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Thermal and biphasic behaviour of a side-chain smectic polyacrylate [1]

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Abstract

The thermal and biphasic behaviour is reported for a side-chain smectic polyacrylate having a number average molecular weight of 59 000 g mol^{-1} and a first polydispersity index of 1.9. Evidence is provided for the existence of smectic Ad and smectic A1 mesophases, the former being enantiotropic and the latter monotropic. The biphasic behaviour was studied by DSC by annealing the polymer inside the apparent biphasic gap associated with the smectic Ad–isotropic transition. A biphasic temperature range in which isotropic and smectic Ad phases coexist at equilibrium was revealed, and the thermodynamic width of this biphasic region was estimated to be about 2.0 K.

INTRODUCTION

The thermodynamic and kinetic aspects of the isotropic–anisotropic biphase equilibria in thermotropic liquid crystalline polymers are presently under extensive investigation [1–14] from both the experimental and theoretical points of view. The occurrence of a thermodynamically stable biphasic region situated between the pure nematic phase and the pure isotropic phase has been described [7–12] in semi-flexible main-chain polymers, with rigid and flexible segments regularly alternating along the polymer backbone. This phase separation has been attributed to the effects of the molecular weight and the molecular weight distribution. A screening mechanism, possibly of entropic origin, in which the lower molar mass species segregate from the longer chain molecules, was invoked [12] as being the thermodynamic driving force toward segregation.

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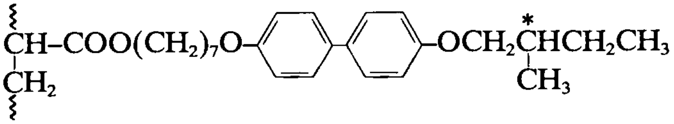
Comparatively very little work has been carried out on the thermodynamic and kinetic features of the isotropic–anisotropic biphasic equilibria in side-chain liquid crystalline polymers [13, 14]. In particular, we have studied [14] some side-chain nematic polymers in which nematic and isotropic phases coexisted and demixed giving rise to macroscopically segregated phases that subsequently underwent different thermal transitions. To gain a better insight into the molecular and structural factors leading to incompatibility in the melt and to assess the possibility of a more general incidence of phase segregation in liquid crystalline polymers, we have started to investigate the effects of the molecular weight and molecular weight distribution on the thermal and biphasic behaviour of the side-chain smectic polyacrylate **1**, based on the 4,4′-biphenylene mesogen spaced from the backbone by a heptamethylene spacer and substituted in the 4-position by an (S)-2-methylbutoxy group.



Polymer 1.

The present paper reports on a differential scanning calorimetric study of the liquid crystalline and biphasic behaviour of a polymer **1** sample with a number average molecular weight M_n of 59 000 g mol^{-1} and a first polydispersity index M_w/M_n of 1.9. The high thermal stability of the mesogenic unit combined with the relatively low transition temperatures should prevent the occurrence of microstructural rearrangements and degradation processes in the melt within the temperature range selected for the investigation.

EXPERIMENTAL

Polymer **1** was synthesised as described in detail in ref. 15. The number average molecular weight M_n and the first polydispersity index M_w/M_n were determined by size exclusion chromatography (SEC) in chloroform solutions using a 590 Waters chromatograph equipped with a Shodex KF-804 column. Thermal transitions were recorded by differential scanning calorimetry (Perkin-Elmer DSC-7) at a scanning rate of 10 K min^{-1} under dry nitrogen flow. Samples of 5–10 mg were employed. The temperature scale was calibrated against the melting temperatures of *n*-hexane, benzoic acid and indium. For the determination of the transition enthalpy, indium was used as a standard material. The transition temperatures were taken from the DSC traces as corresponding to the maximum/minimum of the enthalpic peaks (heating/cooling rate of

10 K min^{-1}) of samples that had been previously heated to the isotropic melt temperature (420 K) and then cooled down to room temperature.

Annealing procedure

The biphasic behaviour was studied by DSC according to a procedure previously described [14]. Polymer **1** was heated for 20 min at 420 K in the isotropic phase, cooled at 1 K min^{-1} to a selected temperature in the biphasic region, annealed at this temperature for 15 h and then rapidly cooled ($\approx$100 K min^{-1}) to room temperature. Finally, the sample was subjected to several heating/cooling cycles at 10 K min^{-1}. For each annealing temperature, a fresh polymer sample was employed.

RESULTS AND DISCUSSION

Liquid crystalline properties

Figure 1 reports the DSC heating and cooling curves of polymer **1** which appears to be practically amorphous at room temperature. On heating, a very broad endothermic transition is observed with a fairly sharp maximum at 407 K (Fig. 1B), whereas on cooling two exothermic peaks occur at 402 and 389 K (Fig. 1A) of comparable intensity ($\Delta H = 5.8$ and 6.3 kJ mol^{-1} respectively). Polarising microscopy observations and X-ray diffraction analysis indicated that the complex mesophase behaviour was in fact the result of the formation of smectic Ad and smectic A1 mesophases [15, 16], which occur within a few degrees of each other. Their individual transitions

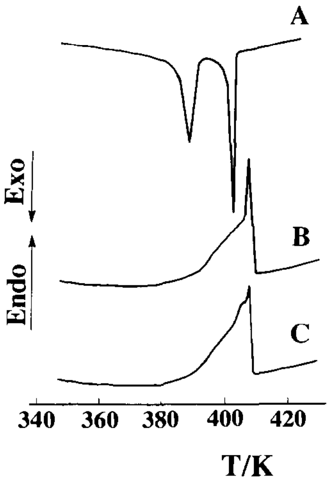


Fig. 1. DSC curves (10 K min^{-1}) for polymer **1**: (A) first cooling; (B) second heating; and (C) heating after annealing in the smectic Ad/isotropic biphase.

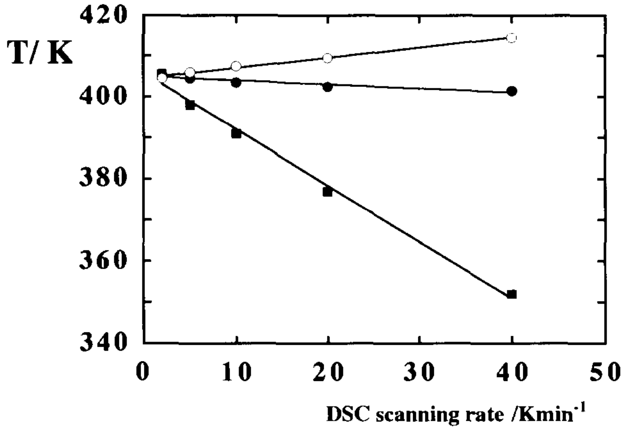


Fig. 2. Trends of the transition temperatures for polymer **1** as functions of the DSC scanning rate: ○, smectic Ad–isotropic (heating mode); ●, isotropic–smectic A1; and ■, smectic A1–smectic Ad (cooling mode).

were clearly observed on cooling, because of the different undercooling propensities of the two mesophases. The low-temperature mesophase remained frozen-in at room temperature. Several smectic A polymorphs are known to exist in liquid crystals [17] and polymer liquid crystals [18]. Specifically, the smectic A1 phase is characterised by a monolayer structure, whereas in the smectic Ad phase a bilayer structure exists with partially interdigitated mesogenic units.

The close proximity of the isotropic–smectic A1 and smectic A1–smectic Ad transitions prompted us to investigate the stability of both mesophases and the influence of the heating and cooling rates on the mesophase transition temperatures. Figure 2 illustrates the trends of the peak temperatures of the endothermic and exothermic transitions shown in Fig. 1, as functions of the DSC scanning rate. With lowering scanning rate, the peak temperature of the endothermic transition (heating mode) decreases, whereas those of the two exothermic transitions (cooling mode) increase in a linear fashion. However, the straight line relevant to the smectic A1–smectic Ad transition shows a more marked rising trend than that of the isotropic–smectic A1 transition, thus determining a crossover point at an estimated scanning rate of about 1 K min^{-1}. This shows that the smectic Ad mesophase is thermodynamically more stable than the smectic A1 mesophase and that the onset of the latter phase was kinetically controlled. Therefore, polymer **1** sample forms an enantiotropic smectic Ad mesophase and a monotropic smectic A1 mesophase, in contrast to the previously described [16] polymer **1** samples ($M_n = 20\,000$–$73\,000\ \mathrm{g\,mol^{-1}}$ and $M_w/M_n = 1.9$–2.7) for which both smectic mesophases were enantiotropic in character. This different behaviour highlights the critical role played by the molecular weight and molecular weight distribution in determining the incidence and stability of the liquid crystalline mesophases of side-chain polymers.

Biphasic behaviour

The biphasic behaviour of polymer **1** sample was studied by DSC according to the following thermal procedure. The sample was heated to the isotropic phase at 420 K, slowly cooled to the predetermined annealing temperature T_a, maintained at this temperature for 15 h and then rapidly quenched to room temperature. The annealing time of 15 h was found to yield the best macroscopic phase separation without any concomitant degradation phenomena. In the DSC heating curves, following annealing at various temperatures, the broad endothermic peak corresponding to the smectic Ad–isotropic transition appears to be composed of several overlapping components (Fig. 1C). Due to this extensive peak overlap, no conclusions could be drawn from the heating curves. In contrast, in the DSC curves recorded on cooling at a 10 K min^{-1} rate from the isotropic state attained by the annealed sample (Fig. 3), the isotropic–smectic A1 and smectic A1–smectic Ad transitions are composed of two well-resolved components (low-temperature component A, and high-temperature component B), whose peak temperatures and relative magnitudes depend on the annealing temperature. From this better resolution of the transition

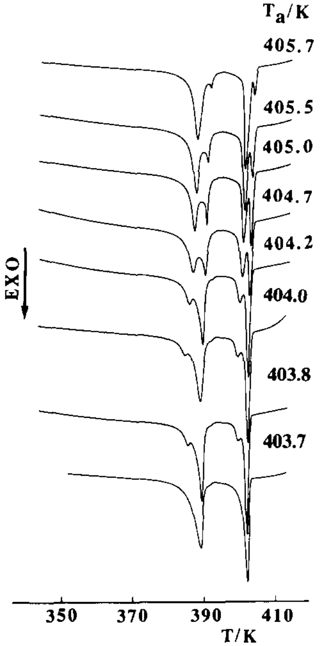


Fig. 3. DSC cooling curves (10 K min^{-1}) for polymer **1** following annealing at different temperatures T_a in the smectic Ad/isotropic biphase (annealing time = 15 h).

TABLE 1

Phase transition parameters[a] of the components A[b] and B[c] of polymer **1** after phase segregation in the smectic Ad/isotropic biphase

T_a[d]/K	$T_{i\text{-}SA1}$/K (B)	$\Delta H_{i\text{-}SA1}$/kJ mol^{-1} (B)	$T_{i\text{-}SA1}$/K (A)	$\Delta H_{i\text{-}SA1}$/kJ mol^{-1} (A)	$T_{SA1\text{-}SAd}$/K (B)	$\Delta H_{SA1\text{-}SAd}$/kJ mol^{-1} (B)	$T_{SA1\text{-}SAd}$/K (A)	$\Delta H_{SA1\text{-}SAd}$/kJ mol^{-1} (A)	F_i[e]	
									i–SA1	SA1–SAd
403.7	402.0	5.8	402.0	0.0	388.5	6.3	388.5	0.0	0.00	0.00
403.8	402.5	5.1	399.9	0.8	389.9	5.5	386.0	0.8	0.14	0.13
404.0	402.6	4.3	399.9	1.5	389.8	4.8	385.9	1.5	0.26	0.24
404.2	402.8	4.1	400.4	1.8	390.2	4.3	386.2	2.0	0.31	0.32
404.7	403.3	2.5	401.2	3.3	390.8	2.9	387.6	3.4	0.57	0.54
405.0	403.5	2.0	402.0	3.9	391.1	2.4	387.8	3.9	0.65	0.62
405.2	403.5	1.8	401.4	4.1	391.0	1.8	387.6	4.5	0.69	0.71
405.5	403.8	1.5	401.7	4.3	391.4	1.5	388.1	4.8	0.74	0.76
405.7	404.1	0.6	402.0	5.3	391.9	0.8	388.4	5.5	0.90	0.87
405.9	402.0	0.0	402.0	5.8	388.5	0.0	388.5	6.3	1.00	1.00

[a] Isotropic–smectic A1 (i–SA1) and smectic A1–smectic Ad (SA1–SAd) transition temperatures and enthalpies (T, ΔH). [b] Component A: formerly isotropic component in the biphase. [c] Component B: formerly smectic Ad component in the biphase. [d] T_a, annealing temperature in the biphasic region (annealing time, 15 h). [e] F_i, fraction of isotropic component in the biphase, as evaluated from the ratio of the enthalpy of component A over the total enthalpy of the isotropic–smectic A1 transition (first column) or of the smectic A1–smectic Ad transition (second column).

peaks, the biphasic behaviour of polymer **1** was delineated by considering the cooling curves alone. The peak temperatures of the components A and B of the two transitions and the relevant areas, evaluated by peak deconvolution, are given in Table 1. The thermal evolution of the isotropic–smectic A1 transition signals closely parallels that of the smectic A1–smectic Ad transition signals. In fact, for both phase transitions, the area of the higher temperature component increases gradually with decreasing T_a. In addition, the peak temperatures of both components of the two transitions increase regularly with increasing annealing temperature (Fig. 4). This dual behaviour at the isotropic–smectic A1 and smectic A1–smectic Ad transitions is attributed [12, 14] to the occurrence of two distinct transitions due to two polymeric fractions with different molecular weights which had segregated during annealing inside the smectic Ad/isotropic biphasic region. The increase in the transition temperatures with increasing T_a reflects the increase in the average molecular weight of the two segregated polymer fractions and indicates that the biphase fractionation process is accompanied by a substantial partition according to molecular weight. By this mechanism the longer chain molecules are selectively retained in the smectic Ad mesophase (component B) and shorter chain molecules are preferentially incorporated into the isotropic phase (component A). The weight fraction F_i of the isotropic component in the smectic Ad/isotropic biphasic region was also evaluated as the ratio of the relevant enthalpy change over the total transition enthalpy (Table 1). It increases monotonically from 0 to 1 with increasing annealing temperature in the range 403.7–405.9 K (Fig. 4). Accordingly, the thermodynamic width

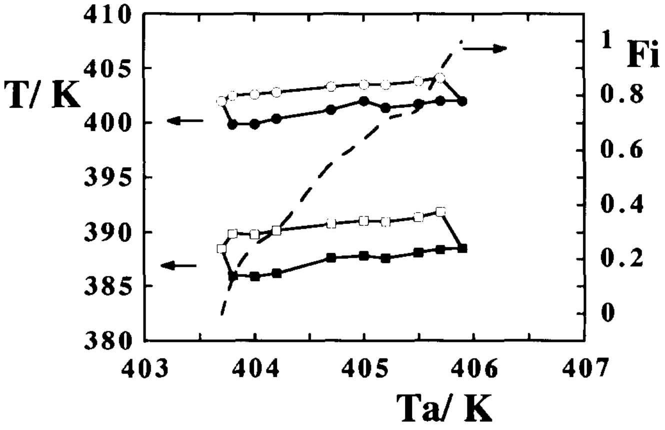


Fig. 4. Trends of the isotropic–smectic A1 (○, ●) and smectic A1–smectic Ad (□, ■) transition temperatures for component A (full symbols) and component B (open symbols) of polymer **1** after segregation in the biphase, and of the fraction of the isotropic component F_i in the smectic Ad/isotropic biphase (broken curve) as functions of the annealing temperature T_a (annealing time = 15 h).

of this biphasic region is about 2.0 K. However, the narrow width of the biphasic region prevented a macroscopic segregation of the coexisting isotropic and smectic Ad phases, making it impossible to gain more quantitative information about the selectivity of this partitioning phenomenon.

CONCLUSIONS

Liquid crystalline polyacrylate **1** is characterised by the formation of a smectic Ad and a smectic A1 mesophase within a very narrow temperature range. The investigation into the transition temperature dependence on the DSC scanning rate allowed determination of the thermodynamic phase sequence and showed that the former phase is enantiotropic whereas the latter is monotropic.

A biphasic temperature range in which isotropic and smectic Ad phases coexist at equilibrium and segregate, was revealed. The two polymer **1** fractions that had demixed during annealing in the smectic Ad/isotropic biphase underwent afterwards distinct isotropic–smectic A1 and smectic A1–smectic Ad transitions. The thermodynamic width of this biphasic region was estimated to be about 2.0 K. The thermal evolution of the transition temperatures of both segregated components indicates that the biphase segregation is driven by partitioning according to the polymer molecular weight, in which the longer chain molecules are selectively retained in the smectic phase. We should like to stress that the observations of a biphasic gap separating the region of stability of the isotropic and smectic Ad mesophases suggest that the overall polymer chain configurations in these phases may differ substantially and reveal that the mesophase transitions of side-chain liquid crystalline polymers are not local-scale phenomena, but rather involve relaxation and equilibration extending over the entire polymer chain.

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