Macromolecules **1990**, *23*, 4347–4350

A Thermodynamic Interpretation of Polymer Molecular Weight Effect on the Phase Transitions of Main-Chain and Side-Chain Liquid-Crystal Polymers

Virgil Percec*,† and Andrew Keller‡

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106-2699, and H.H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, United Kingdom

Received October 25, 1989; Revised Manuscript Received February 21, 1990

ABSTRACT: In this paper we follow up the dependence of the mesomorphic temperature range as a function of the degree of polymerization through simple thermodynamic considerations. In particular, we consider the dependence between the free energies of the crystalline (G_k), liquid crystalline (G_{lc}), and isotropic (G_i) phases on the temperature for different polymerization degrees and three different thermodynamic situations. These dependences were converted into phase-transition temperature–degree of polymerization relationships. The slope of the isotropization temperature (T_i)–polymerization degree dependence is steeper than that of the corresponding dependence of the melting temperature (T_m). It is shown that this has the consequence of promoting or enhancing the mesophase, the exact nature of the effect being determined by the relative positions of the two curves, namely T_i versus molecular weight (M) and T_m versus M. In particular, it explains the enlargement of an enantiotropic mesophase of a monomeric structural unit, and the transformation of a virtual or monotropic monomeric unit mesophase into a monotropic or enantiotropic mesophase upon increasing its degree of polymerization. It shows further why and how the virtual mesophase of the monomeric structural unit is narrowed upon increasing its degree of polymerization. All these predictions are supported by experimental data available in the literature on the phase-transition temperature–molecular weight dependence of both main-chain and side-chain liquid-crystal polymers.

Introduction

This paper will demonstrate that conditions for the realization of mesomorphic states in polymers are readily expressed in terms of the relative thermodynamic stabilities of the crystalline (k), mesomorphic (lc), and liquid (i.e., isotropic, i) phases. The same thermodynamic principles will be used to explain the dependence between phase-transition temperatures and the molecular weight of both main-chain and side-chain liquid-crystalline polymers. For the sake of simplicity within this paper we will refer to the equilibrium state as to be qualified below. Existing experimental data from the literature will be compared with thermodynamically derived relationships. It will be shown that most of the existing experimental data from the literature readily fall within the scheme.

Definitions. For convenience we shall retain the existing nomenclature used in the literature on liquid crystals. First, however, we need to specify each term to maintain consistency.

Enantiotropic Mesophase. This mesophase is observed as reversible both on heating and on cooling. It thus appears as thermodynamically stable with respect to the prevailing crystalline phase regardless of whether the latter is in its own form of highest stability or in a less stable state.

Virtual Mesophase. This refers to a mesophase that is potentially possible, however, is thermodynamically less stable than the crystalline phase at the same temperature. It is unrealizable both on heating and on cooling regardless of whether the crystalline and isotropic phases are in their stablest forms.

Monotropic Mesophase. This refers to a mesophase that is thermodynamically metastable with respect to the crystalline phase. This is a particular case of a virtual mesophase, which under certain kinetic conditions can be observed, however, only on cooling.

Discussion

Let us briefly recapitulate some basic thermodynamic principles. The thermodynamic equation required for this discussion is

$$dG = V\,dp - S\,dT$$

where G is the free energy, S is the entropy, V is the volume, p is the pressure, and T is the temperature. Throughout the entire paper, we will consider phase transitions at constant pressure ($dp = 0$). Therefore, the free energies of the crystal (G_k), liquid crystal (G_{lc}), and liquid or isotropic (G_i) phases decrease with increasing temperature. The decrease of G_i is steeper than G_{lc} and G_k, since

$$S_i > S_{lc} > S_k$$

For the present purpose we take as a starting point the G–T relations for a system having a reversible realizable liquid-crystal temperature regime. This by the definition quoted is enantiotropic and is represented by Figure 1a. Starting from such an enantiotropic mesophase, we can pass on into a virtual mesophase by decreasing either G_i or G_k. G_i is decreased by increasing the disorder or flexibility of the polymer in the isotropic phase, thereby increasing S_i (Figure 1b). G_k is decreased by an increase of the perfection of the crystal and with a consequent increase of T_m (Figure 1c). The monotropic mesophase arises if in a potentially virtual situation as in Figure 1b, we will follow the G_{lc} path on cooling below T_i, with the pathway dropping to G_k at some stage. This case will be illustrated explicitly in another publication.[1] The meaning of the phase-transition temperatures from parts a–c of Figure 1 is explained in the figure caption.

Let us discuss the relationship between phase-transition temperatures and polymer molecular weight for three

---

* To whom correspondence should be addressed.

† Case Western Reserve University.

‡ University of Bristol.

0024-9297/90/2223-4347$02.50/0

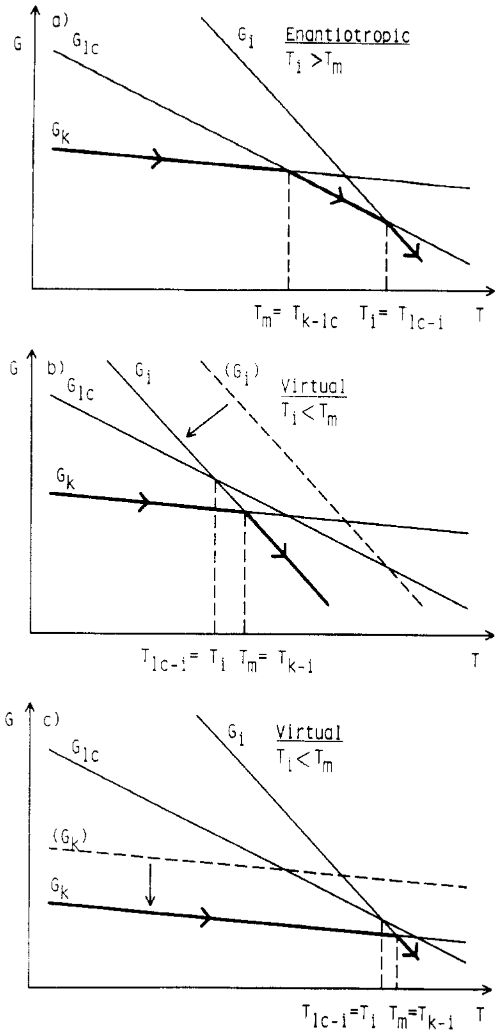

Figure 1. (a) Schematic representation for the dependence between the free energies of the crystalline (G_k), liquid-crystalline (G_{lc}), and isotropic (G_i) phases and temperature for a system displaying an enantiotropic mesophase. The heaviest lines containing an arrow correspond as in parts b and c of Figure 1 to the lowest free energy pathway (on heating for the particular arrow direction), i.e., the stablest state at a given temperature. $T_m = T_{k-lc}$ is the melting of the crystalline phase into a liquid-crystalline phase. $T_i = T_{lc-i}$ is the transition from the liquid-crystalline to the isotropic phase, i.e., isotropization temperature. (b) Schematic representation of the dependence between the free energies of the crystalline (G_k), liquid-crystalline (G_{lc}), and isotropic (G_i) phases and temperature for a system displaying a virtual mesophase. This situation was realized by lowering G_i (i.e., by decreasing the rigidity of the system and therefore, by increasing the entropy of the isotropic phase S_i) from the level outlined in Figure 1a [see the translation of $(G_i) \rightarrow G_i$]. $T_m = T_{k-i}$ is the melting of the crystalline phase into the isotropic phase. $T_i = T_{lc-i}$ is the transition from the liquid-crystalline to the isotropic phase, i.e., isotropization temperature. (c) Schematic representation of the dependence between the free energies of the crystalline (G_k), liquid-crystalline (G_{lc}), and isotropic (G_i) phases and temperature for a system displaying a virtual mesophase. This situation was realized by lowering G_k (i.e., by increasing the crystal perfection with the consequent increase of the melting temperature of the crystalline phase and therefore, by decreasing G_k) from the value outlined in Figure 1a [see the translation of $(G_k) \rightarrow G_k$]. $T_m = T_{k-i}$ is the melting of the crystalline phase into the isotropic phase. $T_i - T_{lc-i}$ is the transition from the liquid crystalline to the isotropic phase, i.e., isotropization temperature. T_m in Figure 1c is higher than T_m in parts a and c of Figure 1.

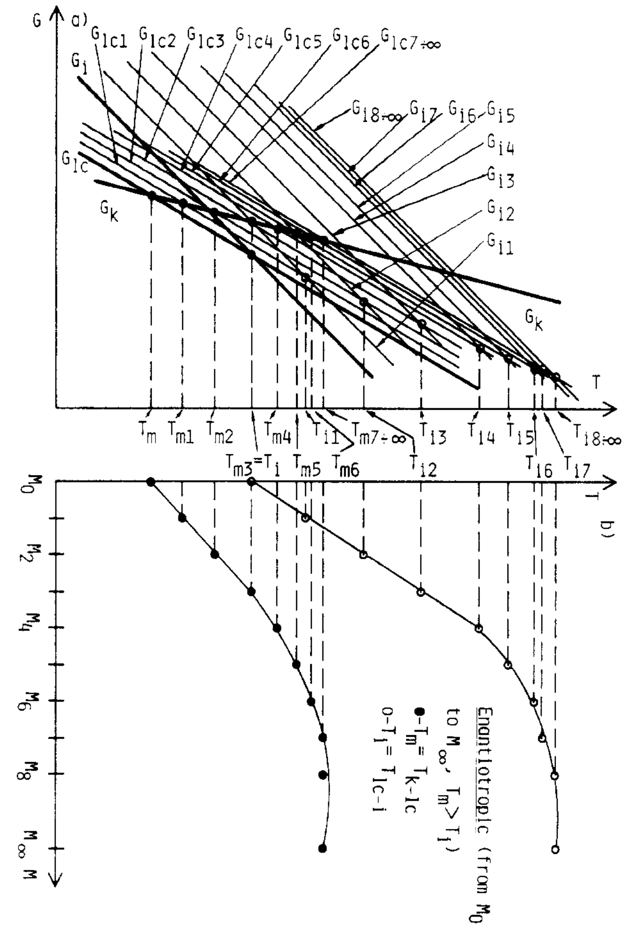

Figure 2. Broadening of the temperature range of an enantiotropic mesophase of the monomeric structural unit (M_0) by increasing the degree of polymerization. The upper part (a) describes the influence of molecular weight on the dependence between the free energies of the crystalline (G_k), liquid-crystalline (G_{lc}), and isotropic (G_i) phases and transition temperatures. The translation of this dependence into the dependence of phase-transition temperature–molecular weight is presented in the lower part (b). The monomeric structural unit having the molecular weight M_0 displays an enantiotropic mesophase. In (a) G_k is taken as molecular weight independent. G_{lc} and G_i refer to the monomeric structural unit (M_0). G_{lc1} to $G_{lc\infty}$ and G_{i1} to $G_{i\infty}$ refer to the increased G_{lc} and G_i values according to the increase in molecular weight from M_1 to M_∞. T_m and T_i values calculated from the upper part of the figure were transferred into temperature transition–molecular weight dependence in the lower part of this figure (best when followed by rotating this figure 90° to the left).

different situations. Upon increasing the molecular weight from monomer to polymer, the entropy of the liquid phase (S_i) decreases. The decrease of the entropies of mesomorphic and crystalline phases is lower than that of the isotropic phase. For simplicity, the decrease of the entropy of the crystalline phase will be neglected. With the decrease in S_i, S_{lc} tends asymptotically to zero with increasing molecular weight. It follows that G_i and G_{lc} increase with the increase of the polymer molecular weight again asymptotically; above a certain molecular weight, we may consider both parameters as remaining constant.

Case 1. Both Monomeric Structural Unit and Polymer Displaying an Enantiotropic Mesophase. The first situation we will consider refers to the case in which the monomeric structural unit displays an enantiotropic mesophase. Upon increasing its molecular weight to dimer, trimer, etc., S_i decreases and, therefore, G_i increases. Beyond a certain molecular weight, G_i remains, for all practical considerations, constant. Figure 2 transforms the free energy (G) versus transition temperature (T) dependence, into a transition temperature (T) versus molecular weight (M) dependence. The T versus M plot in Figure 2 demonstrates that both melting (T_{k-lc}) and isotropization (T_{lc-i}) temperatures increase with increasing molecular weight up to a certain range of M values, beyond which T_{k-lc} and T_{lc-i} remain approximately constant, with the T_i line lying above the line for T_m for all molecular weights. However, the slope of the increase of T_{lc-i} is steeper than that of T_{k-lc}. The difference between these two slopes determines the relative thermodynamic stability of the mesomorphic phase versus that of the crystalline phase at different polymer molecular weights.

For this particular case, the higher slope of the T_{lc-i}–M versus that of the T_{k-lc}–M dependence leads to a widening of the temperature range between the two curves with increasing molecular weights of the polymer. This widening of the liquid-crystal temperature regime with molecular weight agrees with experimental data reported for the case of both main-chain[2-4] and side-chain[5,6] liquid-crystal polymers. This effect has been repeatedly labeled the "polymer effect", especially in the case of side-chain liquid-crystal polymers.[7]

Case 2. Monomeric Structural Unit Displaying a Virtual or a Monotropic Mesophase; the Polymer Displaying a Monotropic or an Enantiotropic Mesophase. The steeper slope of the $T_{lc-k(i)}$–M dependence versus that of the $T_{k-i(lc)}$ dependence has even more important implications on the molecular weight–phase transition temperature dependence for the situation when the monomer structural unit displays only a monotropic or a virtual mesophase (Figure 3).

As seen the two lines T_i versus M and T_m versus M intersect. This arises from the fact that $T_i < T_m$ for low molecular weights with a steeper slope for T_i. Specifically (for the illustration in Figure 3) the T_i (i.e., T_{lc-k}) values are below the corresponding T_m (i.e., T_{k-i}) values for M_0 to M_4; hence, in the range M_0 to M_4, the monomer together with its low oligomers up to 4 displays only a virtual mesophase. Beyond M_4 the mesophase becomes stable; hence, the system is enantiotropic. In addition to the thermodynamic criterion, kinetics also influences the phase transitions. A certain amount of supercooling of the isotropic–mesomorphic transition and especially much more so of the mesomorphic–crystalline transition is possible, which can lead to monotropic behavior for molecular weights slightly below and at the intersection point (i.e., at M_4). In view of the fact that T_i and T_m are expected to be continuous functions of molecular weight, the intersection point can be arbitrarily closely approached (from below); hence, realization of a metastable liquid-crystal phase and consequent monotropic behavior is to be expected for appropriate molecular weights in cases to which Figure 3 pertains. This effect has been observed experimentally both in the cases of main-chain[8-10] and side-chain[11,12] liquid-crystalline polymers and was labeled "transformation of a monotropic mesophase into an enantiotropic mesophase by increasing the molecular weight of the polymer".

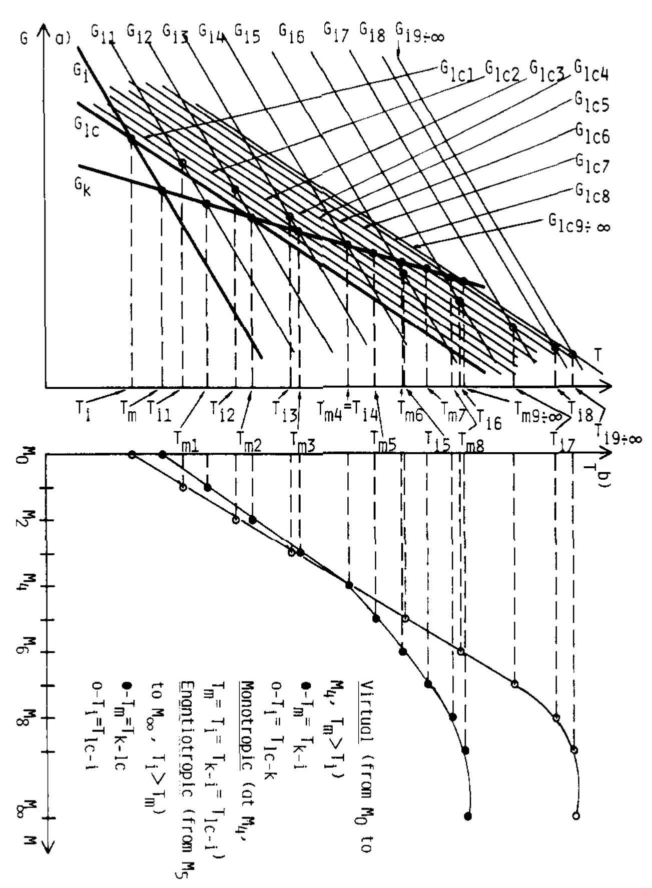

Figure 3. Transformation of a virtual or monotropic mesophase of the monomeric structural unit (M_0) into an enantiotropic mesophase by increasing the degree of polymerization. The upper part (a) describes the influence of molecular weight on the dependence between the free energies of the crystalline (G_k), liquid-crystalline (G_{lc}), and isotropic (G_i) phases and transition temperatures. The translation of this dependence into the dependence of phase-transition temperature–molecular weight is shown in the lower part (b). The monomeric structural unit having the molecular weight (M_0) displays a virtual mesophase. The upper part displays the relationship between G_k, G_{lc}, and G_i versus temperature for different polymer molecular weights M_0 to M_∞. G_k is molecular weight independent. G_{lc} and G_i refer to monomeric structural unit (M_0). G_{lc1} to $G_{lc\infty}$ and G_{i1} to $G_{i\infty}$ refer to the G_{lc} and G_i values corresponding to the increase in molecular weight from M_1 to M_∞. T_m and T_i values determined from the upper part of this figure were transplanted into temperature transition–molecular weight dependence in the lower part (best when followed by rotating the figure 90° to the left).

Case 3. Monomeric Structural Unit Displaying a Virtual Mesophase; the Polymer Displaying a Virtual Mesophase. The third situation is illustrated in Figure 4 and also refers to a different case in which the monomeric unit displays only a virtual mesophase. Here as before, the slope of the T_i–M (i.e., T_{lc-k}–M) dependence is higher than that of the T_m–M (i.e., T_{k-i}–M) dependence. The latter lies above the former throughout; hence, the two curves do not intercept each other. Therefore, the resulting polymer displays also only a virtual mesophase. This thermodynamic situation was recently applied to the synthesis of virtual liquid-crystal polyethers containing both flexible mesogens and flexible spacers. The most thoroughly investigated example so far refers to polyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane and α,ω-dibromoalkanes.[13-15] In this last class of polymers, the transformation of the virtual mesophase of the homopolymer into a monotropic or enantiotropic mesophase was accomplished by increasing the free energy of the crystalline phase (G_k). Theoretically this situation can be envisioned by inspecting parts a and c of Figure 1. Experimentally, the increase of G_k has been accomplished by two different techniques so far. The first involved the copolymerization of 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane with two[13,14] or more than two[15] flexible spacers of different length or the copolymerization of two dissimilar flexible mesogenic bisphenols with one flexible spacer.[16] The resulting copolymers exhibit an increased G_k in comparison to that of their parent homopolymers since their melting temperatures are lower. The second technique is based on blends of two or more homopolymers that display virtual mesophases. When the virtual mesophases of the homopolymers are isomorphic and their crystalline phases are not, the resulting blends display either a monotropic

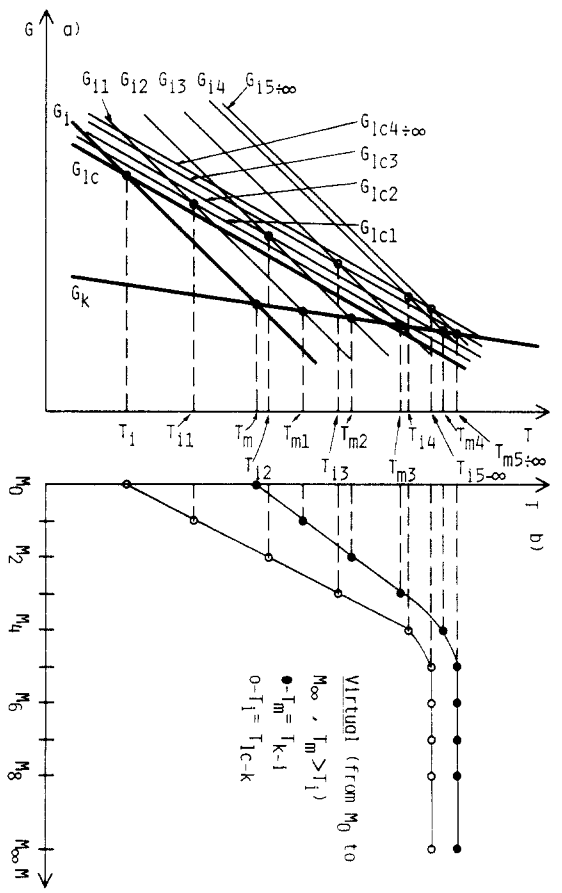

Figure 4. Narrowing of the temperature range of a virtual mesophase of the monomeric structural unit (M_0) by increasing the degree of polymerization. The upper part (a) describes the influence of molecular weight on the dependence between the free energies of the crystalline (G_k), liquid-crystalline (G_{lc}), and isotropic (G_i) phases and transition temperatures. The translation of this dependence into the dependence phase-transition temperature–molecular weight is presented in the lower part (b). The monomeric structural unit (having the molecular weight M_0) displays a virtual mesophase. The upper part (a) displays the relationship between G_k, G_{lc}, and G_i versus temperature for different polymer molecular weights (M_0 to M_∞). G_k is molecular weight independent. G_{lc} and G_i refer to the monomeric structural unit (M_0). G_{lc1} to $G_{lc\infty}$ and G_{i1} to $G_{i\infty}$ refer to the G_{lc} and G_i values corresponding to the increase in molecular weight from M_1 to M_∞. T_m and T_i from the upper part (a) of the figure were transplanted into temperature transition–molecular weight dependence in the lower part (b) (best when followed by rotating the figure 90° to the left).

or an enantiotropic mesophase.[17]

In conclusion, the steeper slope of the isotropization temperature–molecular weight dependence versus that of the melting temperature–molecular weight dependence should have the following effects on going from monomer to polymer. When the monomeric structural unit displays an enantiotropic mesophase, the resulting polymer will display a broader enantiotropic mesophase, i.e., anisotropic temperature interval. When the monomeric unit displays a monotropic mesophase, the resulting polymer will, most probably, display an enantiotropic mesophase. When the monomeric unit displays a virtual mesophase, the resulting polymer may display either an enantiotropic, monotropic, or virtual mesophase. For the case of side-chain[11,12] and main-chain[2,9,10] liquid-crystalline polymers containing flexible spacers and displaying a single mesophase, the nature of the mesophase displayed by the polymer is most frequently identical with that of its monomeric unit. Primarily the molecular weight–phase transition dependences are determined by the relationship between the free energies of the crystalline, liquid-crystalline, and isotropic phases of the monomeric structural unit yet influenced by the molecular weight of the main-chain backbone through its effect on the melt entropy as in case 1 above. Combinations of more than one mesomorphic phases of different thermodynamic stabilities in a monomeric–structural unit will follow the same molecular weight dependence as those described by the monomers displaying a single mesophase.[12,20-22] However, there are few examples where the nature of the mesophase displayed by the main-chain[18,19] and side-chain[22] liquid-crystalline polymers is molecular weight dependent. Both in the case of the main-chain[18,19] and side-chain liquid-crystalline polymers, it has been demonstrated that this change in the mesophase represents a continuous dependence of molecular weight. The interpretation of this dependence based on a similar thermodynamic scheme will represent the subject of further publications.

Acknowledgment. Financial support of this work by the National Science Foundation, Polymers Program (Grant DMR-86-19724) to V.P. and by the U.S. Army European Office, London, to A.K. is gratefully acknowledged.

References and Notes

(1) Keller, A.; Ungar, G.; Percec, V. In *Advances in Liquid Crystalline Polymers*; Ober, C. K., Weiss, R. A., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, in press.
(2) Blumstein, A.; Vilasagar, S.; Ponrathnam, S.; Clough, S. B.; Blumstein, R. B.; Maret, G. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 877.
(3) Percec, V.; Nava, H.; Jonsson, H. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 1943.
(4) Feijoo, J. L.; Ungar, G.; Owen, A. J.; Keller, A.; Percec, V. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 487.
(5) Kostromin, S. G.; Talroze, R. V.; Shibaev, V. P.; Plate, N. A. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 803.
(6) Percec, V.; Hahn, B. *Macromolecules* **1989**, *22*, 1588.
(7) Percec, V.; Pugh, C. In *Side Chain Liquid Crystal Polymers*; McArdle, C. B., Ed.; Blackie and Son Ltd. and Chapman and Hall: Glasgow and New York, 1989; p 30.
(8) Majnusz, J.; Catala, J. M.; Lenz, R. W. *Eur. Polym. J.* **1983**, *19*, 1043.
(9) Zhou, Q. F.; Duan, X. Q.; Liu, Y. L. *Macromolecules* **1986**, *19*, 247.
(10) Percec, V.; Nava, H. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 405.
(11) Stevens, H.; Rehage, G.; Finkelmann, H. *Macromolecules* **1984**, *17*, 851.
(12) Percec, V.; Tomazos, D.; Pugh, C. *Macromolecules* **1989**, *22*, 2259.
(13) Percec, V.; Yourd, R. *Macromolecules* **1989**, *22*, 524 and 3229.
(14) Percec, V.; Tsuda, Y. *Polym. Bull.* **1989**, *22*, 489 and 497.
(15) Percec, V.; Tsuda, Y. *Macromolecules* **1990**, *23*, 3509.
(16) Percec, V.; Howells, B. In preparation.
(17) Percec, V.; Tsuda, Y. *Polymer*, in press.
(18) Kumar, R. S.; Clough, S. B.; Blumstein, A. *Mol. Cryst. Liq. Cryst.* **1988**, *157*, 387.
(19) Blumstein, R. B.; Blumstein, A. *Mol. Cryst. Liq. Cryst.* **1989**, *165*, 361.
(20) Sagane, T.; Lenz, R. W. *Polymer* **1989**, *30*, 2269.
(21) Shibaev, V. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 189.
(22) Percec, V.; Lee, M. *Macromolecules*, in press.