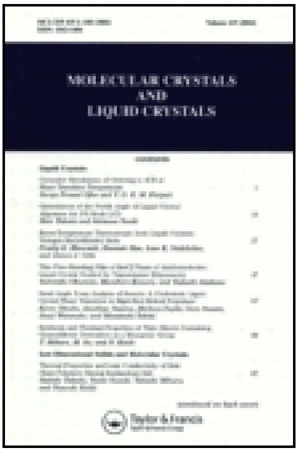

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The Nematic-Isotropic Phase Segregation in a Thermotropic Semiflexible Liquid Crystalline Polyester

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THE NEMATIC - ISOTROPIC PHASE SEGREGATION IN A THERMOTROPIC SEMIFLEXIBLE LIQUID CRYSTALLINE POLYESTER

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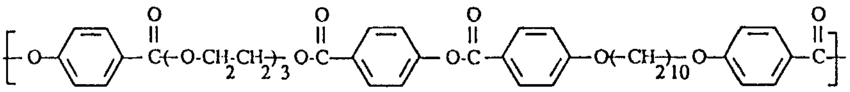
Abstract The isotropic - nematic biphasic segregation has been investigated in a thermotropic main chain polyester by differential scanning calorimetry analysis. The width of biphasic gap has been determined and related to the molecular parameters of the polymer.

Keywords: phase-segregation, differential scanning calorymetry, LC-polyester, main-chain, molecular weight

INTRODUCTION

The occurrence of a biphasic gap separating the region of stability of isotropic and nematic phases has been very recently reported for liquid crystalline polyesters, comprising rodlike and flexible units in alternating sequence in the chain backbone,[1-6] and for the first time in side chain liquid crystalline polymers[7]. The theoretical understanding of this phenomenon is at its very early stage and a comprehensive experimental work is still missing. It appears that the phase separation is promoted by chain length heterogeneity of the sample[8]. A substantial partitioning has been demonstrated of the components with higher molecular weight in the nematic phase, whereas the macromolecular species with smaller molecular weight tend to segregate in the isotropic phase[1-4,6]. The macroscopic separation occuring in the biphasic region may be at least in part retained in the solid state thus markedly influencing its overall morphology and its ultimate physico - mechanical properties.

With the aim of furthering insight into the molecular origin of this phenomenon, in this note we report on the thermal fractionation process inside the nematic - isotropic biphase of a thermotropic main - chain polymer I constituted by two oxybenzoate diads flanked alternatively by triethyleneglycol and decamethylene glycol flexible segments.



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The width of the biphasic gap and the fractionation features were determined under conditions approaching thermodynamic equilibrium. They will be compared to those previously detected[5] for another sample of polymer I characterized by a different molecular weight and molecular weight distribution.

EXPERIMENTAL

Polymer I was synthesized and characterized as described in detail in ref.9. The number - average molecular weight ($\overline{Mn}$) and the first polydispersity index ($\overline{Mw}$ / $\overline{Mn}$) were determined by size exclusion chromatography (SEC) using the universal calibration method and resulted 15400 Da and 1.97 respectivelty. No traces of oligomers were present in the SEC profiles. Thermal analyses were carried out under dry nitrogen flow with a Perkin Elmer DSC-7 instrument equipped with a 3700 data station using Delta standard program on polymer samples of 5 - 10 mg at a scanning rate of 10 K/min. Indium was used for calibration. The maximum in DSC enthalpic peaks was taken as the phase transition temperature. For each annealing temperature (Ta) a fresh polymer sample was employed and the DSC traces were normalized to 1 mg sample.

RESULTS AND DISCUSSION

The thermal properties of polymer I were investigated by differential scanning calorimetry (DSC). In the DSC heating curves, following annealing by cooling at 10 K/min from the isotropic melt, polymer I showed a weak cold - crystallization exotherm at about 385 K followed by two endothermic transitions at 413 K and 427 K. In accordance with a previous study[9], these latter transitions were attributed to the melting transition and to the nematic - isotropic transition respectively.

The isotropization enthalpy and entropy were 7.4 kJ/mol and 17.3 J/molK respectively. These transitional parameters are different from those previously reported[6,9] and consistent with the differences in molecular weight and molecular weight distribution among the samples obtained in three different preparations. The biphasic behaviour of polymer I was investigated by DSC according to the following thermal procedure. The sample, after slow cooling from 443 K in the isotropic phase down to the predetermined annealing temperature (Ta) within the biphasic zone of the nematic - isotropic transition, was annealed for 15 hours and then quenched to room temperature. The sample was then subjected to one heating / cooling cycle. The DSC heating and cooling curves of polymer I following annealing at various temperatures are illustrated in Figs. 1 and 2 respectively.

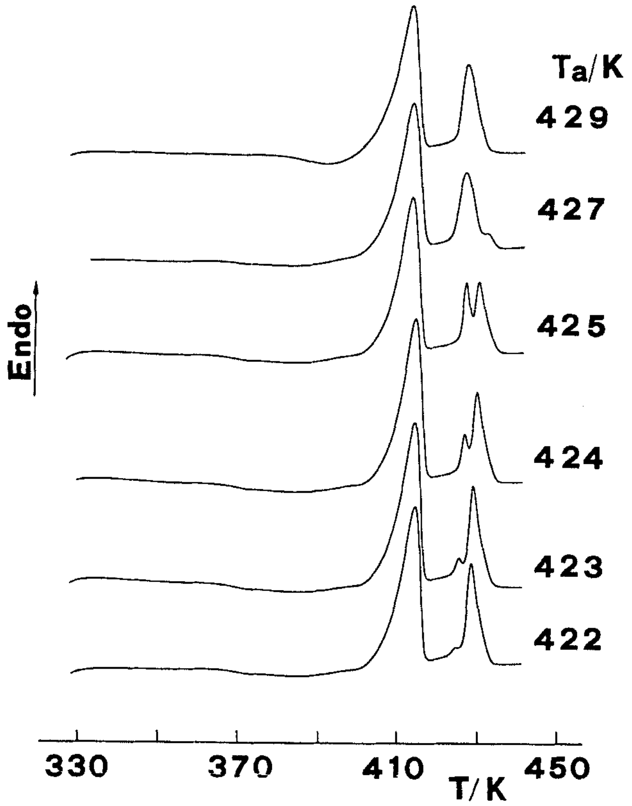

FIGURE 1 DSC heating curves (10 K/min) following annealing at different temperatures Ta in the biphase (annealing time = 15 hours)

On heating (Fig. 1) the endotherm associated to melting is not affected by thermal treatment, whereas the nematic - isotropic transition profile consists of two distinct endotherms, when the annealing temperature ranged from 429 K to 422 K. On cooling the thermal evolution of the isotropic - nematic transition closely resembles that found in the corresponding DSC heating curves (Fig. 2).

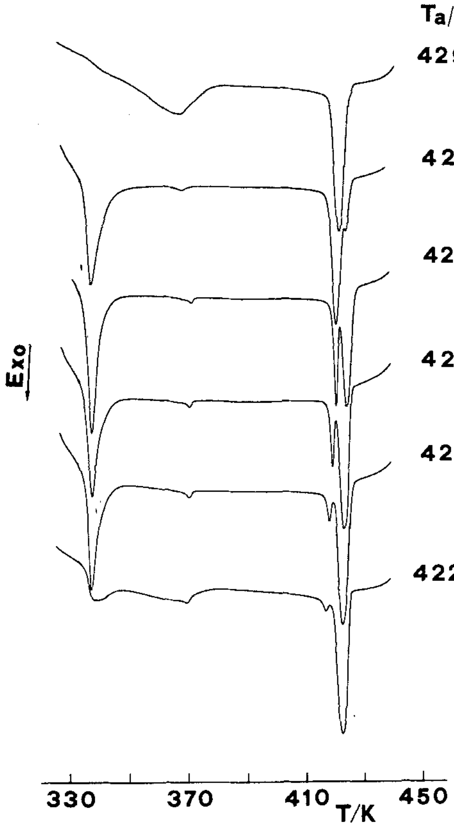

FIGURE 2 DSC cooling curves (10 K/min) following annealing at different temperatures Ta in the biphase (annealing time = 15 hours)

In addition, two distinct crystallization exotherms at about 335 K and 366 K are clearly detectable when the annealing temperature ranged from 429 to 422 K.

The peak temperatures of the nematic-isotropic endotherms in the DSC heating curves and their intesities are collected in Tab. 1. The peak temperatures of both nematic - isotropic transition endotherms regulary increase with increasing annealing temperature. The area of the lower temperature endothermic component increases with annealing temperature, whereas the area of the higher temperature endothermic component decreases. This dual isotropization behaviour reflects the occurrence of a macroscopic separation during annealing in the biphasic region leading to an isotropic phase (fraction A) and a nematic phase (fraction B) coexisting at equilibrium. Once demixed the two fractions undergo independent transitions.

TABLE 1 Isotropization thermodynamic parameters of fractions A[a] and B[b] of polymer I

Ta[c] (K)	T_{iA} (K)	T_i^B (K)	ΔS_{iA} (J/molK)	ΔS_{iB} (J/molK)
422	425.0	428.5	0.9	16.4
423	425.5	429.0	1.5	15.7
424	426.5	430.0	4.3	13.0
425	427.5	431.0	7.4	9.9
427	428.0	433.5	15.4	1.9
429	428.5	436.0	16.4	0.9

[a] A:formerly isotropic component in the biphase
[b] B:formerly nematic component in the biphase
[c] Annealing temperature in the biphasic region of the isotropic - nematic transition (annealing time 15 h)

The difference between the peak temperatures of the isotropization components clearly indicates that the separation process is accompanied by a substantial partitioning of the various macromolecular species between the two phases, the higher molecular weight components being preferentially retained in the nematic phase. The above thermal procedure outlines the thermodynamic biphasic region associated to the nematic - isotropic transition which lays between 429 K and 422 K and accordingly the biphasic gap is 8 degrees.

From a phenomenological point of view, the biphasic behaviour of the present sample is very similar to that of a sample of the same polymer I which was previously investigated[6] and characterized by $\overline{Mn}$ = 10100 Da and $\overline{Mw}$ / $\overline{Mn}$ = 2.34.

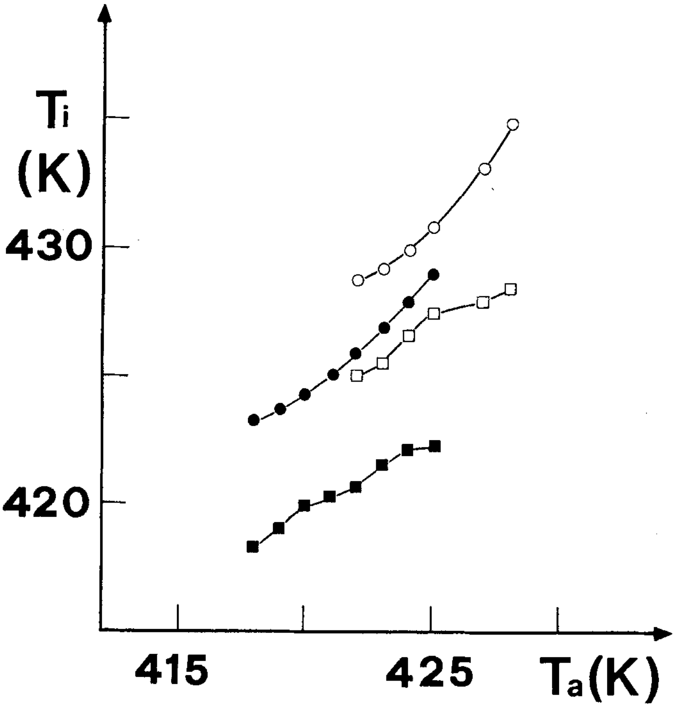

Figure 3 Nematic-isotropic transition temperatures for formerly nematic component in the biphase (●, ○) and formerly isotropic component in the biphase (■, □) for samples of polymer I with $\overline{Mn}$=10100 Da(full symbols, from ref.6) and $\overline{Mn}$=15400 Da (open symbols, this work) as function of the annealing temperature Ta.

For the latter polymer sample the biphasic region associated to the nematic - isotropic phase transition ranged from 418 to 426 K with a biphasic gap of 9 degrees.

However the location of biphasic region is significantly different in the two cases with a shift toward higher temperature values for the present higher molecular weight polymer sample (Fig. 3). In addition, the average difference between the peak temperatures of the nematic - isotropic transition, which is related to the difference between the average molecular weights of the demixed components, is greater for the polymer sample with the wider molar mass distribution.

These results suggest that while the location of the nematic-isotropic biphasic region depends on the number average molecular weight of the sample, the biphasic width and the difference between the transitional parameters of the biphase - demixed fractions, are mainly correlated to the characteristics of the molar mass distribution.

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