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Phase Equilibria in Liquid Crystalline Systems
Part I. Synthesis and Liquid Crystalline Properties of Oligomers of the p-Oxybenzoate Series

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Liquid Crystals / Phase Transitions / Thermodynamics

Syntheses of the trimer (n = 3), tetramer (n = 4) and the pentamer (n = 5) of the p-oxybenzoate series $C_6H_5CO(-OC_6H_4CO)_{n-2}-OC_6H_5$ are reported. Densities and thermal expansion coefficients of the neat liquids were measured and phase transitions in the pure compounds and their binary mixtures were investigated by differential scanning calorimetry (DSC). The nematic-isotropic transition is directly accessible only in the case of the tetramer (melting point 181 °C, nematic-isotropic transition temperature T_{NI} = 254°); the trimer melts to an isotropic liquid at 136°C and the nematic-isotropic transition of the pentamer (melting point 224°C) lies above the range of thermal stability. DSC results for the binary mixtures show the coexistence range of the nematic and the isotropic phases to be very small; it is obscured by pre- and post-transition effects. In satisfactory approximation therefore, the binary mixtures can be treated as one-component systems, and T_{NI} may be identified with the maximum of the DSC peak. Values of T_{NI} thus obtained are linear with respect to composition and may be extrapolated to obtain T_{NI} = 100°C for the pure trimer and 464°C for the pure pentamer. As shown by conformational analysis, all conformers of a given homolog have virtually the same axial ratio. These compounds therefore can be treated as rigid rods.

Introduction

Two factors are dominant in promoting the occurrence of a stable nematic or cholesteric phase: (i) asymmetry of the molecular shape and (ii) anisotropy of the forces between the molecules. The theory of Maier and Saupe [1], which has been extensively applied to low molecular nematogens, considers only the latter factor, thus disregarding the repulsive interactions. A theory which takes into account both features was presented by Flory and Ronca [2]. The steric constraints associated with the accommodation of rigid rods in a limited volume were treated by resort to a lattice model. The theory predicts a transition between discrete isotropic and nematic phases even for "hard" rods, unassisted by "soft" anisotropic intermolecular forces. The predicted transition occurs at a concentration that depends on the axial ratio of the molecule. Soft anisotropic (dispersion)

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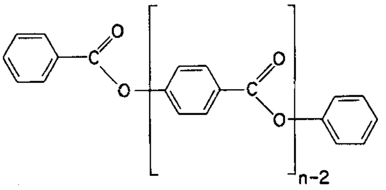
forces were incorporated in the theory through an additional factor in the partition function. The theory has been extended to multicomponent systems [3], i.e., to mixtures of thermotropic nematogenic fluids and to lyotropic systems consisting of long, rodlike molecules in an isotropic solvent. Extensive calculations [4] on thermotropic mixtures of homologous nematogenic species having a most probable distribution of sizes (i.e., length) led to the conclusion that a nematic phase should coexist with the anisotropic phase over a comparatively wide range of temperatures. Furthermore, phase separation was predicted to be accompanied by substantial fractionation, the longer rods being preferentially partitioned into the anisotropic phase [3].

A system ideally suited for testing these predictions should consist of a homologous series of rodlike molecules which are thermally stable at elevated temperatures. Furthermore, their solubility in common organic solvents should be adequate to facilitate the analysis of mixtures of these compounds by standard techniques. The poly-p-phenylenes $H-(C_6H_4)_n-H$ with $n = 4$, 5 and 6 have been the subject of a detailed study recently [5 – 7]. The collinearity of the chain skeleton and the virtually cylindrical symmetry about the long molecular axis in compounds of this series make them uniquely attractive as examples for investigation. However, their solubility in solvents normally used for chromatographic analyses is very low and their transition temperatures are so high (see Ref. [5]) that thermal decomposition presents serious difficulties in the conduct of experiments.

Preliminary experiments [4] indicated that oligomers (I) of the poly-(p-oxybenzoate) series with phenyl and benzoyl terminal groups appended



(I)

are better suited to experiments on phase equilibrium. Mixtures prepared by melt polymerization of phenyl p-hydroxybenzoate according to the procedure of Economy et al. [8] exhibited phase separation into a nematic and an isotropic phase. However, higher oligomers formed in the course of the polycondensation process are not fully soluble in the mixture. This leads to precipitation of a third phase which, incidentally, is crystalline. Analysis by HPLC [9] showed that the content of unreacted hydroxyl groups is appreciable even after formation of high molecular material is substantial. Interpretation of the results is complicated further by the apparent breadth of the distribution of molecular species.

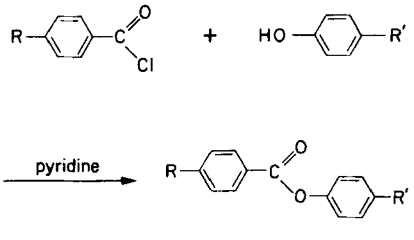
The pure oligomers of the p-oxybenzoate series up to $n = 4$ have been prepared and characterized previously [10]. Their stability at elevated temperatures is sufficient for the present purposes and their solubility is adequate to allow precise analysis by means of liquid chromatography. It is an objective of this communication to describe the preparation of these compounds up to $n = 5$ with special emphasis on high purity and yield.

The recent investigation of the poly-p-phenylenes [5] showed the densities of these fluids to be surprisingly low at the high temperatures T_{NI} of the nematic-isotropic transition. Consequently, their reduced volumes at the transition are large, especially for the higher members of the series. This characteristic turned out to be of utmost importance for an adequate interpretation of the nematic-isotropic transition of the poly-p-phenylenes [6]. Densities and thermal expansion coefficients at temperatures near the T_{NI} of the oligomeric p-oxybenzoates were therefore determined. These data, together with the results of measurements of their Kerr constants and depolarized Rayleigh scattering [11] which serve to elucidate the conformational and optical properties of these compounds, allow a comprehensive test of theory.

Experimental

Synthesis of the Oligomers

Compounds of the structure (I) with $n = 3, 4, 5$ were prepared according to the following route:



The phenolic compounds were prepared as outlined by Fischer and Freudenberg [12] using the carbethoxy group to protect the phenol moiety. Compounds of structure (I) can be regarded as oligomers of poly(p-hydroxybenzoic acid) with specified terminal groups, e.g., the lowest member of the series (compound I.2 below) is the derivative of p-hydroxybenzoic acid with benzoyl and phenyl end groups. For convenience, all oligomers are enumerated according to the number of the phenyl rings; thus, compound I.2 below is the trimer. The melting points reported herein were determined by hot-stage microscopy and are uncorrected. The melting points of the pure oligomers were measured by DSC (see below). All liquid crystalline compounds could be recognized as nematic by the typical Schlieren pattern.

I. Synthesis of the Trimer (Phenyl-4-benzoyloxybenzoate)

I.1 Phenyl 4-hydroxybenzoate

To a solution of phenol (8.7 g, 0.093 mol) in 150 ml water containing sodium hydroxide (4.0 g, 1 equiv) carbethoxybenzoic acid chloride [12] (21.1 g, 1.0 equiv) in 150 ether was added with vigorous stirring. The crude phenyl 4-carbethoxybenzoate which precipitated during the reaction was filtered and dissolved in 300 ml acetone. After addition of 150 ml water and 10 ml of concentrated ammonia solution the mixture was allowed to stand for two hours at room temperature. Following neutralization with ice-cold dilute hydrochloric acid the solvent was evaporated under reduced pressure and the solid residue was washed with water and then recrystallized from ethanol/water (50/50).

Yield: 15 g (75%) m.p.: 176 – 177°C

I.2 Phenyl-4-benzoyloxybenzoate (Trimer)

Phenyl 4-hydroxybenzoate (10.7 g, 0.05 mol) was dissolved in 100 ml ice-cold water containing sodium hydroxide (2 g, 1.0 equiv). To this solution benzoyl chloride (7.7 g, 1.1 equiv) was added dropwise with vigorous stirring. After the last addition the mixture was stirred for an additional 10 min. The trimer which precipitated during the reaction was then filtered off and dried in vacuo.

Yield: 15 g (94%) m.p.: 135 – 136°C (ethanol, 95%)

II. Synthesis of the Tetramer (Phenyl-4-(4-benzoyloxy-)benzoylbenzoate)

II.1 4-Benzoyloxybenzoic acid

To an ice-cold vigorously stirred solution of p-hydroxybenzoic acid (69 g, 0.5 mol) in 400 ml water containing sodium hydroxyde (40 g, 2.0 equiv) benzoyl chloride (77 g, 1.1 equiv) was added dropwise over 15 min. After completion of the addition the mixture was stirred for another 15 min, then ice-cold dilute hydrochloric acid was added and the precipitated p-benzoyloxybenzoic acid was filtered off, washed with water and dried in vacuo.

Yield: 79 g (65%) m.p.: 221 – 223°C (ethanol)

II.2 4-Benzoyloxybenzoyl chloride

4-Benzoyloxybenzoic acid was converted to its acid chloride by refluxing with an excess of thionyl chloride according to the standard procedure [13].

Yield: 80% m.p.: 133 – 134°C (toluene/petrolether 50/50)

II.3 Phenyl-4(4-benzoyloxy)benzoylbenzoate (tetramer)

To a solution of phenyl 4-hydroxybenzoate (compound I.1. 11.6 g, 0.054 mol) in 100 ml dioxane 4-benzoyloxybenzoyl chloride (14 g, 1.0 equiv) in a mixture of 150 ml pyridine and 100 ml dioxane was added with stirring. After allowing the solution to stand 24 h at room temperature, the solid tetramer was filtered off, washed with acetone and recrystallized from dioxane.

Yield: 7.2 g (30%) m.p.: 180 – 182°C nematic, 254°C isotropic

III. Synthesis of the Pentamer (Phenyl-4-[4-benzoyloxy-)benzoyloxy-]benzoyloxybenzoate)

III.1 Phenyl-4-(4-carbethoxybenzoyloxy-)benzoate

To an ice-cold solution of phenyl p-hydroxybenzoate (33.7 g, 0.16 mol) in 400 ml water containing sodium hydroxide (6.3 g, 1.0 equiv) carbethoxy-benzoyl chloride [12] (36 g, 1.07 equiv) in 120 ml dry diethyl ether was added with stirring. The white precipitate was filtered, washed with water and recrystallized from ethyl acetate.

Yield: 53 g (83%) m.p.: 138 – 140°C, nematic, 170°C isotropic

III.2 Phenyl-4-(4-hydroxybenzoyloxy-)benzoate

A portion of compound III.1 (20 g, 0.026 mol) was dispersed in a mixture of 200 ml dioxane and 1 l acetone. Water (40 ml) and concentrated ammonia solution (60 ml) were added. A greenish slurry was formed initially. After ca. 40 min of stirring all the material was dissolved. The clear solution was allowed to stand for an additional 2 h, then neutralized with cold dilute hydrochloric acid, and most of the solvent was evaporated under reduced pressure. The residue was filtered off and washed with water.

Yield: 15 g (90%) m.p.: 224 – 225°C (ethanol, 60%)

III.3 Phenyl-4-[4-(4-benzoyloxy-)benzoyloxy-]benzoyloxybenzoate

To a solution of compound III.2 (8.6 g, 1.0 equiv) in a mixture of pyridine (100 ml) and dioxane (20 ml) was added, a portion of compound II.2 (6.7 g, 1.0 equiv) in 100 ml pyridine. The mixture became turbid at once and was allowed to stand for 24 h at room temperature. The white precipitate was filtered off, washed with acetone and water and dried in vacuo. It was then recrystallized from dry DMSO [13].

Yield: 10.7 g (74%)
m.p.: 223 – 225°C, nematic, ~340°C decomposition

Densities

Densities were determined with a pyknometer (volume ca. 1 ml) which was equipped with a capillary 3 cm long and 0.9 mm in diameter. Calibration was carried out using toluene. The pyknometer was housed in the cavity of an electrically heated aluminium block provided with good thermal insulation. An Omega temperature controller model 4001 JC regulated the heaters. The liquid column could be viewed through a small port transverse to the cavity. The height of the meniscus was measured with a cathetometer. The temperature was determined with an Omega model 871 Digital Thermometer equipped with a thermocouple model type KTC. Temperatures were stable within ±0.3°C.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) measurements were performed using a DuPont Model 1090 thermal analyzer provided with the DSC accessory. Heating rates of 20 deg min^{-1} were employed for studying the pure trimer and tetramer and their mixtures. The pure pentamer and its binary mixtures with the trimer and with the tetramer were investigated using a heating rate of 50 deg/min. Rapid heating was required because of the marginal stability of the higher oligomers at the elevated temperatures of the transitions. The data were accumulated on a diskette during the scan. This eliminated the need to select the sensitivity range in advance of the experiment. Studies on binary mixtures were performed as follows. Weighed amounts of the two components (total weight ca. 60 mg) were mixed above the temperature for complete dissolution of the mixture. The liquid solution was quenched rapidly and ca. 15 to 20 mg of the mixture was encapsulated in a precleaned aluminum pan. The DSC cell was calibrated within ±0.05°C against the melting points of indium and tin.

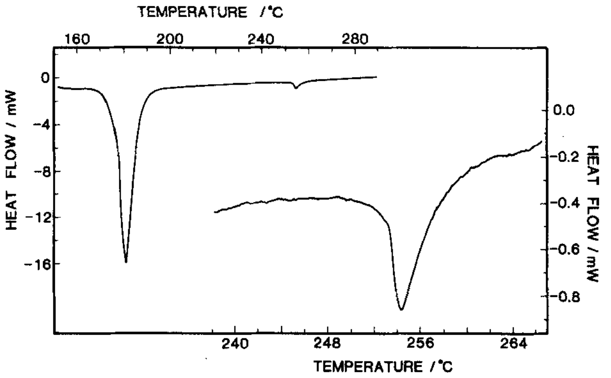


Fig. 1

Upper curve: DSC thermogram for the pure tetramer observed with ascending temperature at 20 deg/min. Transitions are: crystal-nematic and nematic-isotropic. Lower curve: nematic-isotropic transition endotherm obtained at a heating rate of 20 deg/min; enlarged view

Table 1

Transition temperatures, transition enthalpies, densities and axial ratios of the homologous poly(p-oxybenzoates)

Compound	T_f/°C	ΔH_f/kJ mol^{-1}	T_{NI}/°C	ΔH_{NI}/kJ mol^{-1}	$\frac{\Delta S}{R}$	ρ/9 cm^{-1} at T_{NI}	$\alpha \cdot 10^4$/K^{-1}	$\tilde{V}$ at T_{NI}	x
Trimer	136	37.8	100	–	–	1.162_9	6.8	1.216	3.8
Tetramer	181	47.7	254	1.07	0.24	1.109_6	6.7	1.284	5.1
Pentamer	224	65.3	464	3.6	0.60	1.006	6.6	1.364	6.4

Results

Thermodynamic Transitions of the Pure Tetramer

The DSC thermogram in Fig. 1, recorded with rising temperature, reveals two transitions: a crystal-nematic transition at 181 °C and a nematic-isotropic transition at 254°C. The lower curve gives an expanded view of the thermogram in the vicinity of T_{NI}. Most noteworthy are the pronounced pre-transition effects in the isotropic phase. The fairly smooth baseline allows precise integration of the peak, which leads to an enthalpy of the nematic-isotropic transition of 1.07 (±0.03) kJ/mol. The reduced molar latent entropy $\Delta S_{\mathrm{NI}}/R$ is 0.24. The temperature of fusion T_f and the corresponding enthalpy are given in columns 2 and 3 of Table 1. The temperature T_{NI} of the nematic-isotropic phase transition can be determined directly only for the tetramer. For the pure pentamer T_{NI} is located in a temperature range where decomposition prevails. Excessive decomposition cannot be circumvented even by rapid heating. The transition temperature for the trimer lies below its melting point and attempts to observe the transition by supercooling failed. Hence, in order to obtain the desired data for these compounds, it was necessary to determine the T_{NI} for binary mixtures and to extrapolate the results.

Mixtures of Trimer and Tetramer

A typical thermogram for a mixture of the trimer and the tetramer (mole fraction of the tetramer = 0.76) recorded with ascending temperature is shown in Fig. 2. In order of appearance, the transitions displayed are: melting of the eutectic at 115 °C, crystal-to-nematic transition at 174°C and the nematic-isotropic transition at 209°C. The thermogram for the mixture in the vicinity of T_{NI} shown by the lower curve in Fig. 2 differs from the corresponding diagram for the pure tetramer (cf. Fig. 1). The halfwidth of the peak is greater than that of the pure component, which indicates a biphasic gap of finite breadth. The pronounced pre- and post-transition effects do not allow precise determination of the biphasic range. However, the biphasic gap is definitely much smaller then expected from general thermodynamic considerations [6]. In absence of other information, the temperature of the nematic-isotropic transition is identified with the maximum of the peak. Below a mole fraction of approximately 0.75 of tetramer, the nematic-isotropic transition is masked by the much stronger crystal melting transition. Cooling experiments failed to circumvent the difficulty since the high temperatures required to attain isotropy led to appreciable decomposition.

The complete phase diagram presented in Fig. 3 reveals a eutectic at a mole fraction of 0.15 and a temperature of approximately 118°C. Since we are only interested in the nematic-isotropic transition, features pertaining to the crystal melting transition are not discussed in detail in the present paper. The line in Fig. 3 representing T_{NI}, obtained by the above method as a function of composition, is linear, at least in the temperature range where the nematic-isotropic transition is well separated from the crystal melting transition.

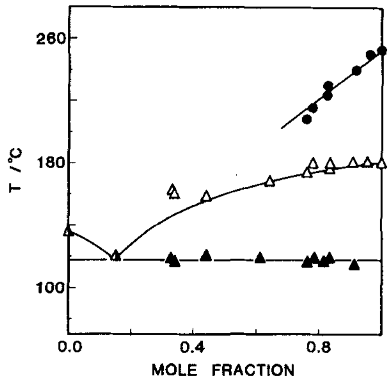


Fig. 3
Phase diagram of the system trimer/tetramer constructed from DSC heating experiments performed at 20 deg/min (see, for example, Fig. 2)

Key: ▲ eutectic, △ crystalline-nematic, ● nematic-isotropic

Mixtures of Tetramer and Pentamer

Thermograms of mixtures of the tetramer and the pentamer exhibit a single melting peak. None of them gave evidence of a eutectic, from which we conclude that these components are miscible in the crystalline state. Fig. 4, showing a thermogram for a mixture with a mole fraction 0.267 of the pentamer recorded with rising temperature, is illustrative. It melts at 180.5 °C and exhibits a nematic-isotropic transition at 308 °C. Both transitions are well separated but T_{NI} is located in a temperature range (especially when the mole fraction of the pentamer exceeds 0.4) where decomposition may become excessive. All DSC measurements therefore were performed at heating rates of 50 deg/min. The results of the measurements are summarized in the phase diagram shown in Fig. 5. The curve indicating T_{NI} is linear over the entire range of composition studied, and may be extrapolated to obtain T_{NI} of the pure pentamer (see below). The slight maximum in the melting curve (see Fig. 5) may indicate compound formation. Since the present investigation focuses on the nematic-isotropic transition of the respective mixtures, the crystal-nematic transition is not discussed further.

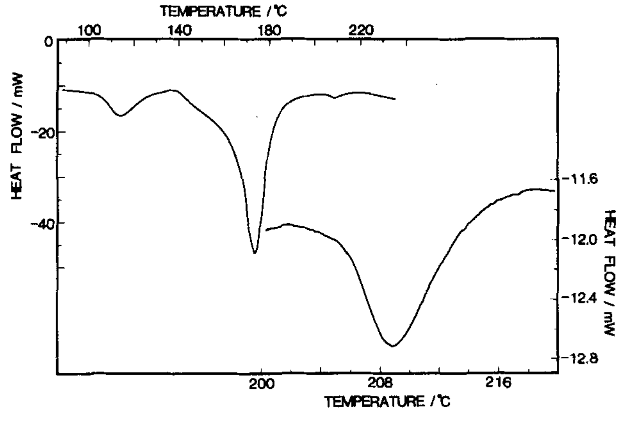


Fig. 2
Upper curve: DSC thermogram for a binary mixture of the trimer and the tetramer (mole fraction of tetramer = 0.76) obtained at a heating rate of 20 deg/min. Lower curve: nematic-isotropic transition on the enlarged scales below and on right

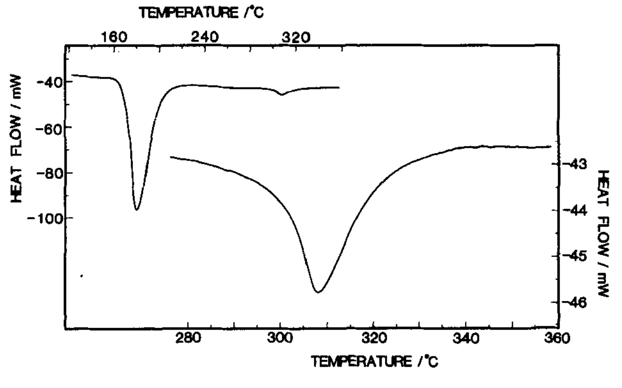


Fig. 4
DSC thermogram for a binary mixture of the tetramer and the pentamer (mole fraction of pentamer = 0.267) recorded with ascending temperature at 50 deg/min. Lower curve: nematic-isotropic transition with expanded scales shown on the lower abscissa and the ordinate on right

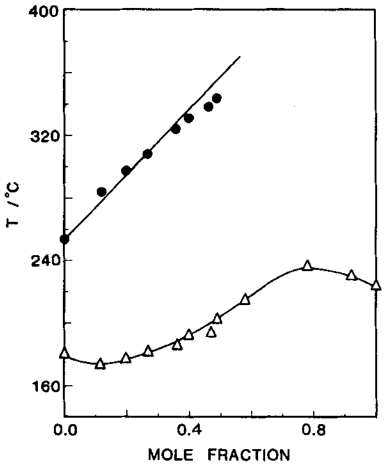


Fig. 5
Phase diagram of the system tetramer/pentamer constructed from DSC heating experiments performed at 50 deg/min (see, for example, Fig. 4)
Key: △ crystalline-nematic, ● nematic-isotropic

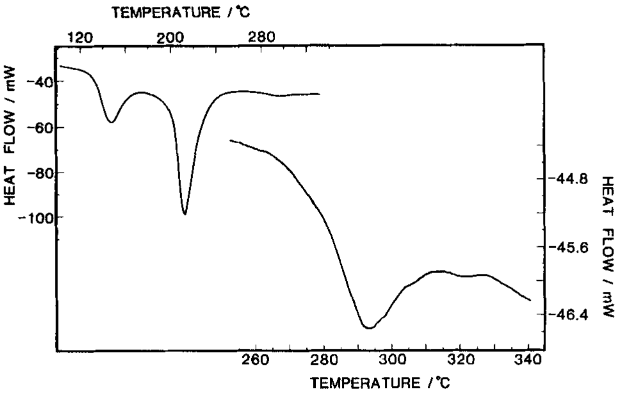


Fig. 6
DSC thermogram for a binary mixture of the trimer and the pentamer (mole fraction of pentamer = 0.521) recorded with ascending temperature at a rate of 50 deg/min. Lower curve: nematic-isotropic transition with expanded scales

Mixtures of Trimer and Pentamer

The temperature range within which mixtures of the trimer and the pentamer can be investigated is restricted due to decomposition at higher temperatures and to masking of the nematic-isotropic transition by the melting peak at lower proportions of the pentamer. The results for T_{NI} obtained in the range $0.4 < x_5 < 0.6$ nevertheless serve to demonstrate linearity and hence to justify extrapolation for the purpose of determining the T_{NI} for the pure compounds. Fig. 6 shows a typical example of the thermogram for a mixture of the trimer and the pentamer ($x = 0.521$) recorded with rising temperature.

Eutectic melting occurs at 145°C, the crystal-nematic transition at 215°C and the nematic-isotropic transition at 292°C. The lower curve shows a detailed view of the nematic-isotropic transition peak. Since the axial ratios of the components differ substantially, one would expect (see Ref. [6]) a much broader biphasic gap. The diagram clearly shows (the "noisier" baseline at higher temperatures notwithstanding) that the breadth of the peak is approximately the same as observed for the mixtures discussed above (cf. Figs. 2 and 4). This observation demonstrates that, even for a mixture of molecules whose axial ratios differ markedly, the two-phase region is much narrower than expected.

The results for all three systems are presented in Fig. 7. They confirm that the linear extrapolations used to determine the T_{NI} for the trimer and the pentamer are of sufficient accuracy (± 5 K).

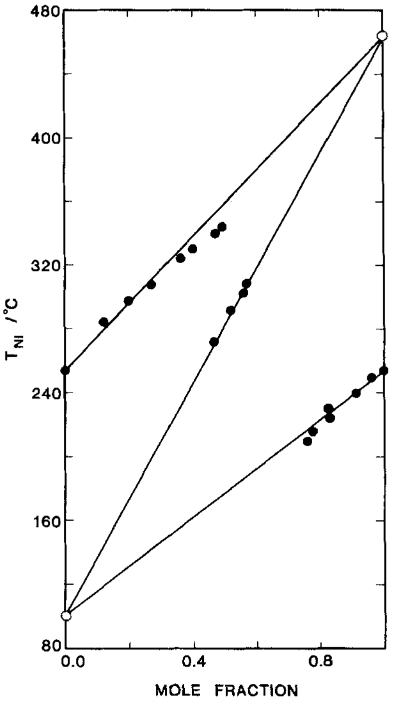


Fig. 7
Extrapolation of the nematic-isotropic transition temperatures of the pure trimer and the pure pentamer: nematic-isotropic temperatures for the systems trimer/tetramer (lower curve), trimer/pentamer (center curve) and tetramer/pentamer (upper curve)

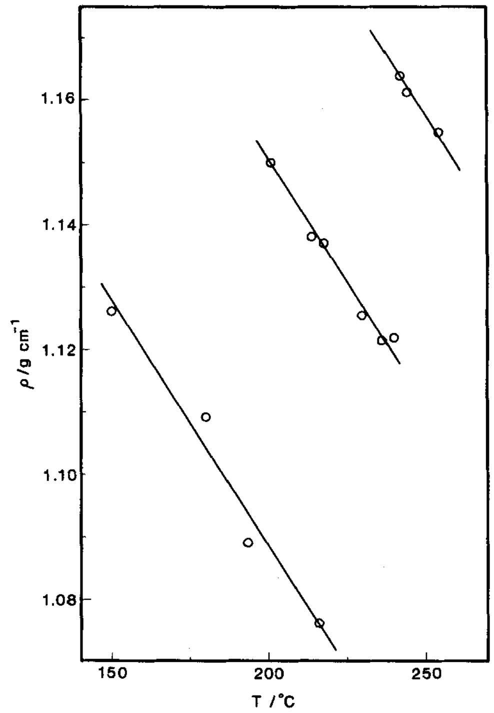


Fig. 8
Plot of measured densities versus temperature for the oligomers

Densities and Thermal Coefficients

Fig. 8 shows the densities of the respective oligomers as functions of temperature. At the temperatures of the measurements all liquids were nematic with the exception of the trimer. The differences between the thermal expansivities in the isotropic and nematic phases are generally small [15]; they would scarcely be detectable by the present pyknometric method. Liquid densities obtained by extrapolation of the data to the transition point are listed in column 7 of Table 1. The thermal expansion coefficients α are given in column 8. Reduced volumes $\tilde{V}$ calculated at $T = T_{NI}$ according to the relation [14]

$$\tilde{V}^{1/3} - 1 = \alpha T/3(1 + \alpha T)$$

are summarized in column 9. As mentioned in the Introduction, the reduced volume is required for satisfactory interpretation of the data according to the lattice theory.

Discussion

Phase Relations

Since the nematic-isotropic transition is of first order, general thermodynamic arguments would lead one to expect a biphasic gap of appreciable magnitude; also, the coexisting phases should differ appreciably in their compositions. These predictions are confirmed by calculations according to the lattice theory [6]. However, it is well-known [15] that binary mixtures of liquid crystals usually exhibit a very narrow biphasic gap. This general observation is confirmed by the results presented here. It suggests that the binary mixtures may be treated in first approximation as systems of one component. The reasons for this unexpected finding will be discussed in more detail in the following paper.

The linearity of the transition temperature with composition does not imply ideal mixing as is sometimes supposed (cf. the discussion of this point in Ref. [15], section 8.8.2). In fact, Osman, Schad and Zeller [16] have shown that ideal solution theory yields a linear relationship between T_{NI} and the mole fraction for a binary mixture only if the difference between the transition temperatures for the respective components is small and their transition entropies are approximately equal. The first condition is not fulfilled in the systems we have investigated inasmuch as the difference in T_{NI} for the two components is typically on the order of 200°C. In order to examine the second condition, ΔH_{NI} for the pure pentamer had to be determined. The experimental molar heats of transition for the system tetramer/pentamer are plotted against the mole fraction in Fig. 9.

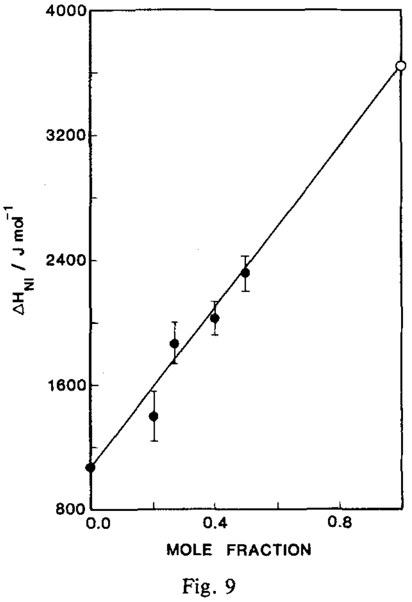


Fig. 9
Molar heats of the nematic-isotropic transition for the system tetramer/pentamer versus composition. Solid circles denote measured values; the open circle is the extrapolated heat of transition

The scattering of the data is due to the "noisy" baselines at elevated temperatures. Within the experimental uncertainties however, the relation between the enthalpy of transition per mole of mixture and the mole fraction is linear, thus allowing one to extrapolate the results to obtain ΔH_{NI} for the pure pentamer. (A similar extrapolation of ΔH_{NI} of the trimer is impossible because of the distortion of the baseline by the crystal-nematic transition; see above). The reduced entropy of the nematic-isotropic transition amounts to approximately 0.6. This is much higher than the corresponding value of 0.24 obtained for the tetramer (see above). Thus, the second ideality condition is not fulfilled, and the linearity of the transition temperature with composition cannot be explained by ideal solution theory. The consequences of these findings are discussed in greater detail in Part II.

Conformational Characteristics and Axial Ratios

A prerequisite for applicability of the theory is full extension of the nematogenic molecule with respect to the long molecular axis. The structural geometry and the conformational characteristics of the poly(p-oxybenzoates) have been exhaustively studied [17, 18]. The torsional angles ϕ and ψ (see Fig. 10) were found to be confined to values near ±60° and to 0°, 180°, respectively [17]. These deductions from analysis of conformational energies and crystallographic data on analogous compounds were confirmed by measurements of the Kerr constant and the depolarized Rayleigh scattering [9]. Inasmuch as the dipolar interactions between the ester groups are small, equal probabilities apply to the states characterized by $\phi = 0$ and $\psi = 180°$. The axes x and x' (see Fig. 10) differ by the angle $\delta \approx 7°$ [17] owing to the difference between the angles $<\mathrm{CC^*O}$ and $<\mathrm{C^*OC^{ph}}$, the carbonyl and the phenyl carbons being denoted by C* and C^{ph}.

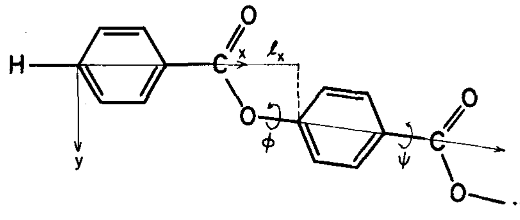


Fig. 10
Coordinate system for calculating the end-to-end vectors and the axial ratios

Pursuant to evaluation of the effective axial ratios of the three oligomers, end-to-end vectors $\mathbf{r}$ were calculated for the conformers of each oligomer generated from various combinations of the torsion angles ϕ and ψ specified above. This vector is dominated by its X-component taken along the axis of a central unit (cf. Ref. [18]); components in lateral directions make only a small contribution to the magnitude r of the chain vector. Values of r for the various conformers of a given oligomer differ by less than ±3%. Moreover, assignment of $\delta = 0$ has little effect on r; hence, the X-axes of consecutive units may be treated as if parallel to one another. In this approximation $\mathbf{r}$ vectors for all conformers have the same X-component, and the effective axial ratio for each oligomer may be calculated on the basis of this length.

Using the structural data given in Ref. [18] we obtain 6.18 Å for the length l_x of the repeating unit (see Fig. 10). The terminal hydrogen atoms are taken into account by adding the C–H bond length (1.08 Å, [2]) and an increment Δl for the additional extension along the long molecular axis due to the van der Waals radius of the hydrogen atom. To estimate Δl, the volume of the hemisphere $(2\pi/3)R^3$ with R being the van der Waals radius of the H atom, which we take to be 1.2 Å may be considered to be distributed over the whole base of the molecule. If a cylindrical shape is assumed, $\Delta l = (2\pi/3)R^3/\pi(d/2)^2 \approx 0.21$ Å where d is the mean molecular diameter equal to 4.7 Å (see below). Thus, the extension of the molecule attributable to the hydrogen atom is $1.08 + 0.21 = \sim 1.3$ Å. The length of an oligomer is therefore

$$l = 6.18\,(n-1) + 2.78 + 2.6 = 6.18n - 0.80$$

in Ångström units, the length of the phenylene ring being 2.78 Å. Crystallographic data for the poly-p-phenylenes yield 4.73 Å for the mean diameter of the phenylene group [6]. A somewhat smaller diameter may be expected for the ester group. The mean diameter of p-oxybenzoate oligomers estimated from the length l and core volume V^* of the repeat unit obtained from densities and reduced volumes (see above) according to the relation

$$d = \sqrt{V^*/l}$$

is 4.65 ± 0.07 Å, which is consistent with the value for the phenylene group. The axial ratios $x = l/d$ calculated for the respective oligomers with $d = 4.7$ Å are summarized in column ten of Table 1. Together with the reduced volumes and the transition temperatures T_{NI}, these data serve for the evaluation of the characteristic temperatures and the phase diagrams, as described in part II.

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Phase Equilibria in Liquid Crystalline Systems
Part II. Theory and Interpretation of Experimental Results

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Liquid Crystals / Phase Transitions / Statistical Mechanics / Thermodynamics

Characteristic temperatures T^* have been evaluated for the oligomeric p-oxybenzoates, $C_6H_5CO(-OC_6H_4CO)_{n-2}-OC_6H_5$ from the transition temperatures T_{NI} presented in the preceding paper. For $n = 3$, 4 and 5 they are, respectively, 343, 316 and 306 K. These parameters that measure the intensities of the orientation-dependent intermolecular interactions are correlated with the optical anisotropy $\Delta\alpha$ and the average intermolecular cohesive energy expressed by the characteristic pressure p^*. The characteristic temperature T^* decreases slightly with chain length. The lattice theory of nematic fluids is extended to include mixtures of rodlike molecules having different characteristic temperatures T^* in order to treat binary and ternary mixtures of the p-oxybenzoate oligomers. The wide biphasic gaps predicted for the several binary systems and the concomitant pronounced partitioning of the components between the nematic and isotropic phases are not confirmed by experiments. Compositions of the coexisting phases in ternary systems were found to be identical within limits of experimental determinations. These marked departures from theory are explicable on the premise that facile rotational diffusion of the nematogens here considered, which are of comparatively low chain length, leads to rapid generation of ordered domains of large dimensions. Subsequent diffusional transport over the required distances consequently is very slow. The transition temperatures observed in binary systems are in excellent agreement with calculations carried out in the "single component" approximation using mean values of the axial ratio and of T^* for the mixture, these being taken to be the same in the two phases at equal concentrations.

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