameter λ_0 decreases and the anisotropic potential parameter λ_2 increases with increasing temperature. Such variations are known to occur also in the case of the corresponding state treat-

TABLE III

	$v_0/$A^3	X	$\lambda_0/$eV	$\lambda_2/$eV
PAA*	230	3.00	2.50	0.200
P(5)*	273	3.25	3.40	0.023
P(14)*	435	2.82	3.77	0.024
C$_6$OCH$_3$	{ 303 / 290	2.65$^+$ / 2.50^{++}	4.66	0.060
PMeC$_6$OCH$_3$ SiC$_6$OCH$_3$	260	2.65	2.00	0.230

*: Data from literature
+: Model, based on the geometry of the mesogenic group
+ +: values obtained for $T = T_{NI}$
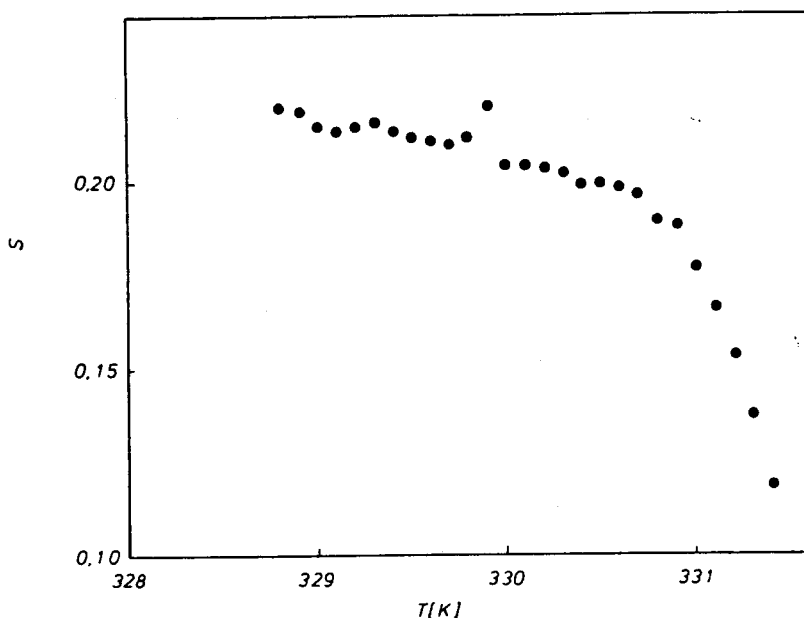P: CH$_3$CH$_2$O—φ—N=N—φ—O(C=O)(CH$_2$)$_n$ CH$_3$

FIGURE 7 Temperature dependence of the order parameter as predicted by the theory for the low molar mass system (C_6O CH_3).

ment of thermodynamic properties where the basic constants v^*, T^* and p^* also vary with the temperature. This reflects the approximate nature of the treatment.

The variation of the order parameter with the temperature corresponds qualitatively to the one found experimentally. The absolute value is, however, predicted to be smaller than found experimentally (Figure 7). This deviation has to be attributed to one of the approximation on which the treatment depends. This problem has been dealt with above. One has to add a constant value of about 0.1 to 0.15 in order to approach the value which would have been obtained for a more rigorous treatment. This still leaves the order parameter unrealistically small, in agreement with previous studies.

In the following we will consider the polymer liquid crystals $PMeC_6OCH_3$. The siloxane polymer will not be considered here in detail, since it gave similar results as the polymer $PMeC_6OCH_3$. The analysis requires the determination of the geometric parameters v_0 and x as well as of the particle densities s_N within the isotropic and anisotropic phase. It has to be pointed out that we consider the particle density rather than the absolute density. The particle density

of the effective structural units will not depend on the inclusion or exclusion of the spacer groups or the chain backbone units within the framework of the theory. This does not hold, however, for its effective volume or its axial ratio.

In a first rather crude model we assume that the mesogenic side groups form locally anisotropic aggregates, which are surrounded by an isotropic state formed by the flexible spacer groups and the flexible chains. We thus consider a segregation model, in agreement with speculations found in the literature. The stability of the anisotropic phase is assumed to be controlled by the interactions within the segregated regions. The molecular volume and the axial ratio is thus taken to be controlled just by the mesogenic group and to amount thus to $v_0 = 303$ A^3 and $x = 2.65$. The particle density within these regions is calculated from the molecular volume and the macroscopic density. The immediate result is, that this set of parameters does not give rise to physically reasonable predictions since one obtains order parameters which are close to 1, independent of the temperature. So this model leads to predictions which are in strong contrast to the experimental results.

The second model corresponds to the approach taken for the low molar mass system. We calculate the effective values for the molecular volume and the axial ratio from the shape and size of the mesogenic group and represent the particle density by that of the total repeat unit. The experimental finding is that both potential parameters turn out to be positive and that the order parameter shows a reasonable temperature variation and magnitude, as long as we consider just the neighborhood of the nematic isotropic transition temperature. The order parameter is found to be smaller just below the nematic to isotropic transition in comparison to the case of the low molar mass system (Figure 8), in agreement with experimental findings. Its absolute value is, as expected from previously published results, unrealistically small.

The potential parameters differ, however, from those found for the low molar mass system at the corresponding transition temperature. The isotropic potential parameter has decreased and the anisotropic potential parameter has increased relative to the values found for the low molar mass system (Table III). This might be taken as an indication that the coupling of the mesogenic groups to the backbone of the chain has induced changes in the molecular interactions which are in excess of the changes induced by the density increase.

Figure 8 shows, however, that the order parameter decreases again at lower temperatures, in strong contrast to all experimental results,
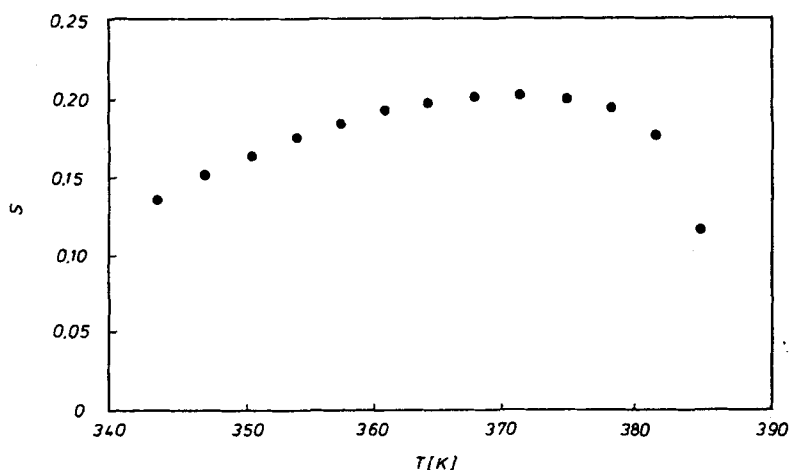
FIGURE 8 Temperature dependence of the order parameter as predicted by the theory for the polymer ($PMeC_6OCH_3$).

provided that we keep the potential parameters constant throughout the nematic range and provided that we keep the geometric parameters constant. Based on the experimental observation that the order parameter increases with decreasing temperature we have adjusted the potential parameters and the geometric parameters in such a way that the predictions of the Van der Waals approach on the variations of the order parameter agree at least qualitatively with experimental results. These variations are shown in Figures 10 and 11. The absolute value of the order parameter remains too small in comparison with experimental results.

We will consider, at first, the differences between the characteristic parameters of the theory at a constant temperature as obtained for the low molar mass system on the one hand and the two polymeric systems on the other (Figs. 10 and 11). We selected as a characteristic temperature the temperature T_{NI} of the low molar mass system. The observation is that the polymer systems display a larger effective volume v_0, a larger magnitude of the isotropic potential parameter λ_0 and a lower axial ratio in comparison to the low molar mass system. These differences can be attributed to a strong coupling of the spacer group and partially of the main chain unit, which are only weakly anisotropic, to the strongly anisotropic rigid mesogenic part: the chain and to a lesser degree the spacer units are nonmesogenic and possess axial ratios which are probably close to one. The coupling of the
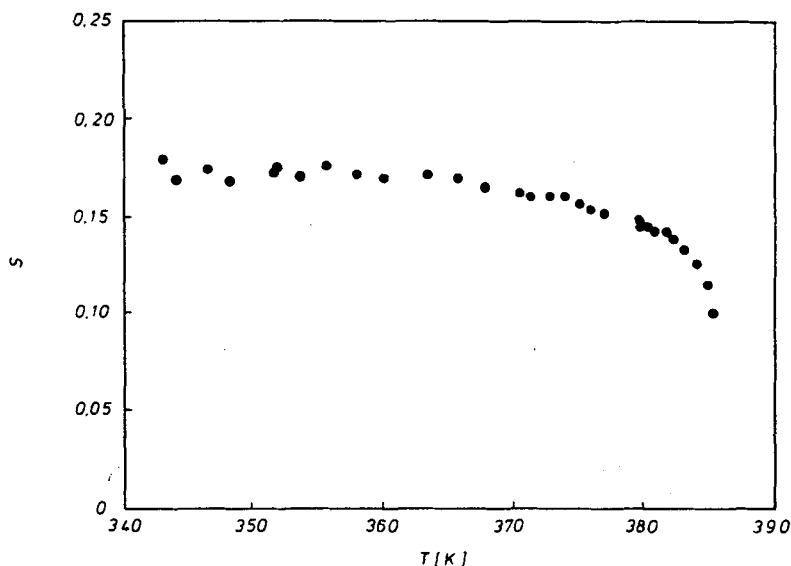
FIGURE 9 Temperature dependence of the order parameter for the polymer (PMeC$_6$OCH$_3$), obtained for effective geometric parameters.

mesogenic units to the chain gives thus rise to a decrease of the axial ratio of the whole unit and to an increase of the effective volume. The total interaction is predominantly controlled by isotropic interactions.

We expect these features to become weaker, as we increase the temperature. The reasoning is that a temperature increase results in stronger decoupling of the rigid parts from the flexible parts of the side chains and from the main chain. This is obviously the case. The isotropic potential parameter is found to decrease with increasing temperature and the anisotropic potential parameter is found to increase with increasing temperature. These variations reflect the growing influence of just the rigid mesogenic part of the side chains on the thermodynamic properties of the anisotropic phase.

The findings that the effective molecular volume decreases and the effective axial ratio increases with increasing temperature are in line with our expectation. Similar variations have been observed for low molar mass system with different length of the flexible tails, if the length of the tail was increased (Table III). The interpretation is again that the effective volume increase due to the coupling of the
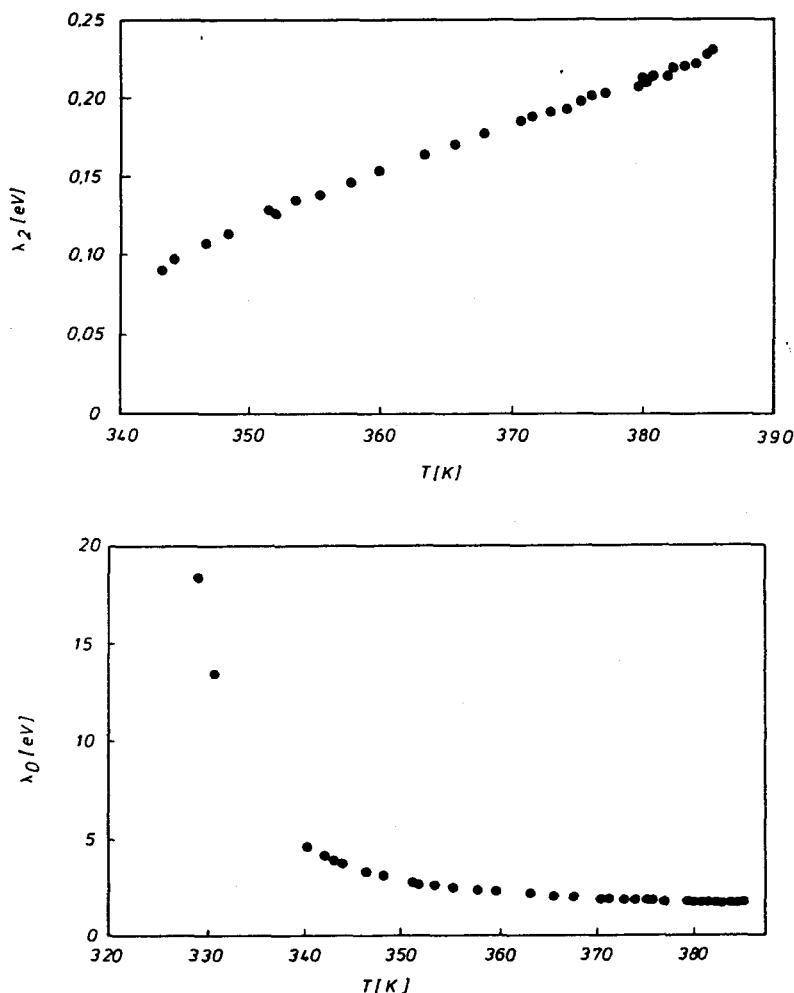
FIGURE 10   Temperature dependence of the potential parameters as predicted by the theory for the polymer $(PMeC_6OCH_3)$.

mesogenic units to a flexible tail and that the coupling decreases with increasing temperature. It is thus the increase of the effective molecular volume and of the effective isotropic attraction, in addition to the increase of the density, which causes an increase of the thermal stability of the anisotropic phase of the polymer systems relative to the low molar mass system. Similar results were obtained for the siloxane polymer.
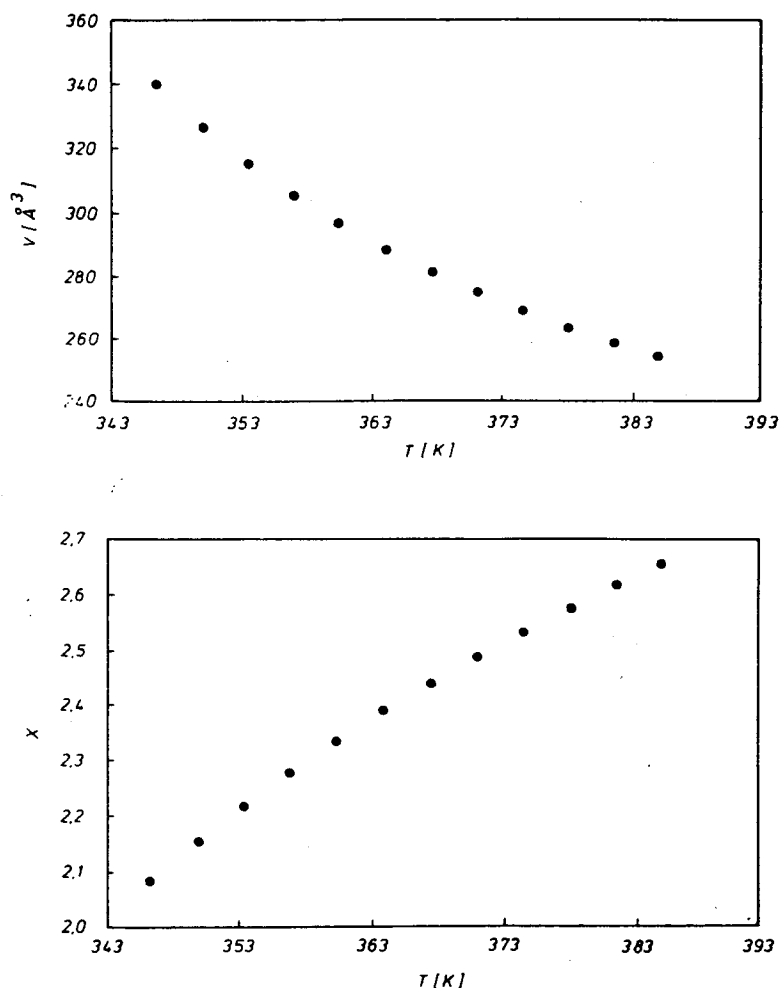
FIGURE 11   Temperature dependence of the effective geometric parameters as predicted by the theory for the polymer ($PMeC_6OCH_3$).

The expectation is that the effective volume and the effective axial ratio will depend on the length of the spacer units, the concentration of mesogenic units along the chain as well as on the tacticity of the chain backbone. In addition, the expectation is that the Van der Waals approach might also be used for disc-like molecules. It seems that the analysis of dilatometric data on the basis of the Van der Waals approach may contribute eventually to our knowledge on the relation

between chemical structure of liquid crystalline side chain polymers and the thermodynamical properties displayed by them.

Acknowledgment

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