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LIQUID-CRYSTALLINE POLYETHERS BASED ON CONFORMATIONAL ISOMERISM: CAN PRESSURE INDUCE SECOND-ORDER PHASE TRANSITIONS IN CRYSTALLINE PHASES PRECEDING THE NEMATIC PHASE?

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ABSTRACT

PVT studies of liquid-crystalline polyethers based on conformational isomerism have evidenced that both the shape of the PVT volume vs temperature curves as well as the phase transition temperatures depend on the mode of operation. Generally, the pressure influence on the first-order phase transitions is higher than on the glass transition. As a consequence, the first-order phases are much more enlarged when increasing the pressure. Additionally, a change of the slope is observed at higher pressures in the volume vs temperature curves of the crystalline phase preceding directly the nematic phase, independent of the order of the phases of the studied LC polyethers. This change of the slope of volume vs temperature is accompanied by both an increased range of the

high temperature crystalline phase and a reduction—and sometimes even disappearance—of the subsequent nematic phase. Taking into account that changes in the slope of volume vs temperature curves are characteristic of second-order phase transitions, the question on the nature of these transitions arises: Can second-order phase transitions be induced really within crystalline phases by pressure? The answer may be of significant applicational relevance.

INTRODUCTION

Percec et al. recently showed that main-chain liquid-crystalline polymers can also be obtained by using flexible rodlike mesogenic units based on conformational isomerism instead of the usual rigid rodlike units. It has been demonstrated that the mesophases, such as nematic [1], smectic [2a] and hexagonal columnar, can be controlled by the chemical structure of these polymers [2b]. First studies were concentrated on polyethers and copolyethers of 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)-ethane [3] and 1,2-bis(4-hydroxyphenyl)ethane [2] without or with flexible spacers based on α,ω-dibromoalkanes. The concept was later extended to synthesize LC polyethers containing combined mesogenic entities of both rigid and flexible units, i.e., 1-(4-hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)-butane (TPB) and flexible alkyl spacers [4].

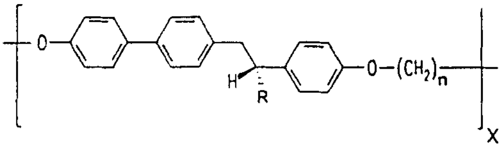
The LC behavior of the copolymers obtained by phase-transfer catalyzed polyetherification with α,ω-dibromoalkanes is controlled by the length of the alkane unit. Whereas the glass temperature of LC copolyethers decreases monotonically with the length of the alkane unit in the main chain, the first-order phase transition temperatures, i.e., crystalline–nematic and nematic–isotrope, additionally exhibit the well-known odd-even effect. Using the combined mesogenic unit 1-(4-hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)-propane (TPP) instead of TPB, two (in the first DSC heating scan even three) crystalline phases [5] are observed besides the nematic phase. Second, the high temperature crystalline phase shows a tilted hexagonal structure, either crystal-G or crystal-H.

PVT studies on main-chain LC polymers have evidenced that the phase behavior is influenced by pressure [6, 7]. To our knowledge, the study of Zoller et al. [7] on LC poly(azomethine ether)s is the only extensive investigation concerning the PVT behavior of main-chain LC polymers. The pressure effect on the relatively high isotropization temperature, however, was not experimentally accessible because of the beginning of thermal degradation. By WAXS, pressure-induced mesomorphic transitions in LC polyesters [8] were observed additionally. Considering the few PVT studies on main-chain LC polymers, it seemed attractive to perform PVT studies on liquid-crystalline polyethers based on conformational isomerism which are characterized by lower isotropization temperatures.

EXPERIMENTAL

For the subsequent PVT measurements, four representative conformational isomerism-based LC polyethers were selected, as characterized by DSC measurements [4, 5] by the following phase transitions: glass–crystalline–isotrope (TPB

TABLE 1. Liquid-Crystalline Polyethers Based on Conformational Isomerism



Polymer	R	*n*	M_W	Phase transitions, °C[a] Cooling	Second heating
TPB 10	C_2H_5	10	37,700	*i* 96 *n* 35 *g*	*g* 43 *n* 112 *i*
TPB 14	C_2H_5	14	33,900	*i* 83 *n* 60 *k* 43 *g*	*g* 49 *k* 85 *n* 96 *i*
TPB 16	C_2H_5	16	30,200	*i* 79 *n* 72 *k* 41 *g*	*g* 54 *k* 97 *i*
TPP 11	CH_3	11	31,800	*i* 156 *n* 136 *k* 95 *k*	*k* 111 *k* 155 *n* 165 *i* *k* 49 *k* 111 *k* 155 *n* 165 *i* (first heating scan)

[a] By DSC, cooling/heating rate 20 K/min.

16), glass-nematic-isotrope (TPB 10), glass-crystalline-nematic-isotrope (TPB 14), and glass-crystalline-crystal-G-nematic-isotrope (TPP 11). The phase structures and the main characteristics of the LC copolyethers studied have been published [4, 5] and are shown in Table 1.

The PVT measurements were carried out by using the commercial GNOMIX PVT apparatus [9]. The polymer samples (1-1.2 g), after annealing for several hours at 250°C, were prepared by press-molding in vacuum at the same temperature. Together with a confining fluid (mercury), the samples were introduced in a rigid piezometer cell closed at one end by a flexible bellows. The deflection of the bellows due to the expansion or contraction of both the sample and the confining fluid is measured by a linear differential transducer, calibrated for converting the data in the corresponding volume changes. The PVT measurements can be carried out in the 10-200 MPa pressure range and from room temperature to 400°C in both the isothermal and isobaric modes of operation. The accuracy of the apparatus used is in the studied temperature range of ±0.002 cm^3/g. Specific volume data are recorded in the isothermal mode of measurement along successive isotherms increasing each time the pressure changes stepwise from 10 to 200 MPa. The values for $P = 0$ can be obtained by extrapolation. In the isobaric mode of operation the PVT measurements can be performed either during heating or during cooling of the sample using constant heating/cooling rates.

RESULTS AND DISCUSSION

In Figs. 1-4 the PVT diagrams of the studied LC polyethers are shown as obtained by the *three* different modes of operation. In the *isotherm mode* the pressure has been increased from 10 to 200 MPa at each temperature in steps of 10

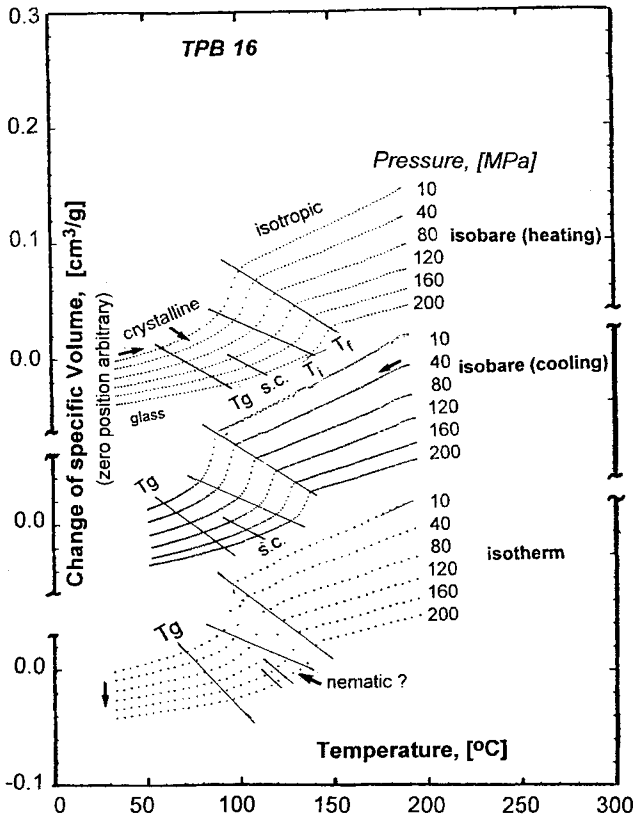


FIG. 1. PVT diagrams of the LC polyether TPB-16 showing the phase transitions: glass–crystalline–isotropic melt. T_g = glass temperature; s.c. = change of the slope of the volume vs temperature curves; T_i, T_f = initial and final temperature, respectively, of the first-order phase transition range.

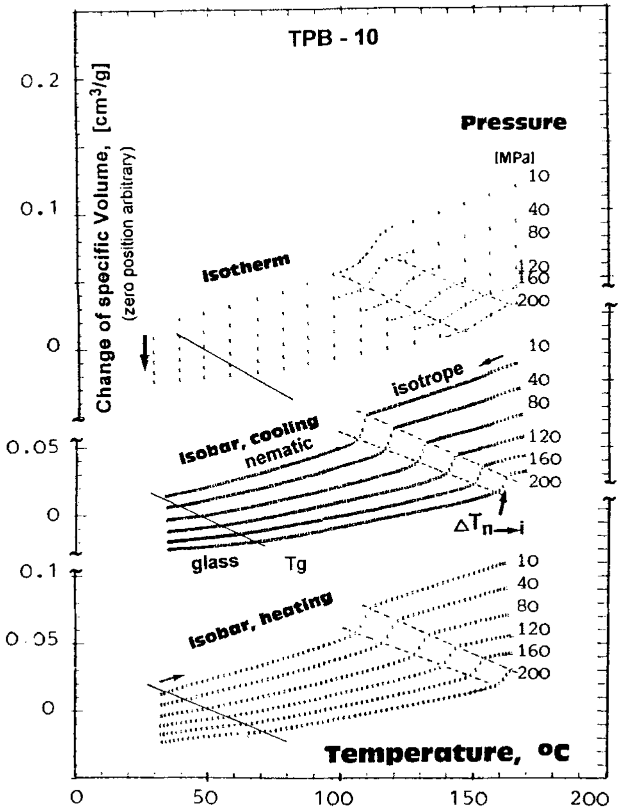


FIG. 2. PVT diagrams of the LC polyether TPB-10 showing the phase transitions: glass–nematic–isotropic melt. $\Delta T_{n \rightarrow i}$ = transition range nematic–isotrope.

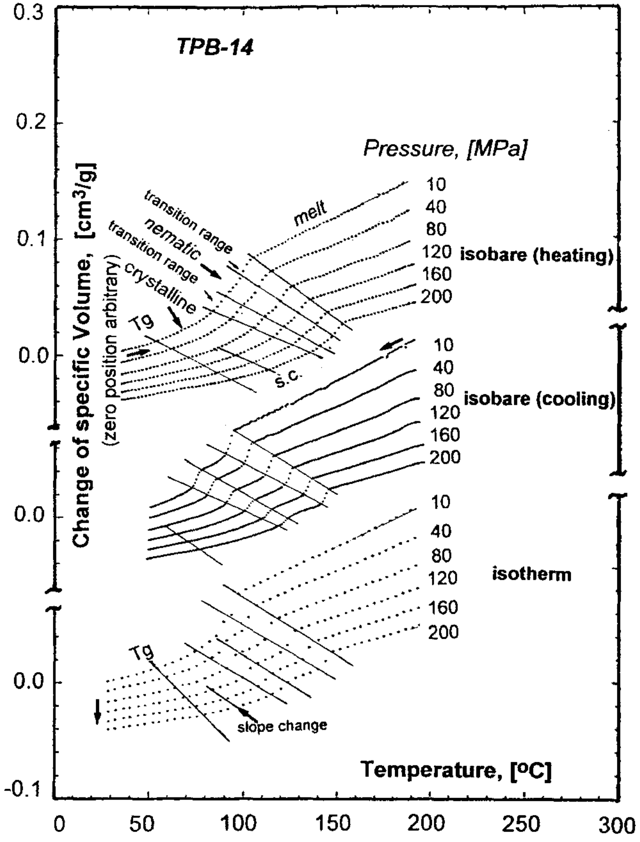


FIG. 3. PVT diagrams of the LC polyether TPB-14 showing the phase transitions: glass-crystalline-nematic-isotropic melt.

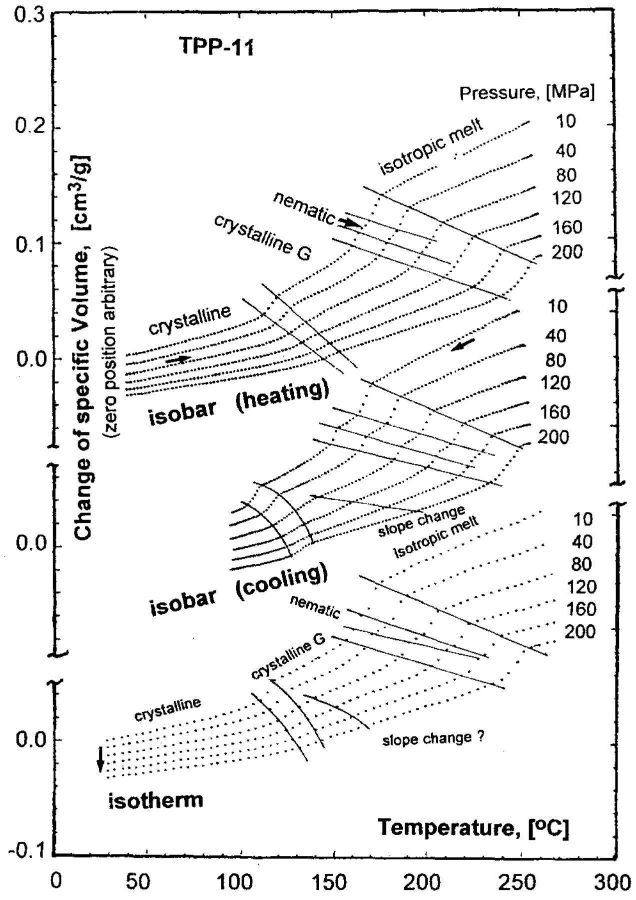


FIG. 4. PVT diagrams of the LC polyether TPP-11 showing the phase transitions: crystalline-crystalline G-nematic-isotropic melt.

MPa. For clarity the data are shown for steps of 40 MPa intervals only. In the *isobar mode*, both *heating* and *cooling* scans were measured. The respective heating and cooling rates were 4 K/min.

It is quite evident that because of the different histories of the samples, the shape of the PVT diagrams depends on the mode of operation. This is mainly seen if the respective phase transition ranges are compared. The first-order phase transition ranges are characterized by the respective initial and final temperatures, T_i and T_f. In the following, some specific features are emphasized.

The PVT curves of TPB 16 (Fig. 1), which exhibit an additional nematic phase in the cooling DSC scan (see Table 1), show a change in the slope of the respective volume–temperature curves of the crystalline phase (marked "s.c." in Fig. 1) in the isobaric scans at pressures above 80 MPa. A change in slope of volume vs temperature curves is characteristic for second-order phase transitions. In the isotherm scan, on the contrary, an additional first-order transition is clearly observed at 200 MPa. Taking into account the DSC data, it is assumed that a crystalline-nematic transition is involved. The dependence on the mode of operation of both the transition temperatures and the first-order transition ranges is illustrated for TPB-16 in Fig. 5. Beside the evident influence of the mode of operation on the phase transition ranges, the higher pressure dependence of the first-order transition temperature crystalline–isotrope of the glass temperature is then observed. The

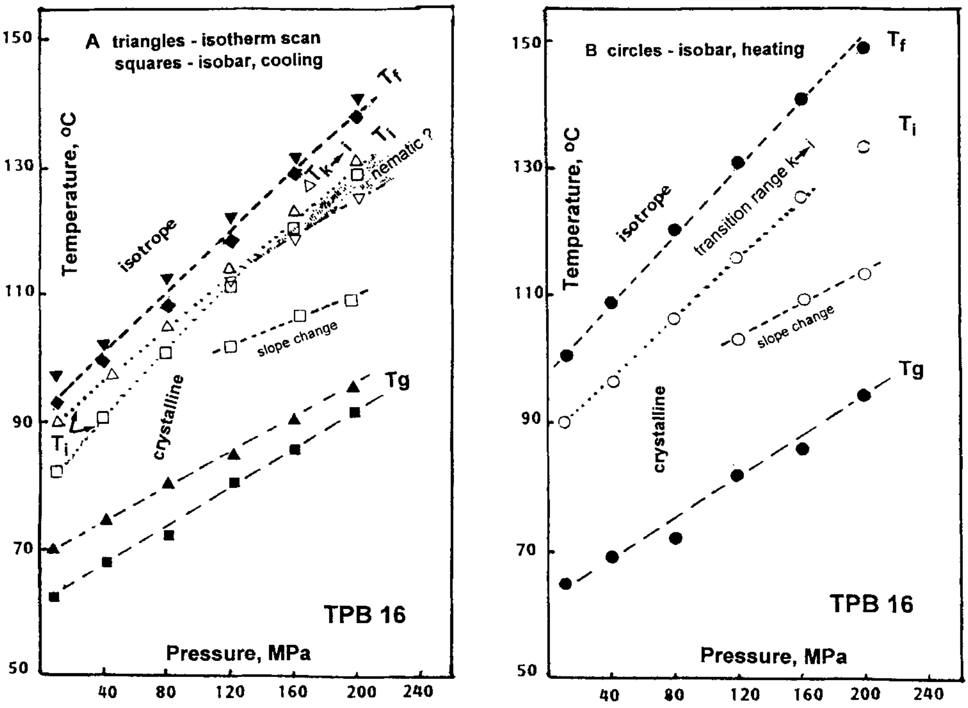


FIG. 5. Pressure dependence of the phase transition temperatures of TPB-16. A: For the isotherm and isobar cooling mode of operation. B: For the isobar heating mode of operation. T_i and T_f temperatures delimiting the first-order transition range crystalline-isotropic melt, $\Delta T_{k\rightarrow i}$.

first-order transition temperature corresponds to T_f of the respective transition ranges. As a consequence, broadening of the crystalline range with pressure results. This enlargement of the crystalline phase is increased additionally at higher pressures where a change is observed in the slope of the respective volume vs temperature curves.

Corresponding observations concerning the influence of pressure on phase transitions are valid for the PVT diagrams of TPB-10 (Fig. 2). It is confirmed once more that the glass transition is mainly influenced by the mode of operation, i.e., by the history of the sample studied (see also Fig. 6). The marked dependence of glass temperature on sample history has been confirmed by an additional study on the glass transition of polystyrenes of different molecular weights [10].

The PVT curves of TPB-14, which show both a crystalline and a nematic phase, are presented in Fig. 3. The result is that the width of the two first-order phase transition ranges are affected differently by the mode of operation. Taking into account that the glass temperature is less influenced by pressure than the subsequent first-order transition, the crystalline phase is much more enlarged by the increasing pressure than is the nematic one (see Fig. 7). In the PVT curves obtained in the isobar heating and the isotherm modes of operation, a change of the slope of the volume vs temperature curves of the crystalline phase is also observed at higher pressures.

It has been shown by DSC that the LC polyether TPP-11 is characterized by two crystalline phases. A change in slope of the volume vs temperature curves at

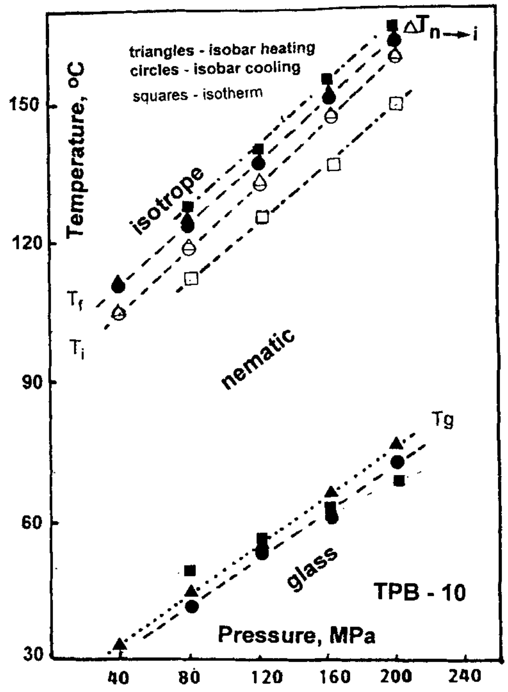


FIG. 6. Pressure dependence of the phase transition temperatures of TPB-10. $\Delta T_{n \to i}$ = transition range nematic–isotropic melt delimited by T_i and T_f.

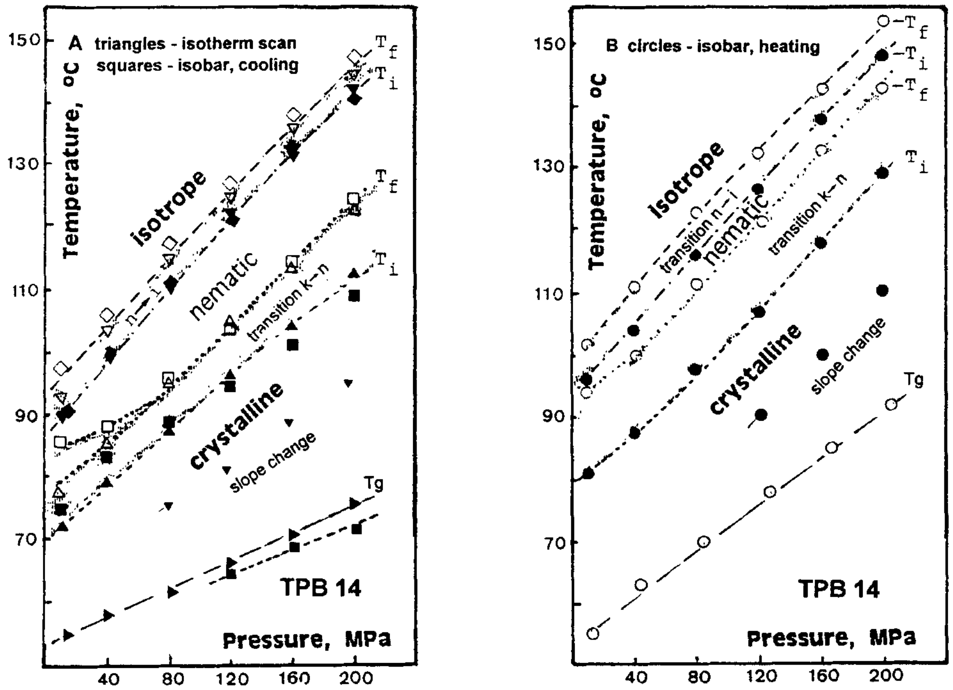


FIG. 7. Pressure dependence of the phase transition temperatures of TPB-14. A: For the isotherm and isobar cooling mode of operation. B: For the isobar heating mode of operation.

higher pressures is observed; however, this occurs only at higher temperatures in the crystal-G phase. This change of the slope of the volume vs temperature curves is accompanied by an increased enlargement of the respective phases and by a decrease (or even disappearance) of the subsequent nematic phase. Additionally, the dependence of the first-order transition of crystal–crystal G on pressure is no longer linear. It shows, however, a tendency to level off with increasing pressure (see Fig. 8). Additional studies are needed to explain this unusual behavior.

In Fig. 9 the pressure dependences of the temperature ranges of the mesophases of TPB-14 and TPP-11 are compared. TPP-11 shows a second, high temperature crystalline phase. There is excessive reduction with increasing pressure of the temperature range of the nematic phase of TPP-11 because of the presence of a second crystalline phase.

Finally, in Figs. 10 and 11 the pressure influences on the expansion coefficients of the studied LC copolyethers are illustrated. The data confirm the dependence of the expansion coefficients on the operating conditions used in the PVT measurements. As expected, the glass and crystalline phases always show lower expansion coefficients. It is remarkable, however, that for LC copolyethers showing both a crystalline and a nematic phase (i.e., TPB-14 and TPP-11), the expansion coefficients are larger for the nematic phase when compared with those of the isotropic one. Surprisingly, even the two expansion coefficients of the crystal-G phase are higher than those of the isotropic phase. The expansion coefficients of TPB-10,

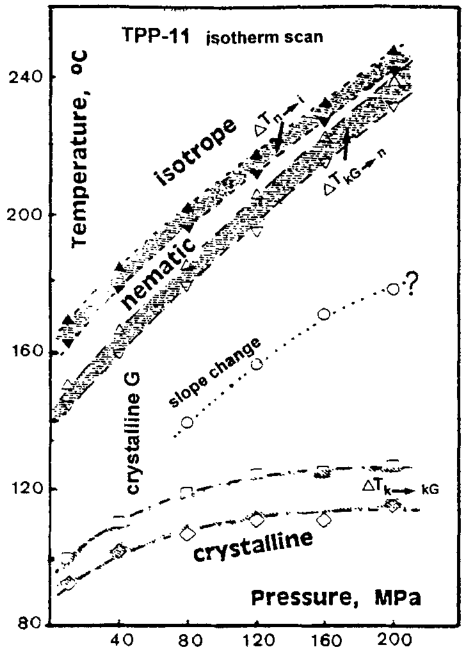


FIG. 8. Pressure dependence of the phase transition temperatures of TPP-11 for the isotherm mode of operation. First-order phase transition ranges: crystalline-crystalline G-$\Delta T_{k\to kG}$, crystalline G-nematic-$\Delta T_{kG\to n}$, and nematic-isotropic melt-$\Delta T_{n\to i}$.

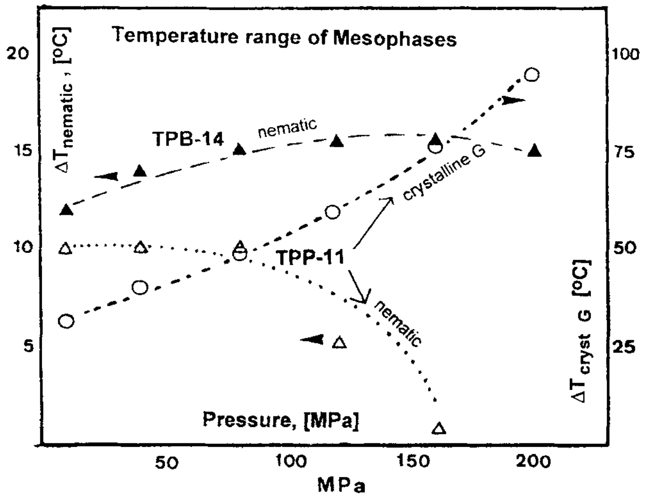


FIG. 9. Pressure dependence of the temperature ranges of the nematic and of the high temperature crystalline G phases of TPB-14 and TPP-11.

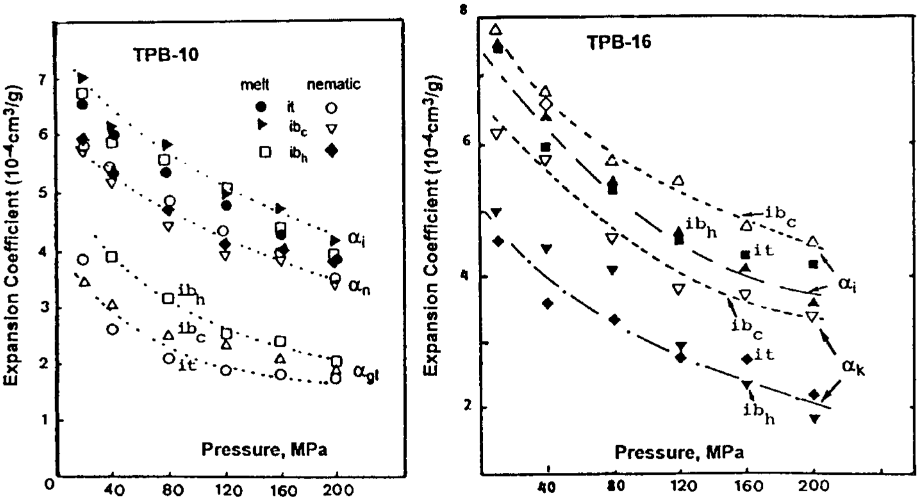


FIG. 10. Pressure influence on the expansion coefficients of TPB-10 and TPB-16. it = isotherm, ib_h = isobar heating, and ib_c = isobar cooling mode of operation.

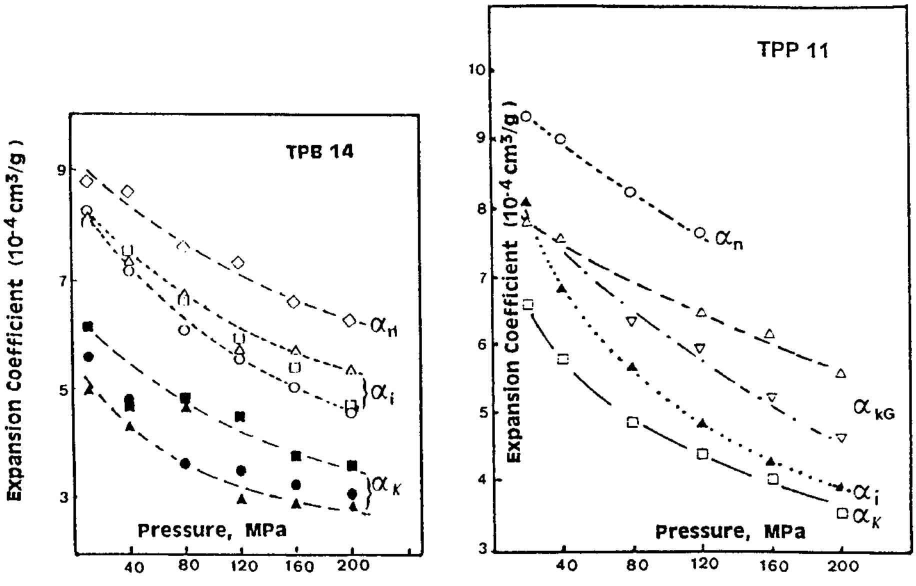


FIG. 11. Pressure influence on the expansion coefficients of TPB-14 and TPP-1 (for the significance of the marks used for TPB-14, see Fig. 10; TPP-11 data for isotherm mode of operation).

where an intermediary crystalline phase is missing, show the expected order, i.e., $\alpha_{gl} < \alpha_n < \alpha_i$.

It is worthwhile to note that independent of the phases of the LC polyethers based on the conformational isomerism studied, a change in the volume vs temperature curves is observed at higher pressures only in the crystalline phase directly preceding a nematic phase. Further studies are needed for a justifiable explanation of this unexpected result.

It is well known that slope changes in volume vs temperature curves are generally characteristic for second-order phase transitions. Thus, the question arises whether second-order transitions can be induced by pressure in crystalline phases preceding nematic phases: What is the molecular background of these second-order phase transitions? It is of interest to note that the pressure-induced slope change in the respective volume vs temperature curves is always accompanied by an increased enlargement of the high temperature crystalline phase with pressure and by a reduction of the subsequent nematic phase. Without additional investigations applying other methods at high pressures, it will not be possible to offer an unequivocal explanation for these observations.

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