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Phase Transformations of Liquid Crystalline Side-Chain Oligomers[†]

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ABSTRACT: Liquid crystalline (l.c.) oligomers were synthesized in order to obtain a more detailed understanding of the change of the phase behavior from the monomer to the polymer of l.c. side-chain polymers. The phase transformation temperatures of oligomers were determined as a function of the degree of polymerization r. For $3 < r < 10$ a steep increase in phase transformation temperature is observed for all systems. With growing r the stability range of the nematic phase is more extended than the stability range of the smectic phase. In analogy to the pressure–temperature behavior of low molar mass l.c's, this effect can be attributed to progressively denser packing of the mesogenic side chains of the oligomers with growing degree of polymerization. This is macroscopically seen in a decrease of specific volume at the phase transformation temperature with r.

Introduction

Recently, an increasing interest has been devoted to thermotropic liquid crystalline (l.c.) polymers which have linked mesogenic groups in the main chain[1] or in the side chain.[2] The linkage of low molar mass mesogenic molecules to a polymer as side chains via flexible spacers provides a method for the systematic synthesis of liquid crystalline side-chain polymers.[3] The formation of liquid crystalline phases of mesogenic groups, which are decoupled from the main chain by flexible spacers, follows principles similar to those of low molar mass liquid crystals involving nematic, smectic, and cholesteric phases.[4,5]

Although main and side chains are regarded to be essentially decoupled, two principal rules have been established for relating phase behavior with the polymerization of mesogenic molecules to a l.c. side-chain polymer.

(i) The coupling of mesogenic molecules to the polymer main chain always shifts their phase transformation temperatures toward higher temperatures. If, e.g., a metastable nematic monomer (metastable with regard to the crystalline state) is linked to a polymer backbone, stable nematic polymers can be obtained.

(ii) Attaching liquid crystalline molecules to a polymer backbone tends to form higher ordered phases. If, e.g., a nematic monomer is polymerized, in most cases smectic polymers will be obtained.[2,6] To get a more quantitative understanding of the extent to which the degree of polymerization influences the liquid crystalline state we investigated the phase behavior of monodisperse oligo(methylsiloxane) with mesogenic side chains.

Experimental Section

Preparation of the Oligomers. Fractionation of the oligomers was carried out by size exclusion chromatography (SEC). The SEC system supplied by WFN-Labortechnik, Köln, consists of the following components: (a) a high-pressure pump in which the flow rate is uniform to within 0.4% at 1 m/min, (b) a Shodex GPC 2000 column of 50-cm length and 20-mm i.d., (c) a variable-loop sample injection port, and (d) a differential refractometer as a concentration detector.

Chloroform, stabilized with 500 ppm *N*-methylmorpholine, was used as eluent. Calibration of the column was accomplished with narrow-distribution polystyrenes and by the peak elution volumes of the lower l.c. side-chain oligomers. The narrow molecular weight distribution polystyrenes were obtained from the Pressure Chemical Co.. The calibration curve of retention volume vs. the logarithm of the molecular weight was linear. The injection volume was always 1.0 mL, with concentrations ranging from 10 mg/mL for the highest molar mass to 25 mg/mL for the lowest molar mass.

Table I
Synthesized and Investigated Oligomers

oligomer system	m	R
A3	3	$-OCH_3$
A4	4	
A5	5	
A6	6	
B4	4	$-COOCH_2C^*H(CH_3)(C_2H_5)$
B5	5	
B6	6	

In order to obtain sufficient amounts of the monodisperse liquid crystalline oligomers, the fractionation procedure was carried out several times to obtain 500–700 mg of monodisperse oligosiloxane. Figure 1 shows a chromatogram of the oligomers of systems A3. The fractions were collected in steps of 1 count = 1 mL. The purity of the fractions was confirmed by analytical SEC and for selected samples by vapor pressure osmometry.

The fractions were freed from chloroform at about 333 K under reduced pressure. Residues were dissolved in benzene and freeze-dried to remove the stabilizer. The samples were then stored in the dark at a temperature of 250 K.

DSC Measurements. Phase transformation temperatures were determined by differential scanning calorimetry (DSC 2B, Perkin-Elmer) using the same heating and cooling rate (10 K/min). First, samples were heated to a temperature 10 K above the l.c.-to-isotropic transformation, and then they were cooled at a rate of 10 K/min. During the succeeding thermogram the l.c. phase transformations and the melting point of monomers and dimers were always determined at the same heating rate of 10 K/min. The crystallization temperature of the partially crystalline system A5 was also determined at the cooling rate of 10 K/min. Peak maximum temperatures of a DSC thermogram were taken as the phase transformation temperatures. Sample size varied from 4.0 to 7.0 mg.

Microscopic investigations were performed by means of a Leitz Ortholux-II-Pol-BK microscope supplied with a Mettler FP 5–FP 52 hot stage. The samples were studied at both decreasing and increasing temperatures.

Synthesis. Mesogenic derivatives (II) of vinyl-substituted benzoic acid phenyl esters were chosen for study. They were easily attached to the oligo(hydrogenmethylsiloxane) backbone (I) in the presence of a platinum catalyst according to the reaction scheme shown in Figure 2. If R consists of nonchiral alkoxy groups, nematic or smectic side-chain oligomers are obtained, depending on the spacer length m. The replacement of the alkoxy substituent with an optically active ester group yields cholesteric homooligomers when the spacers are short ($m = 4$). The resulting oligomers are summarized in Table I.

[†] Dedicated to Professor Walter H. Stockmayer on the occasion of his 70th birthday.

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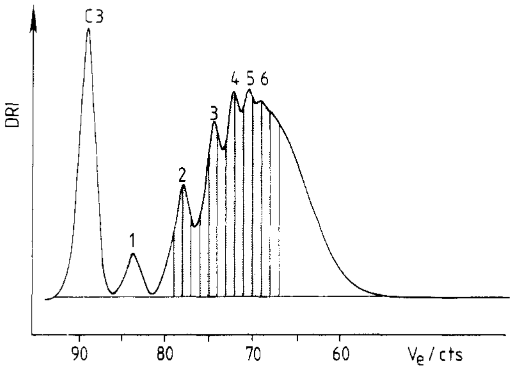

Figure 1. SEC chromatogram of the oligomer system A3 (refer to Table I). No. indicates the degree of polymerization *r*.

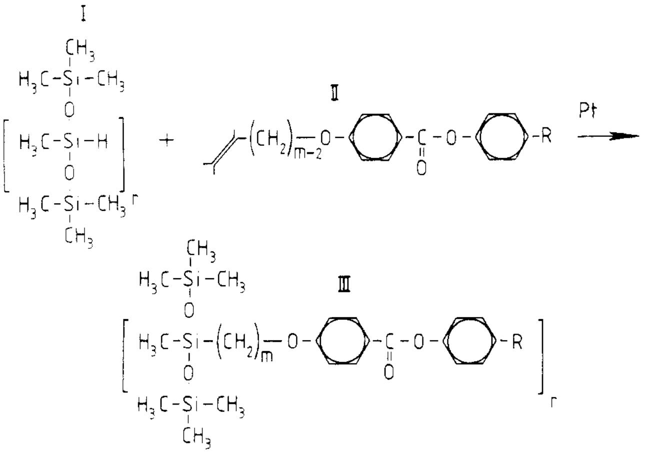

Figure 2. Reaction scheme for the preparation of the l.c. oligomers.

Results and Discussion

As mentioned above, polymerization always changes the phase behavior of a l.c. monomer. The most evident effect is the shift of the liquid crystalline-to-isotropic transformation toward higher temperatures. Therefore the following questions are of interest:

(i) What effect does degree of polymerization have on phase transformation temperatures?

(ii) Does *r* influence the nematic-to-isotropic transformation in the same way as the smectic-to nematic or the smectic-to-isotropic transformations?

(iii) Is the change in phase transformation temperature dependent on the length of flexible spacer if the polymer backbone and the mesogenic group are unchanged?

Before we discuss these questions in detail we will describe phase behavior as a function of *r* for three representative examples.

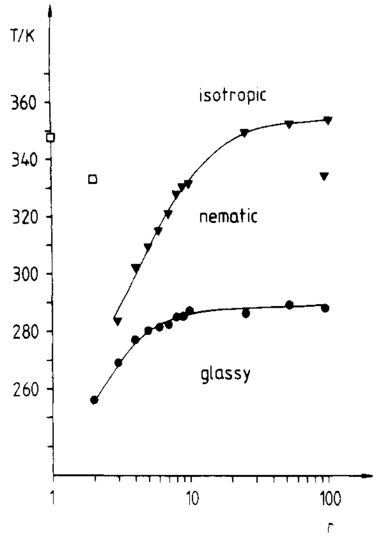

Figure 3. System A3. Phase transformation temperatures T_{tr} and glass temperatures T_g vs. *r*: (●) phase transition glassy to nematic or smectic, respectively, (▼) phase transformation nematic to isotropic; (□) phase transformation crystalline to isotropic.

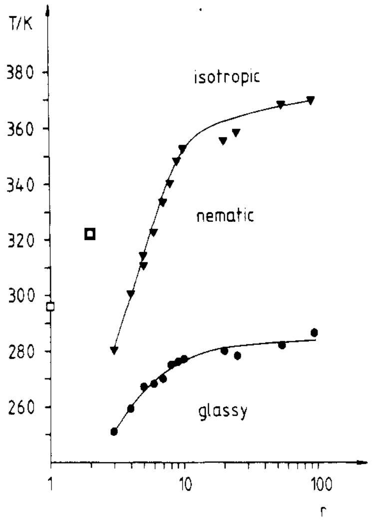

Figure 4. System A4. T_{tr} and T_g vs. *r*. Symbols refer to Figure 3.

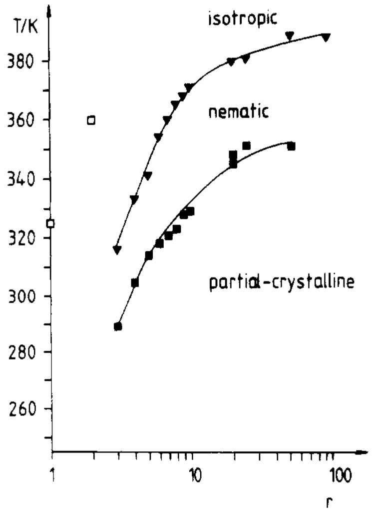

Figure 5. System A5. T_{tr} and T_g vs. *r*: (■) phase transformation partial crystalline to nematic; other symbols refer to Figure 3.

Phase transformation temperatures of the oligomer (A3 of Table I) with the shortest spacer ($m = 3$) are shown as a function of *r* in Figure 3. The monomer ($r = 1$) and dimer ($r = 2$) do not form liquid crystals. The monomer crystallizes rapidly and has a melting point of 348 K. The melting of the dimer is observed at 333 K, but the rate of crystallization is lower than that of the monomer. Therefore the dimer can be supercooled and a transition into the glassy state is found at 255 K. The trimer forms a nematic liquid crystalline phase, exhibiting a liquid crystalline-to-isotropic transformation at a clearing temperature (T_c) of 285 K and a glass transition temperature (T_g) of 270 K. The mesophase is stable within a temperature interval of 15 K. With each additional lengthening of the siloxane backbone, T_c increases steeply up to $r \leq 10$. Thereafter *r* has a slight effect on T_c. Figure 3 indicates that T_g also shifts to higher temperatures with increasing *r*, but the increase of T_g with *r* is much smaller than the increase in the liquid crystalline-to-isotropic

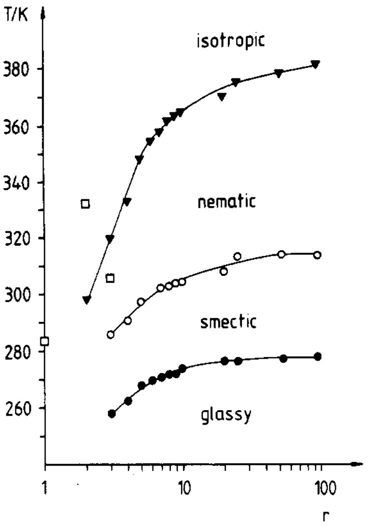

Figure 6. System A6. T_{tr} and T_g vs. r: (O) phase transformation smectic to nematic.

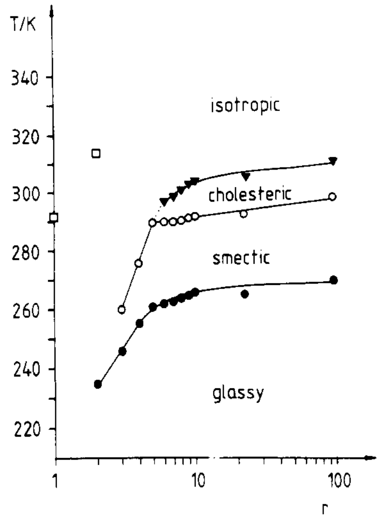

Figure 7. System B4. T_{tr} and T_g vs. r: (O) phase transformation smectic to isotropic and cholesteric; other symbols refer to Figures 3 and 6.

transformation temperature. A similar behavior with regard to T_c is shown by the systems A4 and A5 (Figures 4 and 5, respectively). System A5 does not become entirely glassy but instead is semicrystalline.

System A6 from Table I is discussed in more detail. It deviates from the first example by the length $m = 6$ of the flexible spacer. Earlier investigations of polymer A6 revealed[8,9] that in addition to the glassy and nematic states, the polymer exhibits a (metastable) smectic state. By annealing the smectic phase above the glass transition temperature, a crystallization occurs. The crystallites melt over a broad temperature range and the melting temperature is 10 K higher than the smectic-to-nematic transformation temperature. This means that the smectic phase is thermodynamically metastable. For our experiments, however, we will not consider the crystalline phase, which is only obtained by annealing.

The monomer of A6 is crystalline like the monomer of the oligomer system A3. But in contrast to the previous example, the dimer exhibits a monotropic l.c. phase, which can be observed at cooling rates >10 K/min. The peak preceding crystallization in the DSC thermogram indicates this transformation. It was reconfirmed by polarizing microscopy that this phase is l.c. The trimer is the first oligomer of A6 where a stable mesophase is observed. The nematic phase becomes isotropic at $T_c = 320$ K. By DSC cooling measurements we find a low-temperature nematic-to-smectic transformation. Crystallization can be suppressed by freezing the smectic phase into the glassy state. If this frozen sample is heated, the DSC thermogram shows a strong endothermal crystallization peak, and at 306 K the partially crystalline phase is transformed into the nematic phase. The growth of crystals can be easily observed under the polarizing microscope by annealing the sample at the temperature of the nematic-to-smectic transformation.

As we can see from Figure 6 the clearing temperatures increase steeply with r at first. The glass transition and the smectic-to-nematic transformation temperatures also increase with r, but not as strongly as the corresponding clearing temperatures. Therefore, with growing siloxane backbone, the l.c. interval increases with r. The range of stability of the nematic state is affected more than the smectic state by increasing r.

The third example, B4 ($m = 4$) from Table I, differs from A6 in the chemical constitution of the mesogenic group. It exhibits both a smectic and a cholesteric phase due to a chiral substituent. The phase transformation temperatures for the oligomers are plotted vs. the degree of polymerization in Figure 7. The monomer and dimer are crystalline, but the trimer exhibits liquid crystalline behavior. DSC measurements indicate that above $T_g = 246$ K this liquid crystalline phase is stable within a temperature range of 14 K. A growing siloxane chain again causes a steep increase in the clearing temperature at the outset.

While only one l.c. phase is observed for $r < 6$, two l.c. phases for $r > 6$ appear, where the high-temperature phase broadens only slightly with increasing r. If we refer to the polymer with $r_n = 95$ (r_n is the number-average degree of polymerization), we have to conclude that this high-temperature phase is the cholesteric phase.[9] The low-temperature phase, which was already observed for the trimer, is the smectic phase. The hexamer is smectic above $T_g = 263$ K, and at 290 K it becomes cholesteric with a clearing temperature of 294.5 K. The temperature of the smectic-to-isotropic transformation increases similarly like the glass temperature with growing r. Consequently, the temperature range in which the smectic phase occurs is only slightly affected by $r > 7$.

It has to be emphasized that in addition to the smectic phase in these oligomers where $r > 6$, the high-temperature cholesteric phase becomes stable due to the polymerization. This is the first time this effect has been observed.

We have seen in the three examples described above that the phase behavior is strongly influenced by the degree of polymerization up to $r \leq 10$ for all systems. The phase transformation temperatures for $r > 10$ change only slightly with r. We have seen, however, that $T_{s,i}$ still changes with r, whereas $T_{s,n}$ remains nearly constant. The analysis of all systems confirms these results. We have therefore demonstrated the following principal behavior:

(1) In all systems where $r > 100$, the l.c. range remains constant and the phase transformation temperatures do not depend on r.

(2) The clearing temperatures of side-chain polymers exhibiting a nematic mesophase increase slightly with r within the range $10 < r < 100$. Therefore the extent of the nematic phase still grows for $10 < r < 100$.

(3) Within the accuracy of measurements, the temperature of the smectic-to-nematic and smectic-to-isotropic transformations no longer changes when $r > 10$. Consequently, the stability range of a smectic phase is not altered by r, if $r > 10$.

Table II
Differences of the Phase Transition Temperatures between Trimer and Polymer

m	$\Delta T_{n,i}$	$\Delta T_{s,i}$	$\Delta T_{s,n}$	$\Delta T_{g,n}$	$\Delta T_{g,s}$
3	(A3) 71			(A3) 20	
4	(A4) 88		(B4) 39	(A4) 34	(B4) 21
5	(A5) 74	(B5) 62			(B5) 24
6	(A6) 61	(B6) 50	(A6) 28		(A6) 20 (B6) 16

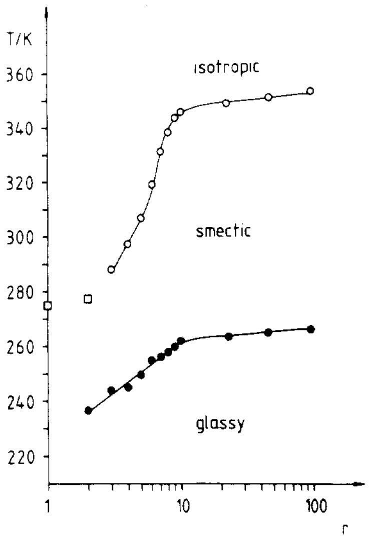

Figure 8. System B5. T_{tr} and T_g vs. r. Symbols refer to Figure 7.

(4) The most drastic increase of transition temperatures with r is observed for $3 < r < 10$ for the nematic as well as for the smectic state.

We will now discuss the extent to which the degree of polymerization shifts the phase transformation temperatures $T_{s,i}$, $T_{s,n}$, and $T_{n,i}$ toward higher temperatures. For these considerations we compare the difference, ΔT, in transition temperatures between the trimers and the corresponding polymer having $r_n = 95$. The results derived from all systems, shown in Figures 3–9, are summarized in Table II.

If we consider the temperature differences $\Delta T_{n,i}$, where the nematic phase becomes isotropic, we find a strong shift of the clearing temperatures from the trimer to the polymer (71 K for system A3 and 88 K for system A4). In comparison to this strong shift in nematic phase transformation temperatures, the smectic systems B5 and B6 (refer to Figures 8 and 9) show a smaller shift ($\Delta T_{s,i} = 62$ and 50 K, respectively) for the transition from trimer to polymer. This obviously indicates that the temperature of the smectic-to-isotropic transformation $\Delta T_{s,i}$ is less influenced by polymerization than $T_{n,i}$. The third transformation to be considered is the smectic-to-nematic transformation. Here we find only a small increase of $\Delta T_{s,n}$, and we can conclude that this type of phase transformation is at least influenced by r. These results can be summarized by the following rule: Transformations of the highly ordered smectic phase are less sensitive to changes of r than those of the nematic phase, as shown in the following sequence:

$$\frac{\Delta T_{n,i}}{\Delta r} > \frac{\Delta T_{s,i}}{\Delta r} > \frac{\Delta T_{s,n}}{\Delta r}$$

We chose systems where the mesogenic group and the main chain remained constant but the flexible spacer was varied in length. Simple model considerations[5] indicate that the flexible spacer decouples the motions of the main and side chains. Accordingly, we should expect that the transformation temperatures are less influenced by r as the spacer length increases. If we look at our diagrams, no substantial differences are evident at first sight. However, more detailed information can be obtained by comparing l.c.-to-isotropic transformation temperatures with the extrapolated clearing temperatures $T_{c,r\to\infty}$ for the corresponding polymer with infinite molar mass. This has been done in Figure 10. This diagram, representing the behavior of system A, shows that the increase of $T_c/T_{c,r=\infty}$ with rising r depends on the spacer length (m = 4–6). The shorter the flexible spacer, the stronger is the dependence at low degrees of polymerization ($r < 10$). This result is consistent with that of a simple model.[5]

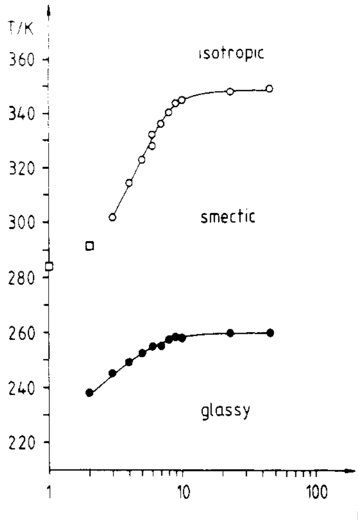

Figure 9. System B6. T_{tr} and T_g vs. r. Symbols refer to Figure 7.

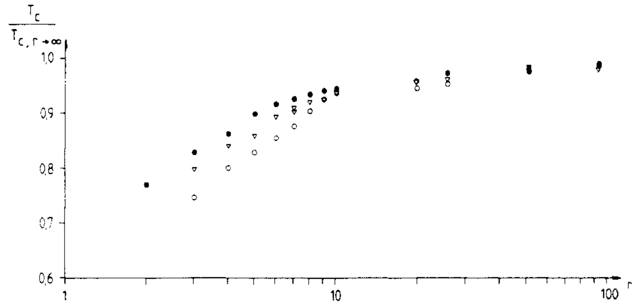

Figure 10. Normalized phase transformation temperatures $T_{c,r}/T_{c,r=\infty}$ of oligomer and polymer vs. r: (●) system A6; (▼) system A5; (○) system A4. $T_{c,r}$ is the clearing temperature of the oligomer and $T_{c,r=\infty}$ is the extrapolated clearing temperature of the polymer with $r = \infty$.

Conclusions

A summary of results for these systems reveals that the most drastic effect of the degree of polymerization, r, on the phase transition temperatures is observed for $r < 10$. Furthermore, it could be established that the smectic-to-nematic or smectic-to-isotropic phase transformation temperatures are less influenced by r than the nematic-to-isotropic transformation. Obviously, a reason for the shift in the phase transformations with growing polymer backbone should be sought. One explanation is that the influence of the trimethylsiloxane end groups of the polymer main chain becomes less pronounced on the phase behavior with increasing chain length. If it is assumed that these voluminous end groups suppress the extent of the

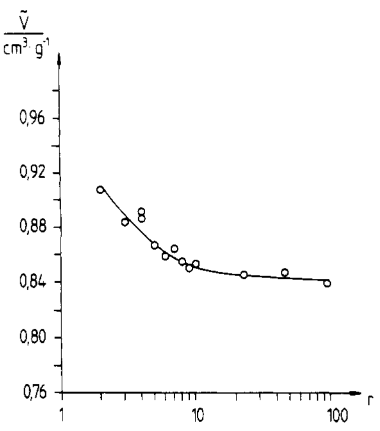

Figure 11. Specific volume $\tilde{V}$ of the oligomers A6 vs. r at constant temperature 298 K.

l.c. phase, then the phase transformation temperatures should also increase with increasing length of the polymer backbone. The temperature difference $T_{n,i}$ from the trimer to the polymer with $r_n = 95$ is 60–90 K for these oligomers. If we compare, on the other hand, the influence of alkyl end groups of different length on the l.c. phase behavior of low molar mass benzoic acid phenyl ester,[10] $T_{n,i}$ is only slightly affected if the length of the alkyl chain varies from 1 to 12 methylene units. Furthermore, $T_{s,n}$ is influenced more than $T_{n,i}$, which is an opposite effect from that observed for the oligomers. Therefore it is possible that the effect of the end groups is less important in the oligomers.

Without making any explicit speculations on molecular effects, an argument can be made which relates the linkage of the mesogenic molecules to the polymer main chain if we refer to the specific volume of the oligomers as a function of r. In Figure 11 the isothermal specific volume $\tilde{V}$ of the oligomer system A6 at 298 K is shown as a function of the degree of polymerization. Because of the small amounts available from SEC, $\tilde{V}$ has been determined roughly by assuming that a few milligrams of the respective oligomers is suspended in solution. Since densities are the same, the samples are in mechanical equilibrium. For samples $2 < r < 10$, the isothermal specific volume decreases and levels off to a constant value for $r > 10$. The specific volume changes about 5.3% from dimer to a polymer of $r_n = 95$. Accordingly, with decreasing r the l.c.-to-isotropic phase transformation is shifted toward higher temperatures. It is important to determine whether a relationship exists between the phase transformation temperatures of conventional low molar mass l.c. and their specific volume $\tilde{V}$.

The first-order phase transformations of liquid crystals can be described by the well-known Clausius–Clapeyron equation

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\mathrm{tr}} = \frac{\Delta\tilde{H}}{T_{\mathrm{tr}}\Delta\tilde{V}} \qquad (1)$$

where $\Delta\tilde{H}$ is the specific phase transformation enthalpy and $\Delta\tilde{V} = \tilde{V}' - \tilde{V}''$ is the difference between the specific volumes of the coexisting phases at the phase transformation temperature (and pressure). If we want to know the change of specific volume $\tilde{V}$ with the phase transformation temperature of the l.c. phase (indexed with a single prime) which coexists with the isotropic phase, we have to differentiate $\tilde{V}'(T,P)$ with respect to T along the coexisting curve

$$\left(\frac{\mathrm{d}\tilde{V}'}{\mathrm{d}T}\right)_{\mathrm{tr}} = \left(\frac{\partial\tilde{V}'}{\partial T}\right)_P + \left(\frac{\partial\tilde{V}'}{\partial P}\right)_T\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\mathrm{tr}} \qquad (2)$$

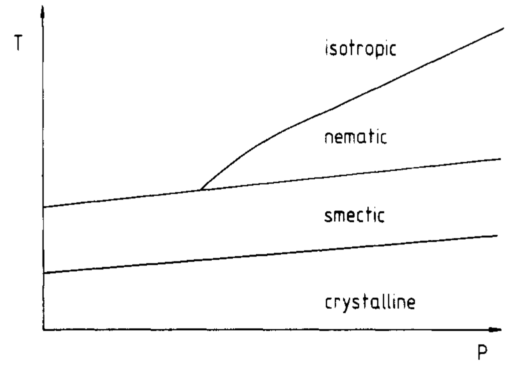

Figure 12. Schematic diagram of the P–T behavior of a low molar mass l.c.

where $(\mathrm{d}P/\mathrm{d}T)_{\mathrm{tr}}$ is given by eq 1. Introducing the specific isobaric expansion coefficient α^* and the isothermal specific compressibility $\varkappa^*$ at the phase transformation

$$\alpha^*_{\mathrm{tr}} = \frac{1}{\tilde{V}'_{\mathrm{tr}}}\left(\frac{\partial\tilde{V}'}{\partial T}\right)_P$$

$$\varkappa^*_{\mathrm{tr}} = -\frac{1}{\tilde{V}'_{\mathrm{tr}}}\left(\frac{\partial\tilde{V}'}{\partial P}\right)_T$$

eq 2 becomes

$$\left(\frac{\mathrm{d}\tilde{V}'}{\mathrm{d}T}\right)_{\mathrm{tr}} = \tilde{V}'_{\mathrm{tr}}\left[\alpha^*_{\mathrm{tr}} - \varkappa^*\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\mathrm{tr}}\right] \qquad (3)$$

Equation 3 relates the slope of the specific volume $\tilde{V}'$ with temperature and the slope of the pressure with temperature at the phase transformation. For conventional low molar mass l.c.'s, measurements of the pressure–temperature behavior have shown[12,13] that $(\mathrm{d}P/\mathrm{d}T)_{\mathrm{tr}} > 0$ for all l.c. phase transformations as shown schematically in Figure 12. Furthermore, two important aspects have been generally established: (i) The phase transformation temperatures $T_{n,i}$ are changed more by pressure than are $T_{s,n}$ or $T_{s,i}$

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{n,i} < \left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{s,n} \approx \left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{s,i}; \quad \left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\mathrm{tr}} > 0 \qquad (4)$$

(ii) Increasing pressure on smectic systems can induce[12,13] a nematic phase as shown schematically in Figure 12.

According to the experimental results,[7,12,13] the slope of the specific volume $\tilde{V}$ of the l.c. phases (indexed with a single prime) with temperature is $(\mathrm{d}\tilde{V}'/\mathrm{d}T)_{\mathrm{tr}} < 0$. This indicates that in eq 3 the isobaric specific expansion coefficient is smaller than the second term.

Analogies to the phase behavior of the l.c. oligomers become apparent on varying P in low molecular weight l.c.'s. In Figure 11 we have seen that the isothermal specific volume at $T = 298$ K falls with increasing r. This also holds if we roughly estimate the specific volume $\tilde{V}'_{\mathrm{tr}}$ of the l.c. phase at the transformation temperature using the isobaric expansion coefficient α^* of about 5×10^{-4} cm^3 g^{-1} K^{-1}, which was found for polymer A6 at 1 bar and 298 K.[7] Consequently, referring to the specific volume $\tilde{V}'_{\mathrm{tr}}$, an analogy in the behavior of the phase transformation temperatures can be observed for low molecular weight l.c.'s, where $\tilde{V}'_{\mathrm{tr}}$ changes with pressure, and for oligomers, where $\tilde{V}'_{\mathrm{tr}}$ changes with the degree of polymerization. Other analogies can be found between the effect of pressure on low molar mass l.c.'s and the degree of polymerization on l.c. oligomers. We observed the following relationship between the oligomers (see Table II)

$$\left(\frac{\Delta r}{\Delta T}\right)_{\mathrm{n,i}} < \left(\frac{\Delta r}{\Delta T}\right)_{\mathrm{s,n}} \lesssim \left(\frac{\Delta r}{\Delta T}\right)_{\mathrm{s,i}}$$

which shows the same effect on r on the phase transformation temperature as P has for low molar mass l.c.'s. This interpretation makes the $T_{\mathrm{tr}}(r)$ behavior of the oligomer system B4 in Figure 7 easier to understand.

While a nematic phase can be induced by pressure on low molar mass l.c.'s (Figure 12), a cholesteric phase is induced by increasing r of the B4 oligomers. So far the experiments show that the phase transformation temperatures of oligomers are changed by r in a way similar to the change in phase transformation temperatures of low molar mass l.c.'s with pressure. The specific volume decreases with increasing r of the oligomers and increasing pressure on the low molar mass l.c.'s, indicating a denser packing of the molecules. This denser packing of the mesogenic molecules due to their linkage to the polymer backbone might be a major factor for increasing the phase transformation temperature with r.

We think that detailed $P-V-T$ measurements on l.c. monomers and the corresponding oligomers and polymers are necessary to gain a better understanding of the change of the l.c. phase behavior with polymerization.

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Mesophase Formation by Semirigid Polymers: Poly(*n*-hexyl isocyanate) in Dichloromethane and Toluene

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ABSTRACT: The liquid crystal phase behavior of solutions of poly(*n*-hexyl isocyanate) (PHIC) in dichloromethane and toluene was investigated by using unfractionated and fractionated samples of PHIC covering the molecular weight range from 24 000 to 524 000. The volume fractions of polymer in the coexisting isotropic and anisotropic phases, v_2' and v_2'', were determined by microscopic and analytical techniques, and the molecular weight and molecular weight distribution of the polymer in the coexisting phases were determined by solution viscosity and gel permeation chromatography. The persistence lengths, q, of PHIC in dichloromethane and toluene, 185 ± 15 and 375 ± 25 Å, were evaluated by using the hydrodynamic theory of wormlike chains. Since the contour length for the lowest molecular weight is approximately equal to the persistence length for PHIC in toluene, the dependence of v_2' could be investigated in the region where PHIC changes from rigid to semirigid chain behavior. None of the existing theories for freely jointed or wormlike chains offers a quantitative description of this dependence or of the fractionation effect, and only the qualitative trend of the molecular weight dependence is in line with the approximate virial treatment of wormlike chains.

Introduction

Rigid and semirigid polymers can be differentiated on the basis of the relative magnitudes of the contour length L and the persistence length q. We will arbitrarily define as rigid those polymers having $L \leq q$, and as semirigid those for which $L > q$. It is clear from this definition that a rigid polymer must have a large persistence length (e.g., $q > 100$ Å), while semirigid polymers may either have more flexible chains ($q < 100$ Å) or have a large persistence length coupled with very high molecular weight. The phase behavior of rigid-chain liquid crystalline polymers has been extensively investigated, both theoretically[1] and experimentally.[2] In this case the formation of the mesophase is controlled by the axial ratio, $x = L/d$, where d is the diameter of the chain. By contrast, our understanding of the phase behavior of semirigid mesogenic polymers is more rudimentary.[1,2] Although the wormlike chain model has received preliminary consideration,[3] most theoretical treatments of the mesophase behavior have involved the Kuhn model chain.[1,4] The latter is predicted[4] to be equivalent to a collection of rigid rods having axial ratio $x = 2q/d$, so that the critical concentration for the appearance of the mesophase should be independent of both the contour length and molecular weight distribution of the polymer.

(Hydroxypropyl)cellulose (HPC) is the most extensively studied[5,6] example of a semirigid polymer. HPC obeys the definition of semirigid chains given above, even at low molecular weight, because $q = 65$ Å.[5] This polymer may

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