Phase transitions in narrow-molar-mass samples of side-chain liquid-crystalline polymers: molar-mass dependence

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The molar-mass dependence of phase transitions in narrow-molar-mass samples of smectic side-chain poly(vinyl ether)s is discussed with reference to earlier data by Stevens *et al.* and Percec *et al.* on narrow fractions of smectic side-chain polysiloxanes and polymethacrylates. The constant heat of isotropization (Δh_i) and the proportionality between the glass transition temperature (T_g) and the reciprocal degree of polymerization (DP) observed for polysiloxanes and polymethacrylates indicate that the order within the smectic layers and the penetration of the flexible main chains of the smectic layers was not appreciably affected by changes in DP. The poly(vinyl ether)s on the other hand exhibited a pronounced decrease in Δh_i with increasing DP and a more complex correlation between T_g and DP indicative of an increasing disturbance by the flexible main chains of the smectic layers with increasing DP. These differences between polysiloxanes/polymethacrylates and poly(vinyl ether)s were also found to have profound effects on the DP dependence of the isotropization temperature.

(Keywords: side-chain smectic polymers; narrow molar mass; phase transitions; molar-mass dependence; poly(vinyl ether)s)

INTRODUCTION

The molar-mass dependence of phase transitions occurring in liquid-crystalline (LC) polymers has been studied in both main-chain and side-chain polymers[1–14]. It is established that the glass transition temperature and the isotropization temperature increase strongly with molar mass in the low-molar-mass range. These quantities level off at higher molar masses and finally approach a constant value. The molar-mass dependence of the heat of isotropization is currently under discussion.

Comprehensive work on narrow-molar-mass samples has been reported by Stevens *et al.*[6] on fractionated samples of side-chain polysiloxanes and more recently by Percec *et al.*[10,11] on side-chain polysiloxanes and polymethacrylates. These data are here critically compared with data recently presented by Percec *et al.*[12–14] on side-chain poly(vinyl ether)s prepared by living cationic polymerization. The latter technique permits the production of samples of narrow molar-mass distribution. Different expressions for the molar-mass dependence of the glass transition temperature and isotropization temperature and the enthalpy and entropy change associated with isotropization are tested, and the results are discussed with reference to current views concerning the structure of these polymers. The effect of the length of the spacer group consisting of seven to nine methylene groups is also discussed.

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RESULTS AND DISCUSSION

The synthesis and structure of the poly(vinyl ether)s have been presented in earlier papers by Percec *et al.*[12–14]. The molecular structure of the narrow-molar-mass poly(vinyl ether)s ($M_m/M_n = 1.1$) is shown in *Figure 1*. The number of methylene groups in the spacer unit is seven, eight or nine. These polymers are referred to as C7, C8 and C9 respectively. The degree of polymerization (DP) of the different polymers (oligomers) ranged from 2 to 32.

Phase transitions in these polymers were detected by differential scanning calorimetry (d.s.c.) and polarized light microscopy at a scanning rate of 20 K min^{-1} (refs. 12–14). The glass transition temperature measured during cooling refers either to smectic A (s_A) or to an unknown smectic phase (s_X). The isotropization of the mesomorphic structure involved unanimously s_A phases.

Feijoo *et al.*[15] recently showed that high-molar-mass samples of a nematic main-chain polyether exhibited non-equilibrium behaviour. A significant increase in both isotropization temperature (T_i) and heat of isotropization (Δh_i) was observed in nematic samples annealed at temperatures above the crystal melting point. Equilibrium was reached after several hours of annealing. It was observed that traces of nematic order remained typically several minutes after heating the samples above the clearing temperature. Samples of poly(vinyl ether) C7 ($DP = 5$ and 30) were therefore annealed in the smectic LC state, but no significant changes in T_i or Δh_i were

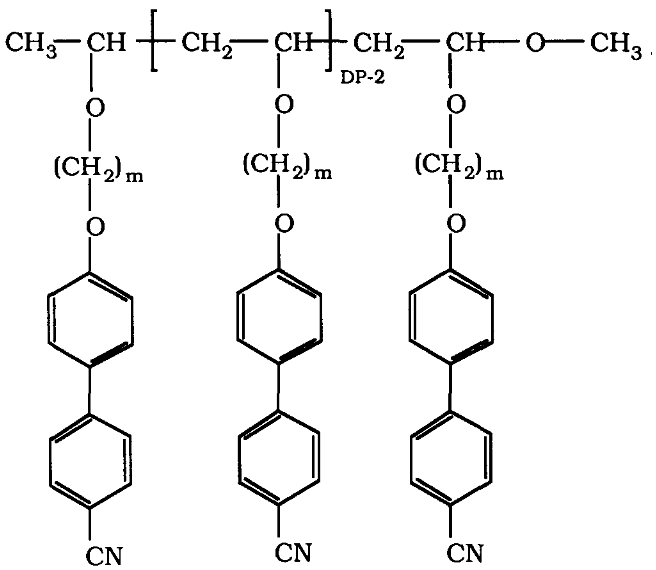

Figure 1 Structure of side-chain liquid-crystalline poly(vinyl ether)s C7, C8 and C9

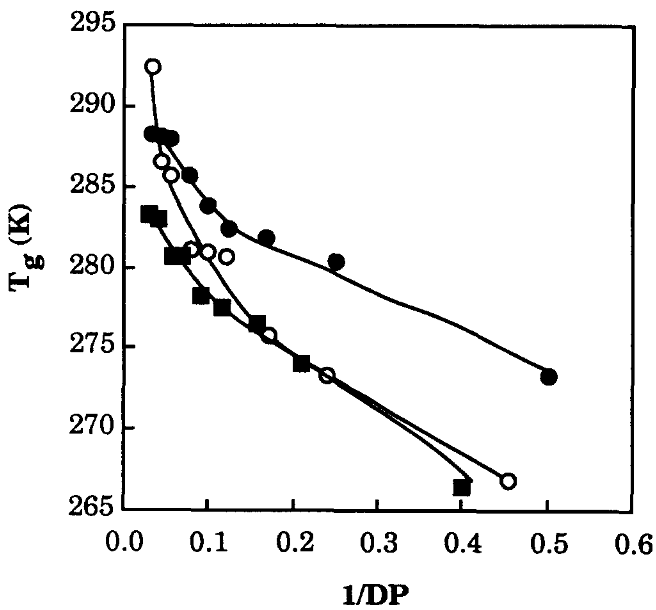

Figure 2 The glass transition temperature (T_g, recorded on cooling) of poly(vinyl ether)s as a function of the reciprocal degree of polymerization (DP): (●) C7; (○) C8; (■) C9

observed. Nor was the time spent above T_i significant for the recorded values of T_i or Δh_i. Thus, we can safely state that the smectic poly(vinyl ether)s studied here were in a near-equilibrium state.

Glass transition

Figure 2 presents the glass transition temperature (T_g) as a function of the reciprocal of the degree of polymerization (DP), and it is evident that the molar-mass dependence of T_g in the case of the side-chain poly(vinyl ether)s is different from that observed in fully amorphous polymers[16]. Stevens *et al.*[6] reported T_g data as a function of DP for narrow-molar-mass fractions of polysiloxanes with four (PS4) and six (PS6) methylene groups in the spacer. The LC phases involved were nematic for PS4 and smectic for PS6. *Figure 3* shows that T_g was proportional to $(DP)^{-1}$ for the polysiloxanes, in agreement with the behaviour of fully amorphous polymers. Percec *et al.*[10,11] reported the same trend for poly((6-4(4-methoxy-β-methylstyryl)phenoxy)hexyl methacrylate) (4-6-PMA) and polysiloxanes.

The plasticizing effect of the chain ends leads to a linear trend in the T_g *versus* $(DP)^{-1}$ plot, which indicates that the behaviour of amorphous polymers cannot alone explain the presented data for the side-chain poly(vinyl ether)s. In addition to the effect of the chain ends on the free volume, a possible influence of the molar mass on the morphology must also be considered. The morphology may in turn affect the free volume of the disordered backbone chain segments.

On the basis of data by n.m.r.[17], small-angle neutron scattering (SANS)[18] and thermal analysis[19], it has been suggested that two microphases exist in these polymers: (a) smectic layers of the mesogenic groups and (b) disordered microdomains essentially consisting of the backbone chains sandwiched between the mesomorphic layers. The two microphases are connected *via* the spacer groups, which decouple the main chain from the mesogens and allow it to attain an anisotropic 'random' chain configuration. Keller *et al.*[18] showed that the ratio of the radius of gyration perpendicular to the mesogenic group to that parallel to the mesogenic group of the polymer main chain in a smectic polymethacrylate with six methylene groups in the spacer was 4. The size of the radius of gyration parallel to the smectic group was found to be comparable with the layer spacing, indicating interpenetration between the smectic layers and the polymer chain[18]. Thus, phase separation may not be complete.

The glass transition is associated with the disordered phase. The plasticizing effect of the chain ends must indeed have an important influenced on T_g. However, as discussed above, the decoupling of the disordered main chain is only partial and the constraints imposed by the

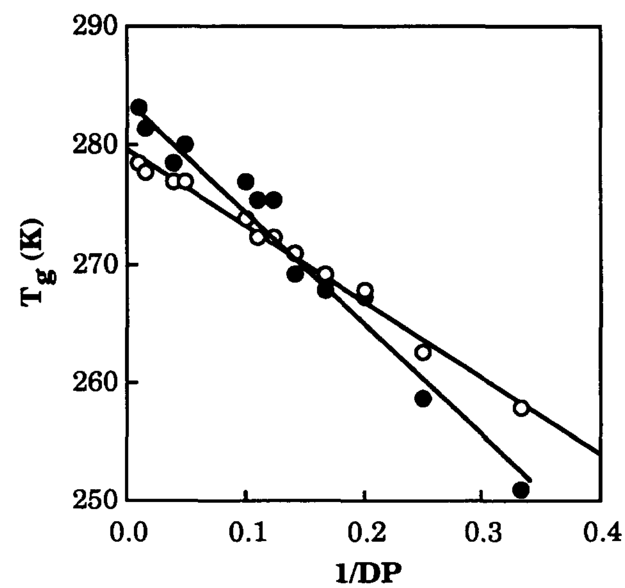

Figure 3 The glass transition temperature (T_g, recorded on cooling) of polysiloxanes as a function of reciprocal degree of polymerization (DP): (●) PS4; (○) PS6. Calculated from data of Stevens *et al.*[6]

smectic layers on the main chain may in some cases be substantial. The data on polysiloxanes[6,10] and polymethacrylates[11] indicate nevertheless that the degree of constraint imposed by the smectic layers is independent of molar mass for these polymers. For the poly(vinyl ether)s, on the other hand, it may be postulated that the statistical nature of the main chain means that the probability of the polymer chain penetrating a smectic layer increases with increasing length of the main chain. It is therefore assumed that phase separation was more complete in the low-molar-mass samples and that the constraints imposed by the smectic layers on the disordered phase increased with increasing molar mass. The reduction in free volume resulting from the reduction in concentration of chain ends in the case of the poly(vinyl ether)s is accompanied by additional interfacial constraints on the disordered layers in the high-molar-mass samples, resulting in the displayed non-linear trend in the T_g *versus* $(DP)^{-1}$ plot. This picture is consistent with the observation that the order of the smectic layers was higher in the low-molar-mass samples (*Figure 4*). The difference in curve shape (T_g *versus* $(DP)^{-1}$) may thus reflect this difference between the two groups of polymers, polysiloxanes/polymethacrylates on the one hand and poly(vinyl ether)s on the other, in molar-mass dependence of the smectic layer perfection.

Another important tendency in the T_g data, in agreement with earlier reported data[20,21], is that T_g increased progressively with decreasing length of the spacer group, again demonstrating the significance of the constraints imposed by the smectic layers on the disordered phase.

Isotropization

The most contradictory issue remaining unsolved is perhaps the molar-mass dependence of the heat of isotropization (Δh_i). *Figure 4* shows that Δh_i decreases with increasing *DP* in agreement with the following logarithmic function:

$$\Delta h_i = a_0 - a_1 \log DP \quad (1)$$

The scatter plot presented in *Figure 5* confirms that the deviation of the experimental data from the regression

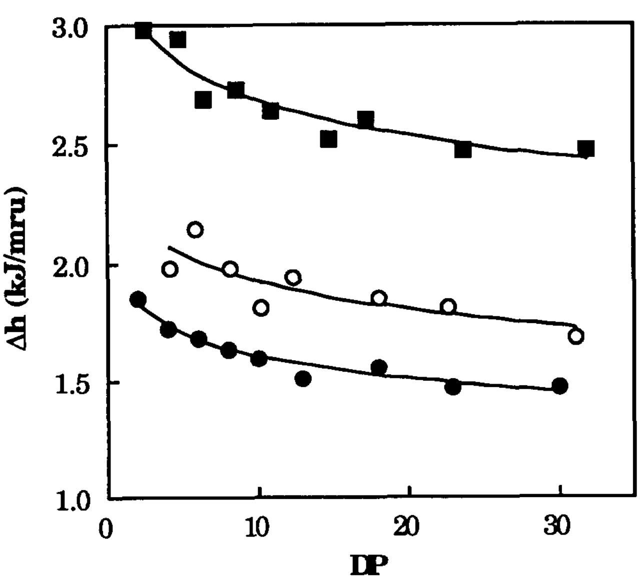

Figure 4 The heat of isotropization (Δh_i) of poly(vinyl ether)s plotted as a function of degree of polymerization (*DP*): (●) C7; (○) C8; (■) C9. The full curves were obtained by fitting equation (1)

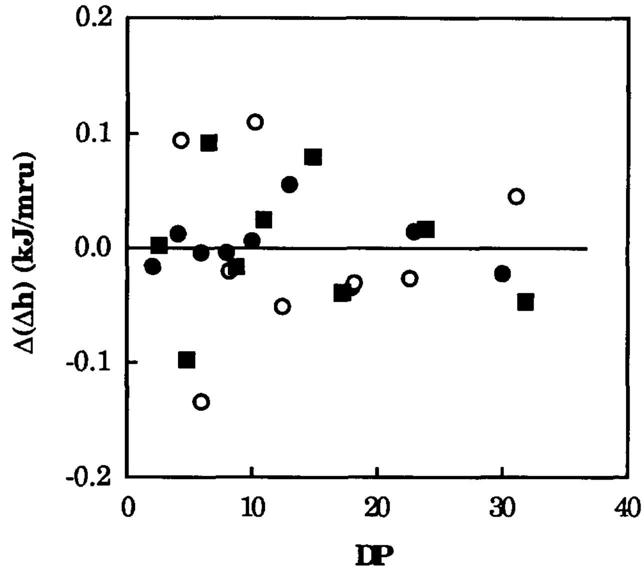

Figure 5 The difference between Δh_i (regression) and experimental Δh_i of poly(vinyl ether)s plotted as a function of degree of polymerization (*DP*): (●) C7; (○) C8; (■) C9

line is due to normal scatter in the data. The decrease in Δh_i with increasing molar mass may first seem anomalous. In fact, polysiloxanes and polymethacrylates (4-6-PMA) exhibited a molar-mass-independent Δh_i except for monomers and dimers of 4-6-PMA, which exhibited a lower Δh_i than their higher homologues[10,11]. It may be suggested that the packing and order of the smectic layers were not appreciably affected by molar mass in the latter cases, whereas for the poly(vinyl ether)s, longer backbone chains penetrated and disturbed the smectic layers causing less perfect smectic layers.

The length of the spacer group affected Δh_i more than did the molar mass (*Figure 4*). The longer spacer group decouples the smectic group more efficiently from the backbone and allows the former to attain higher perfection, which is reflected in the higher enthalpy change (Δh_i).

The relationship between temperature of isotropization for the poly(vinyl ether)s and *DP*, presented in *Figure 6*, resembles the pattern reported on samples with a broader molar-mass distribution[1-4]. The increase in T_i with increasing number of methylene carbons (*m*) in the spacer group evident in *Figure 6* parallels the increase in Δh_i with *m* (*Figure 4*). The increase in Δh when *m* increases from 7 to 9 is approximately 100%, which is significantly greater than the observed 5% increase in T_i. The increase in Δs_i with increasing *m* displayed in *Figure 9* is thus almost as great as the increase in Δh_i. The isotropization temperature data of the poly(vinyl ether)s were successfully adapted to the Broadhurst equation (equation (2); *Figure 6*):

$$T_i = T_i^\circ \frac{DP + a_2}{DP + a_3} \quad (a_2 \text{ and } a_3 \text{ are constants}) \quad (2)$$

The scatter plot shows only temporary errors in the data with a significant deviation from the fitted curve only for dimers (*Figure 7*). The behaviours of silane polymers and 4-6-PMA are very different (*Figure 8*). Equation (3) represents the data for these polymers in the studied molar-mass range:

$$T_i = T_i^\circ - \frac{a_4}{DP} \quad (a_4 \text{ is a constant}) \quad (3)$$

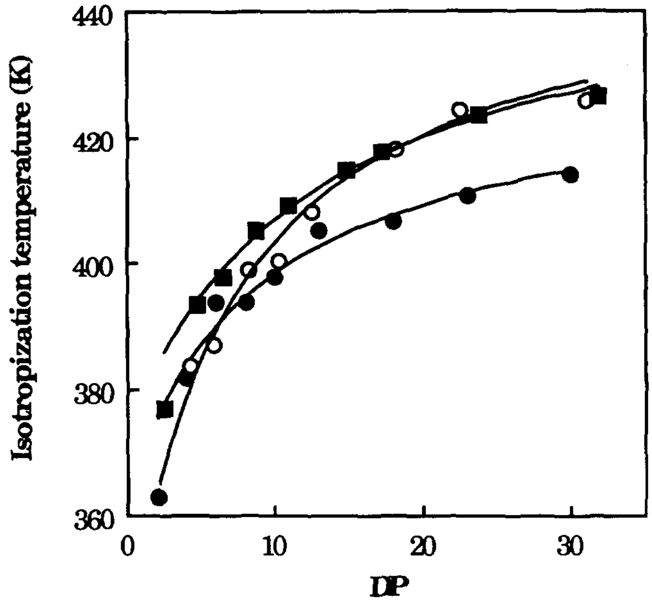

Figure 6 Temperature of isotropization (T_i, recorded by d.s.c. on heating) for poly(vinyl ether)s as a function of degree of polymerization (*DP*): (●) C7; (○) C8; (■) C9. The full curves were obtained by fitting equation (2)

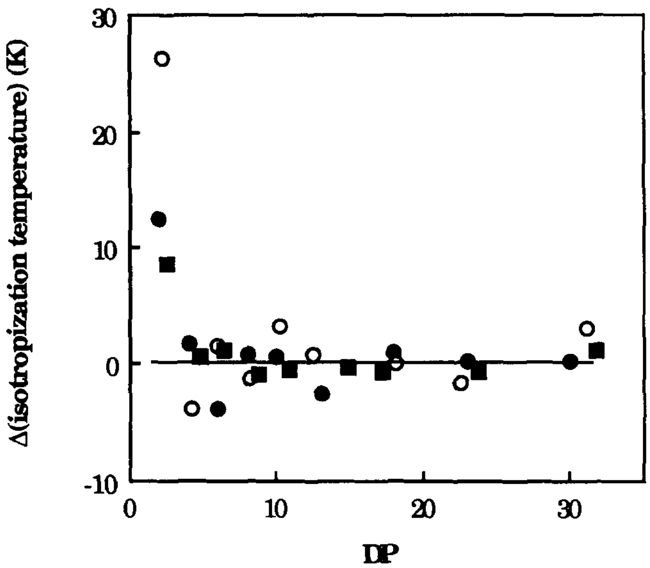

Figure 7 The difference between T_i (regression) and experimental T_i of poly(vinyl ether)s as a function of degree of polymerization (*DP*): (●) C7; (○) C8; (■(C9

Table 1 presents a summary of the fitted parameters of equations (1) and (2).

Equation (2) can be rewritten in the form:

$$T_i = \frac{T_i^\circ}{1 + (a_3 - a_2)/(DP + a_2)} \tag{4}$$

which is similar to equations derived for crystalline polymer melting[22].

The entropy of isotropization (Δs_i) was obtained by combining Δh_i and T_i data according to $\Delta s_i = \Delta h_i / T_i$. *Figure 9* shows that Δs_i decreases strongly with increasing molar mass and that the data are well represented by the fitted parameters a_1, a_2, a_3 and T_i in accordance with:

$$\Delta s_i = \frac{(a_0 - a_1 \log DP)(DP + a_3)}{T_i^\circ (DP + a_2)} \tag{5}$$

The consistency of the data within the two groups of polymers indicates that the trends are real and not due to stochastic variations in the data. The pronounced differences between poly(vinyl ether)s and the polysiloxanes illustrate the complexity of this problem.

Figures 10 and *11* present overviews of the thermodynamics of isotropization for poly(vinyl ether) C7 and a smectic polysiloxane. The experimental data cover only the low-molar-mass range. The poly(vinyl ether) exhibits

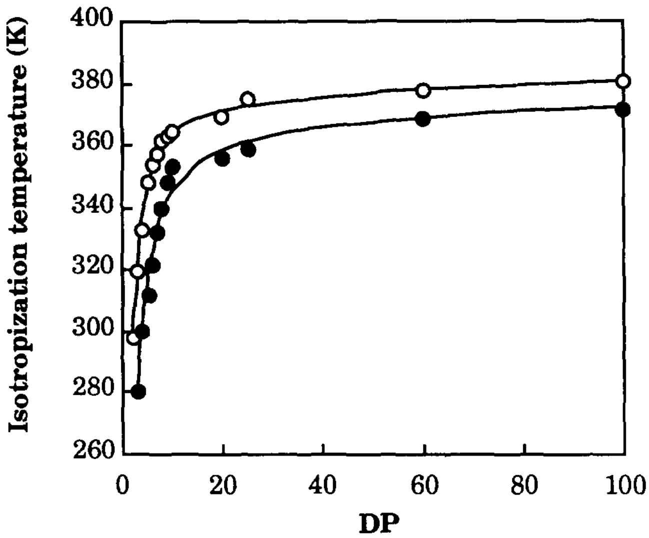

Figure 8 The isotropization temperature of polysiloxanes as a function of degree of polymerization (*DP*): (●) PS4; (○) PS6. Calculated from data of Stevens *et al.*[6]. The full curves were obtained by fitting equation (3)

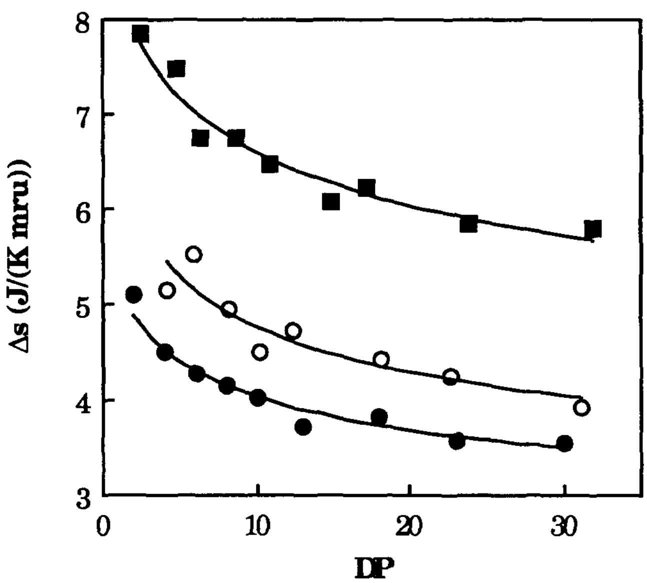

Figure 9 The entropy of isotropization (Δs_i) of poly(vinyl ether)s plotted as a function of degree of polymerization (*DP*): (●) C7; (○) C8; (■) C9. The full curves were obtained by fitting equation (5)

Table 1 Fitted parameters according to equations (1) and (2)

Polymer	a_0 (kJ mru^{-1})	a_1 (kJ mru^{-1})	a_2	a_3	T_i° (K)
C7	1.930	0.327	7.7265	9.1396	430
C8	2.313	0.392	5.5749	7.3829	450
C9	3.183	0.500	10.528	12.704	450

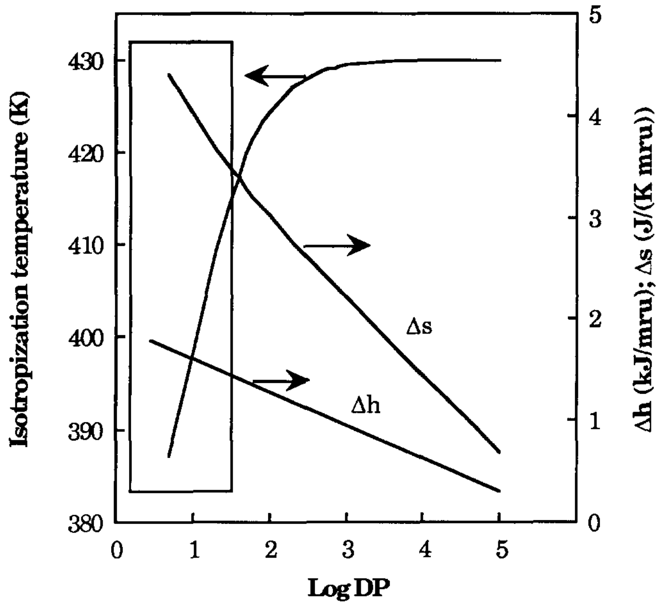

Figure 10 Molar-mass (DP) dependence of temperature, enthalpy and entropy of isotropization for poly(vinyl ether) C7. The window covering the experimental data is shown in the graph and the extrapolations were performed from best fits of equation (1), (2) and (5)

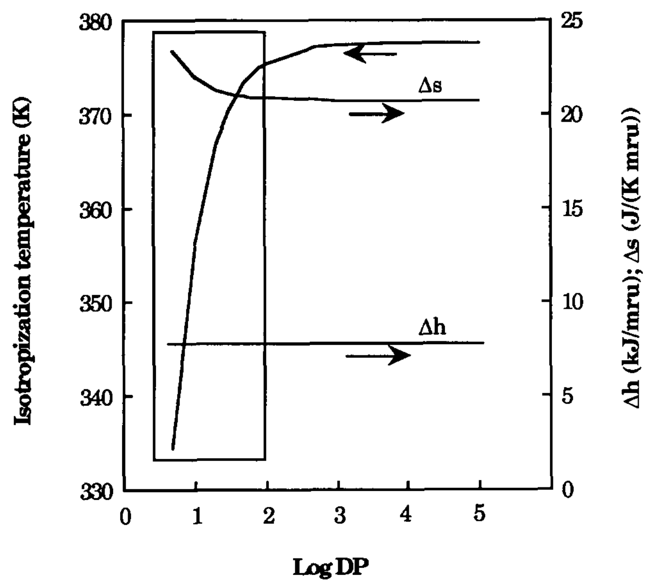

Figure 11 Molar-mass (DP) dependence of temperature, enthalpy and entropy of isotropization of a polysiloxane containing 2-[4-(2(*S*)-methyl-1-butoxy)phenyl]-5-(11-undecane-1-yl)-1,3,2-dioxaborinane. Calculated from data of Percec and Hahn[10]. The window covering the experimental data is shown in the graph and the extrapolations were performed from best fits of equations (1) and (3)

continuous and strong depressions in both Δs_i and Δh_i whereas the polysiloxane displays a constant Δh_i and a very moderately decreasing trend in Δs_i with increasing molar mass. The latter quantity reaches a constant value at high molar masses.

CONCLUSIONS

The side-chain smectic polymers considered in this paper exhibited two distinctly different types of thermal behaviour:

(1) Polysiloxanes and polymethacrylates possessed a heat of isotropization (Δh_i) independent of molar mass. The order within the smectic layers, deduced from measurements of heat of isotropization, of these polymers was not affected by molar mass. This conclusion indicates that phase separation between the mesogenic groups and the flexible parts was relatively complete and not appreciably affected by the molar mass. The decrease in the change in entropy on isotropization with increasing molar mass was moderate (10–20%) and is predicted to reach a constant value at DP levels between 100 and 1000. The molar-mass dependence of the isotropization temperature (T_i) for these polymers followed the simple equation $T_i = T_i^{\circ} - a_4/DP$, where a_4 is a constant. The disordered phase supposedly existing between the smectic layers behaved as a solitary entity, as was manifested in the simple molar-mass dependence of the glass transition temperature (T_g), i.e. $T_g \propto (DP)^{-1}$. The constraints imposed by the smectic layers were not affected by molar mass and the change in T_g was controlled by the concentration of chain ends, as observed for fully amorphous, flexible-chain polymers[16].

(2) Poly(vinyl ether)s exhibited a pronounced decrease in Δh_i with increasing molar mass, i.e. $\Delta h_i = a_0 - a_1 \log DP$, where a_0 and a_1 are constants. The order of the smectic layers decreased with increasing molar mass. An extension of the backbone chain reduced the perfection of the smectic layers. It is possible that the statistical nature of the main chain led to penetration of the smectic layer by the main chain and that this occurred more frequently in higher-molar-mass samples. The molar-mass dependence of T_i, although qualitatively similar to the behaviour of polysiloxanes or polymethacrylates, followed the Broadhurst equation $T_i = T_i^{\circ}(DP + a_2)/(DP + a_3)$. The decrease in Δs_i with increasing molar mass is due to lower perfection of the smectic layers and lower entropy of the isotropic phase. The continuous decrease in smectic layer perfection with increasing molar mass caused a continuous decrease in Δs_i with increasing M. The molar-mass dependence of the coupling between disordered and ordered phases led to a non-linear decrease in the glass transition temperature with increasing reciprocal molar mass. It may be suggested that a molar-mass increase led to both a reduction in concentration of chain ends and an additional penetration of the flexible backbone of the smectic layers and hence to the development of additional constraints.

ACKNOWLEDGEMENTS

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