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Phase Transitions in Narrow Molecular Mass Samples of Side-Chain Liquid Crystalline Polymers: Molecular Mass Dependence

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PHASE TRANSITIONS IN NARROW MOLECULAR MASS SAMPLES OF SIDE-CHAIN LIQUID-CRYSTALLINE POLYMERS: MOLECULAR MASS DEPENDENCE

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ABSTRACT

The molecular mass dependence of phase transitions in narrow molecular mass samples of smectic side-chain poly(vinyl ether)s is discussed in this paper with reference to earlier data by Stevens et al[6] and Percec et al[10,11] on narrow fractions of smectic side-chain polysiloxanes and polymethacrylates. The constant heat of isotropization (Δh_i) and the proportionality between glass temperature (T_g) and 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 on 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.

Key words: Side-chain smectic polymers, narrow molecular mass samples, phase transitions, molecular mass dependence

Abbreviated title: Phase transitions in liquid-crystalline polymers

INTRODUCTION

The molecular mass dependence of phase transitions appearing in liquid-crystalline polymers have been studied both in main-chain and side-chain polymers[1-14]. It is established that the glass temperature and the isotropization temperature increases strongly with molecular mass in the low molecular mass range. The increase in these quantities levels-off at higher molecular masses to finally approach a constant value. Under discussion is currently the molecular mass dependence of the heat of isotropization.

Comprehensive work reported on narrow molecular mass samples have been made 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 in this paper critically compared with recent data presented by Percec et al[12-14] on side-chain poly(vinyl ether)s prepared by living cationic polymerisation. The latter permits the production of samples of narrow molecular mass distribution. Different expressions for the molecular mass dependence of the glass temperature and isotropization temperature, and the enthalpy and entropy change associated with isotropization are tested and the results are discussed with reference to the prevailing views of the structure of these polymers. The effect of the length of the spacer group consisting of 7-9 methylene groups is also discussed.

RESULTS AND DISCUSSION

The synthesis and structure of the poly(vinyl ether)s considered in this paper have been presented in earlier papers by Percec et al[12-14]. The molecular structure of the narrow molecular mass poly(vinyl ethers) $\left(\frac{M_m}{M_n} = 1.1\right)$ is shown in Fig. 1. The number of methylene groups in the spacer unit is 7, 8 or 9. These polymers are correspondingly referred to as C7, C8 and C9 respectively. The degree of polymerization of the different polymers (oligomers) ranged from 2 to 32.

<u>FIGURE 1</u>

Phase transitions in these polymers were detected by differential scanning calorimetry (DSC) and polarized light microscopy at a scanning rate of 20 K(min)$^{-1}$ [12-14]. In this paper the molecular mass dependence of the glass transition and the isotropization is considered. 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] showed recently that high molecular 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 also after heating the samples above the clearing temperature. Samples of poly(vinyl ether) C7 (DP= 5 and 30) was therefore annealed in the smectic LC state but no significant changes in T_i and Δh_i were observed. Neither was the time spent above T_i of any significants for the recorded values of T_i or Δh_i. Thus, we can safely state that the smectic poly(vinyl ether)s here studied were in a near-equilibrium-state.

Glass transition

Figure 2 presents the glass temperature (T_g) as a function of the reciprocal degree of polymerization (DP) and it evident that the molecular mass dependence of T_g 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 molecular mass fractions of polysiloxanes with 4 (PS4) and 6 (PS6) methylene groups in the spacer. The LC phases involved were nematic for PS4 and smectic for PS6. Fig. 3 shows that T_g was proportional to 1/DP 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 revealing a linear trend in the T_g vs. $(DP)^{-1}$ plot which explains 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, we must also consider a possible influence of the molecular mass on the morphology. The latter may in turn affect the free volume of the disordered backbone chain segments.

Essentially on the basis of data by n.m.r.[17], small-angle neutron scattering (s.a.n.s)[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 in between the mesomorphic layers. The two microphases are connected via the spacer groups which decouples the main chain from the mesogens and allows 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 with the mesogenic group of the polymer main chain in a smectic polymethacrylate with 6 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 be one important influence on T_g. However, as discussed above the decoupling of the disordered main chain is only partial and the constraints imposed by the smectic layers on the main chain may in some cases be substantial. The data on polysiloxanes [6,10] and polymethacrylates[11] indicate however that the degree of constrain imposed by the smectic layers is for these polymers molecular mass independent. For the poly(vinyl ether)s, on the other hand, it may be postulated that the statistical nature of the main chain increases the probability for the polymer chain to penetrate a smectic layer with increasing length of the main chain. It is therefore expected that phase separation was more complete in the low molecular mass samples and that the constraints imposed by the smectic layers on the disordered phase increased with increasing molecular mass. The reduction in free volume resulting from the reduction in concentration of chain ends is for the poly(vinyl ether)s accompanied by the additional interfacial constraints on the disordered layers in the high molecular mass samples resulting in the displayed non-linear trend in the T_g vs. $(DP)^{-1}$ plot. This picture is consistent with the observation made that the perfection of the smectic layers was greater in the low molecular mass samples (Fig. 4). The difference in curve shape (T_g vs. $(DP)^{-1}$) may thus reflect this difference between the two groups of polymers, polysiloxanes and polymethacrylates vs. poly(vinyl ether)s, in molecular 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 molecular mass dependence of the heat of isotropization (Δh_i). Fig. 4 shows that Δh_i decreases with increasing DP in agreement with the following logarithmic function:

$$\Delta h_i = a_o - a_1 \log DP \qquad ...(1)$$

The scatter plot presented in Fig. 5 confirms that the deviation of the experimental data from the regression line is due to normal scatter in the data. The decrease in Δh_i with increasing molecular mass may first seem anomalous. In fact, polysiloxanes and polymethacrylates (4-6 PMA) exhibited a molecular mass-independent Δh_i except for monomers and dimers of 4-6 PMA which exhibited lower Δh_i than their higher homologs[10,11]. It may be suggested that the packing and order of the smectic layers was not affected appreciable by molecular mass in the latter cases, whereas for the poly(vinyl ethers) longer backbone chains penetrated and disturbed the smectic layers causing lower perfection of the smectic layers.

FIGURES 4,5

The length of the spacer group affected Δh_i more than the molecular mass (Fig. 4). The longer spacer group decouples the smectic group more efficiently from the backbone and allows the former to attain higher perfection reflected in the lower enthalpy.

FIGURES 6-8

TABLE 1

Fig. 6 presenting the temperature of isotropization for the poly(vinyl ether)s as a function of DP resemblance the pattern reported on samples with broader molecular mass distribution[1-4]. The increase in T_i with increasing number of methylene carbons (m) in the spacer group evident in Fig. 6 parallels the increase in Δh_i with m (Fig. 4). The increase in Δh on increasing m 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 Fig. 9 is thus almost as great 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 (eq. (2); Fig. 6). The scatter plot shows only temporary errors in the data with a significant deviation from the fitted curve only for dimers (Fig. 7). The behaviour of silane polymers and 4-6-PMA is very different (Fig.8). Eq. (3) represents the data of these polymers in the studied molecular mass range. Table 1 presents a summary of the fitted parameters of eqs. (1,2).

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

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

Eq. (2) can be rewritten in the form

$$T_i = \frac{T^{\circ}_i}{1 + \frac{a_3 - a_2}{DP+a_2}} \qquad ...(4)$$

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 $\Delta s_i = \frac{\Delta h_i}{T_i}$. Fig. 9 shows that Δs_i decreases strongly with increasing molecular mass and that the data is well represented from the fitted parameters a_1, a_2, a_3 and T_i in accordance to eq. (5):

$$\Delta s_i = \frac{(a_0 - a_1 \log DP)(DP+a_3)}{T^\circ_i(DP+a_2)} \qquad ...(5)$$

FIGURE 9

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

FIGURES 10,11

Figs. 10 and 11 present overviews of the thermodynamics of isotropization for poly(vinyl ether) C7 and a smectic polysiloxane. The experimental data covers only the low molecular mass range. The poly(vinyl ether)s exhibit continuous and strong depressions in both Δs_i and Δh_i whereas the other polymers display constant Δh_i and a very moderately decreasing trend in Δs_i with increasing molecular mass. The latter quantity reaches at high molecular masses a constant value.

CONCLUSIONS

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

(1) Polysiloxanes and polymethacrylates possessed a molecular mass independent heat of isotropization (Δh_i). The order within the smectic

layers of these polymers was not affected by molecular mass. This conclusion point in the direction that phase separation between the mesogenic groups and the flexible parts was relatively complete and not appreciably affected by molecular mass. The decrease in change in entropy on isotropization with increasing molecular mass was moderate (10-20%) and is predicted to reach a constant value at DP levels between 100 and 1000. The molecular mass dependence of the isotropization temperature (T_i) for these polymers followed the simple equation $T_i = T^{\circ}_i - \frac{a_2}{DP}$ (a_2 is a constant). The disordered phase supposedly existing between the smectic layers behaved as a solitary entity as was manifested in the simple molecular mass (M) dependence of the glass temperature (T_g), i.e. $T_g \alpha \frac{1}{M}$. The constraints imposed by the smectic layers were not affected by molecular mass and the changes in T_g was controlled by the concentration of chain ends as have been observed for fully amorphous, flexible-chain polymers[16].

(2) Poly(vinyl ether)s exhibited a pronounced decrease in Δh_i with increasing molecular mass, i.e. $\Delta h_i = a_o - a_1 \log DP$ (a_o and a_1 are constants). The order of the smectic layers decreased with increasing molecular 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 lead to penetration of the smectic layer by the main chain and that these occasions occurred more frequently in higher molecular mass samples. The molecular mass dependence of T_i although qualitatively similar to the behaviour of polysiloxanes or polymethacrylates followed the Broadhurst equation ($T_i = T^{\circ}_i \frac{DP + a_2}{DP + a_3}$). The decrease in Δs_i with increasing molecular 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 molecular mass caused a continuous decrease in Δs_i with increasing M. The molecular mass dependence of the coupling between disordered and ordered phases lead to that the glass temperature decreased in a non-linear way with increasing reciprocal molecular mass. It may be suggested that a molecular mass increase lead to both a reduction in concentration of chain ends as well as additional penetration of the flexible backbone of the smectic layers and hence the formation of additional constrains.

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Table 1. Fitted parameters according to eqs. (1,2)

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

LEGENDS TO FIGURES

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

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

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

Figure 4. The heat of isotropization (Δh_i) of poly(vinyl ether)s plotted as a function of degree of polymerisation (DP):● C7;○ C8;■ C9. The solid lines were obtained by fitting eq. (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.

Figure 6. Temperature of isotropization (T_i, recorded by DSC on heating) for poly(vinyl ether)s as a function of degree of polymerization (DP): ● C7;○ C8;■ C9. The solid lines were obtained by fitting eq. (2).

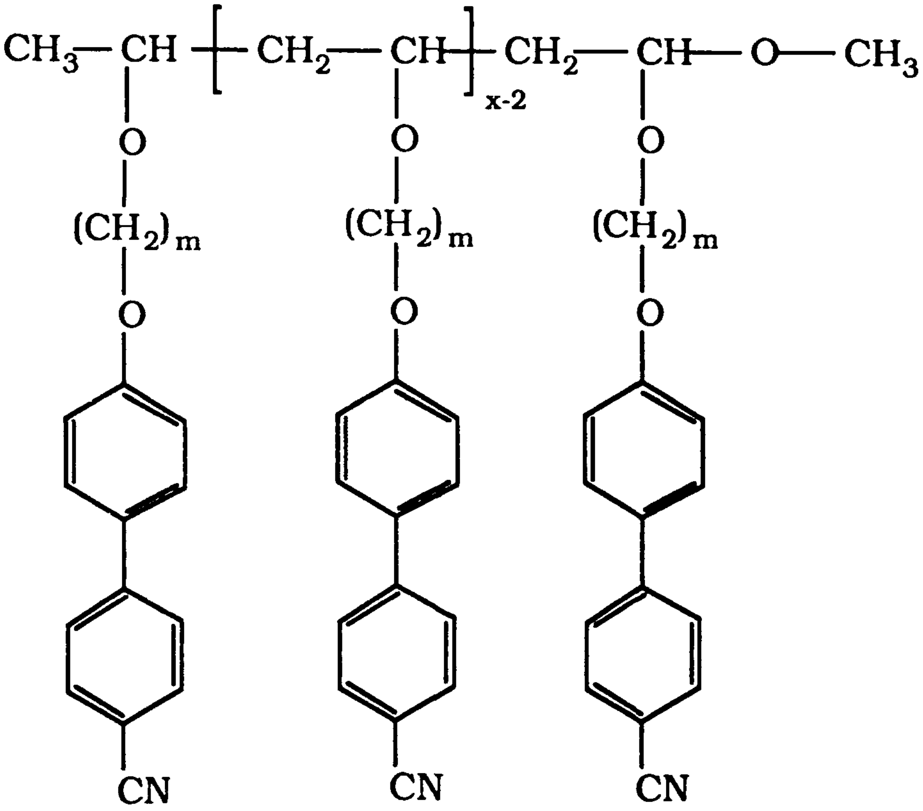
Figure 7. The difference between T_i (regression) and experimental T_i of poly(vinyl ether)s as a function of degree of polymerization (DP): ● C7;○ C8;■ C9.

Figure 8. The isotropization temperature of polysiloxanes PS4 and PS6 as a function of reciprocal degree of polymerisation (DP): ● PS4; ○ PS6. Calculated from data of Stevens et al[6]. The solid lines were obtained by fitting eq. (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 solid lines were obtained by fitting eq. (5).

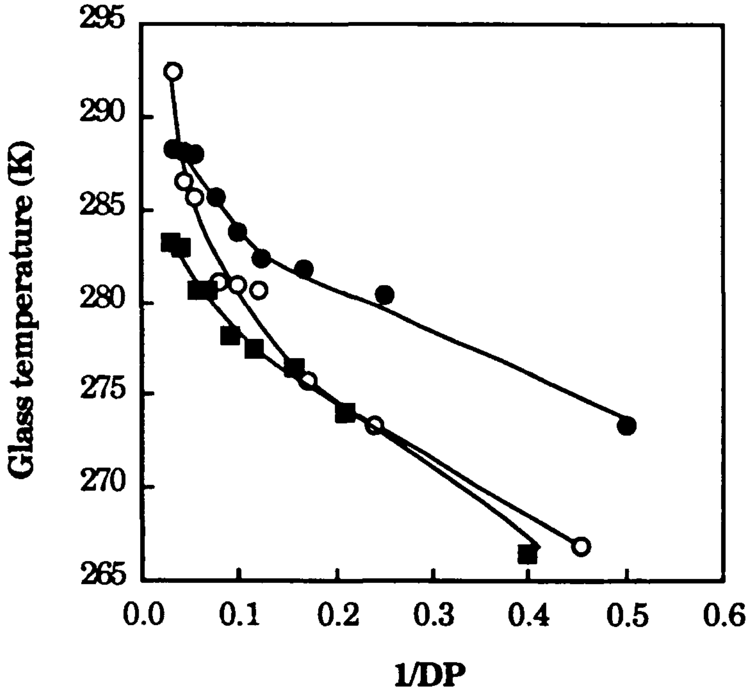
Figure 10. Molecular mass (DP) dependence of temperature, enthalpy and entropy of isotropization for poly(vinyl ether) C7. The window covering the experimental data is shown in the graph and the extrapolations were performed from best fits of eqs. (1,2,5).

Figure 11. Molecular mass (DP) dependence of temperature, enthalpy and entropy of isotropization of a polysiloxane containing 2-[4-(2(S)-methyl-1-butoxy)phenyl]-5-(11-undecan-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 eqs. (1,3).



m =7,8 or 9

Figure 1. Gedde et al



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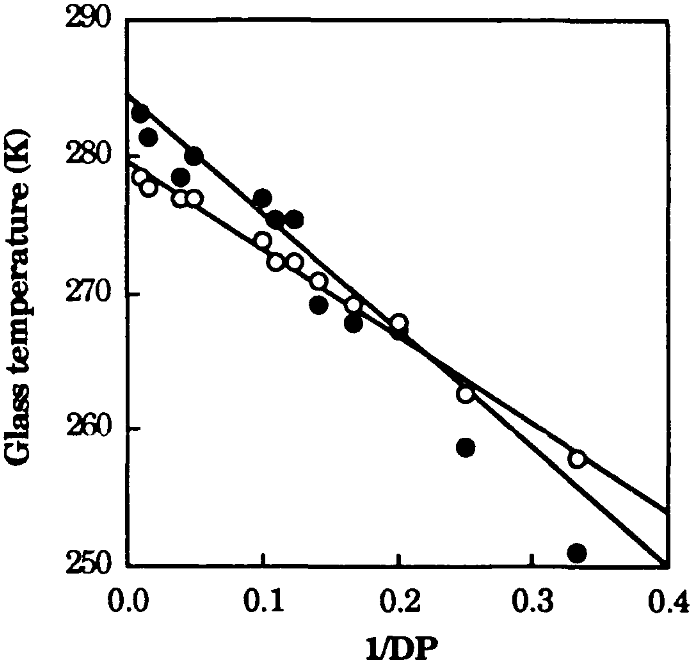

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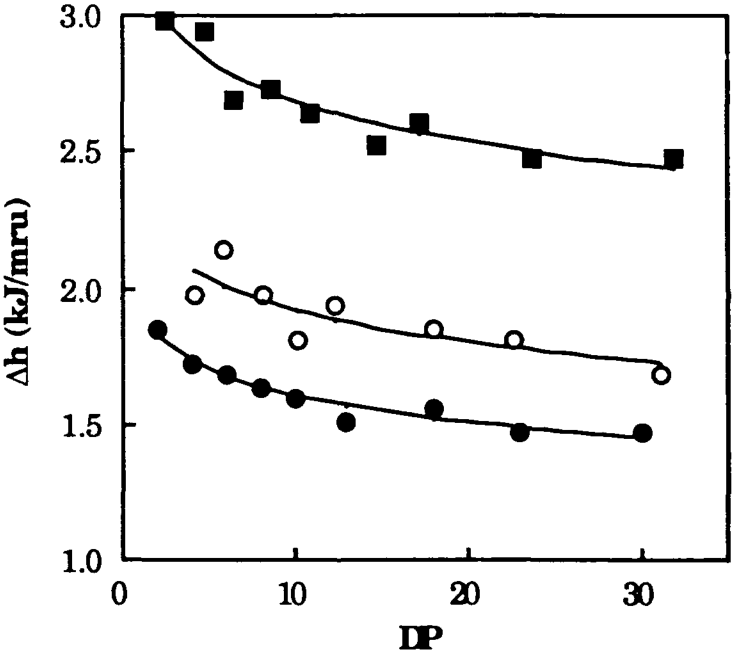

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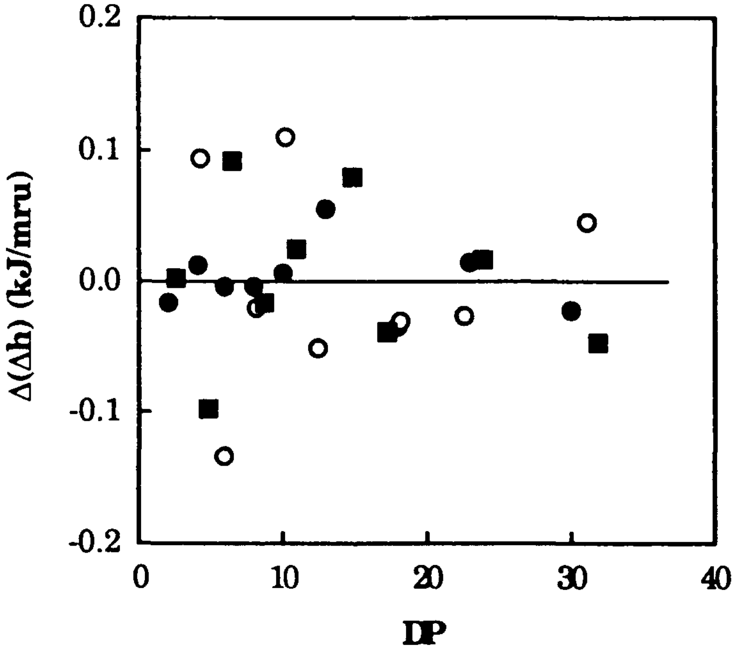

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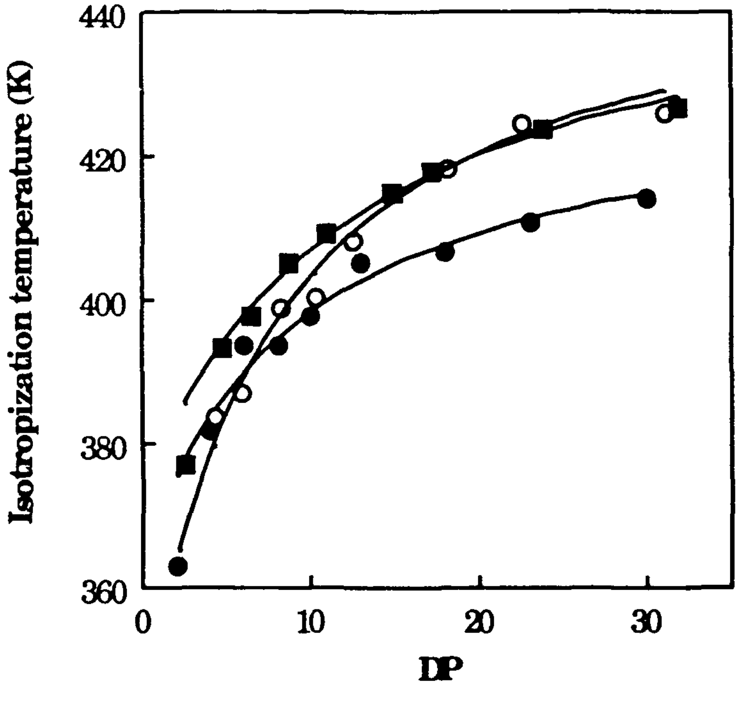

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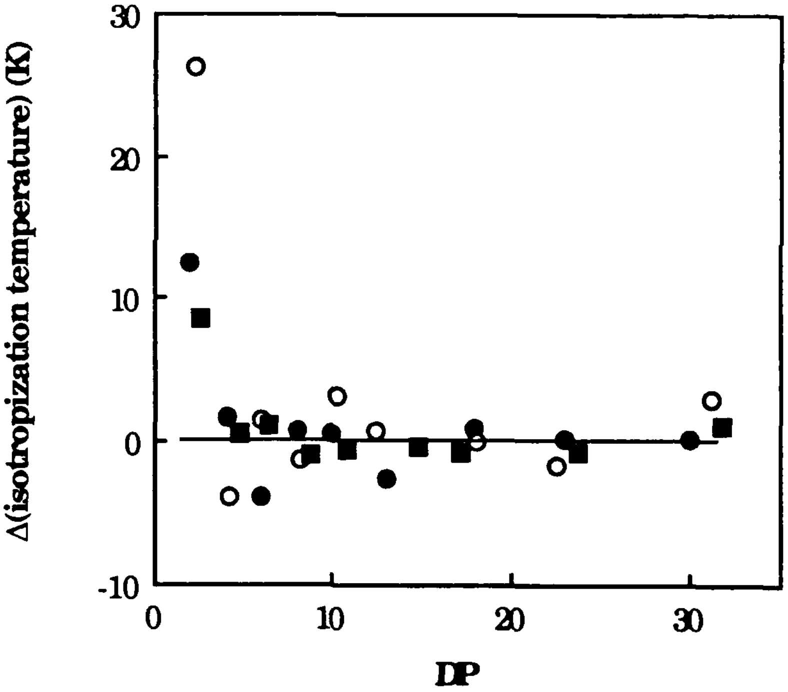

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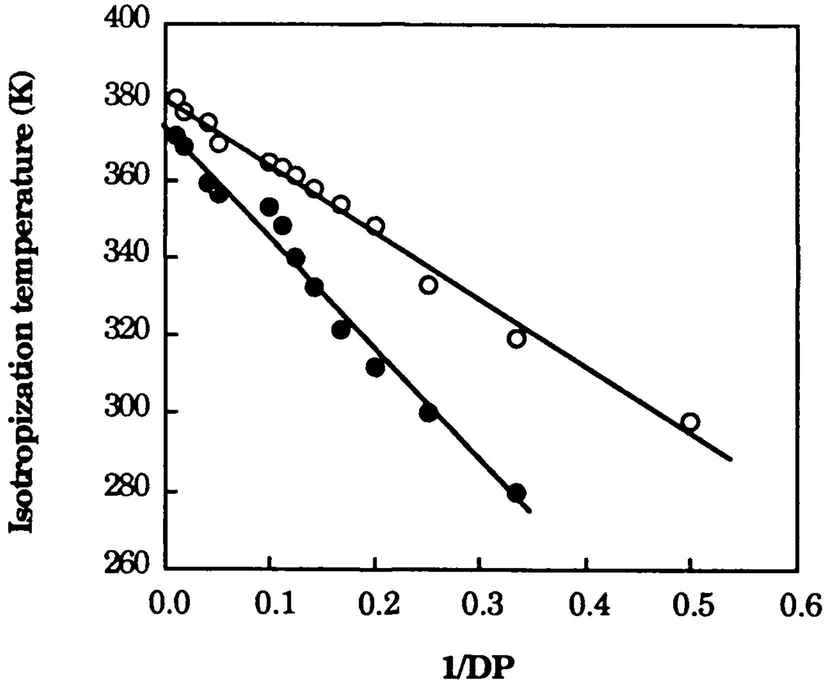

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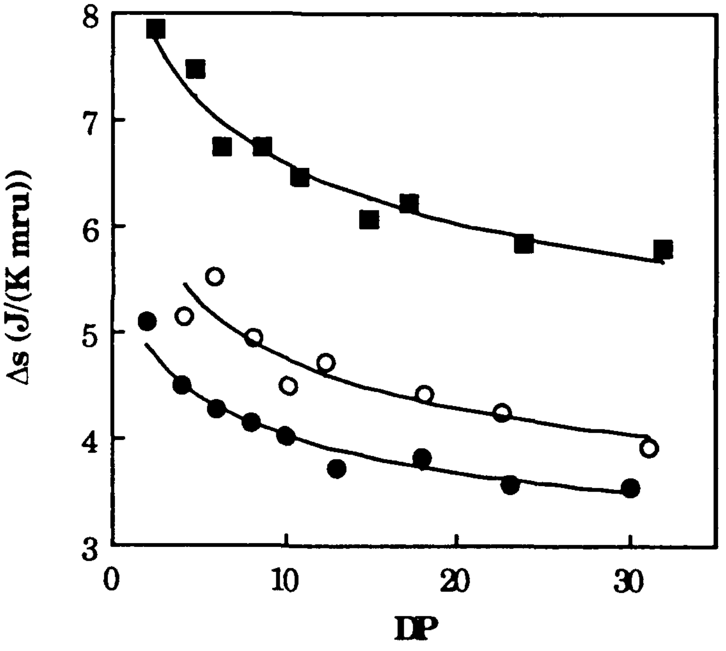

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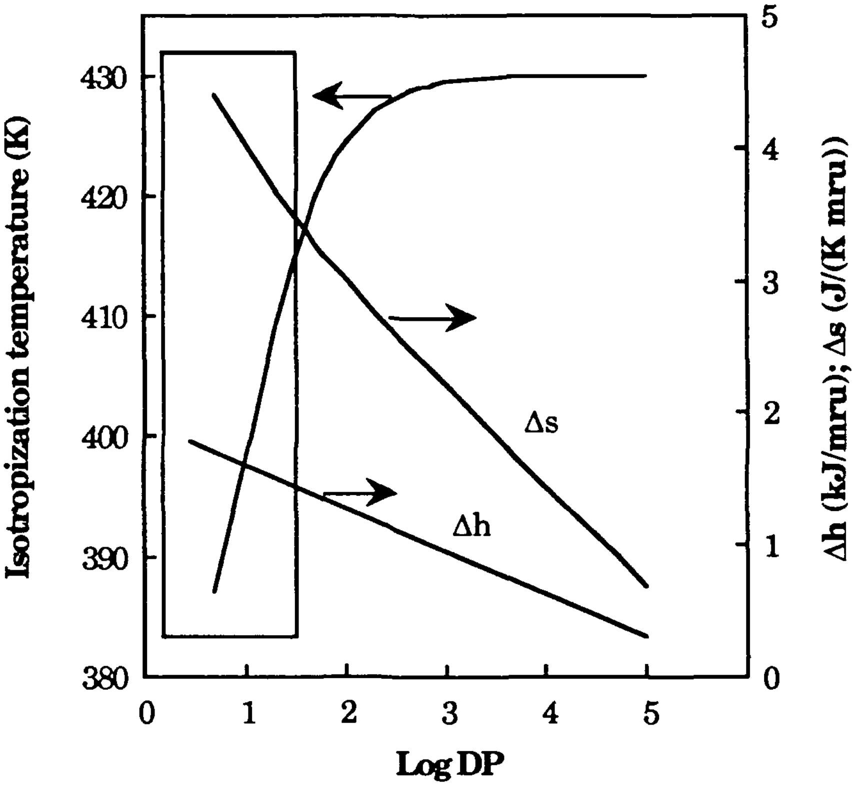

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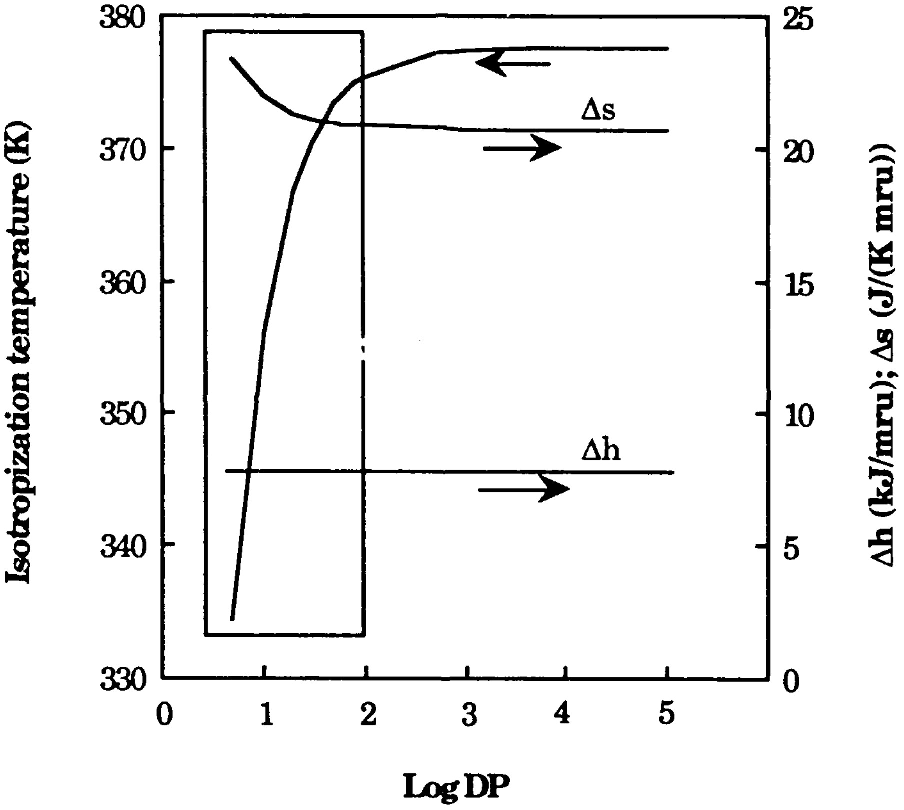

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