Biphasic Behavior of a Thermotropic Polymesomorphic Polyester. 2. Temperature Evolution of Phase Separation

Maria Cristina Righetti

Centro di Studio per la Fisica delle Macromolecole, CNR, Via Selmi 2, 40126 Bologna, Italy

Michele Laus*

Dipartimento di Scienze e Tecnologie Avanzate, Università del Piemonte Orientale "A. Avogadro", Corso Borsalino 54, 15100 Alessandria, Italy

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ABSTRACT: The temperature evolution of biphase segregation at the N−I as well as S_A−N and S_B−S_A transitions of a main chain polyester I was studied by annealing the sample inside the relevant biphasic gaps. The thermodynamic width of the mesophasic transitions were 2 °C for the N−I transition and 6 and 4 °C for the S_A−N and S_B−S_A transitions, respectively. The maximum efficiency of the biphase demixing, in terms of peak resolution, was found for the transitions at which the demixing was performed. It was suggested that the system lowers its free energy by selective redistribution of species of different molar masses between two different phases. The analysis of polyester I fractions with different molar masses and molar mass distributions showed that the location of the peaks moves to higher temperatures as the average molar mass increases. In addition, the width of the overall biphase segregation process was wider for the sample with the widest molar mass distribution, thus clearly indicating that the molar mass parameters are key factors in determining the overall biphase segregation phenomenology.

Introduction

The occurrence of a thermodynamically stable biphasic region located between the pure nematic phase and the pure isotropic phase has been described in semiflexible main chain copolymers with statistical distribution of rigid and flexible segments along the chain backbone.[1−7] The statistical fluctuations in the chain composition of these copolymers are supposed to produce a distribution of chain flexibilities, called polyflexibility, capable of promoting partitioning between the nematic and isotropic liquid phases which coexist over a range of temperatures. A substantial incorporation of the more rigid chains into the nematic mesophase is expected. Broad biphasic regions are usually detected in these systems.

In contrast, the nematic−isotropic biphasic behavior of main chain polymers with regular structure is ascribed[8−14] to the molar mass distribution of the samples which produces a distribution of persistence lengths. In fact, it was clearly demonstrated that the average molar mass values of the two biphase segregated components at the N−I transition are different, with the lower molar mass species being selectively incorporated into the isotropic phase.[13] In addition, to observe a nematic−isotropic biphase separation, the average molar mass of the sample should be fairly high and the mass distribution quite wide, so that the phase transition parameters of the individual species differ substantially.[14] The biphasic behavior of these polymers is usually observed in a somewhat narrower temperature range.

LC polymers with regular structure presenting smectic and nematic mesophases are of special interest for the present investigation because the comparison between the biphasic behavior at the nematic−isotropic as well as at the smectic−nematic or smectic−smectic transitions should allow the driving force toward microphase segregation to be better understood and the structural and molecular factors conducive to separation in the various LC phases, differing in their stability and degree of order, to be delineated. Accordingly, new aspects of the segregation phenomena can be highlighted by improving the knowledge of the thermodynamics of semiflexible chain molecules.

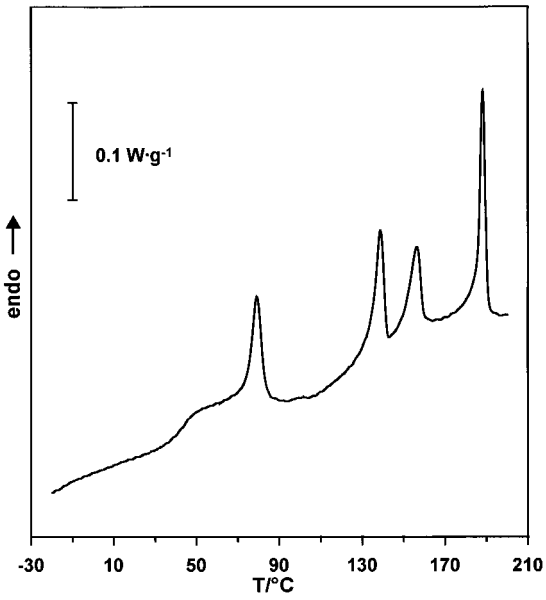

Figure 1. DSC heating curve (10 °C/min) for polymer **I** after thermal treatment at 60 °C for 24 h.

The time evolution of biphase segregation at the N−I as well as S_A−N and S_B−S_A transitions of a main chain polyester, containing a sequence of rigid anisometric units and two flexible spacer segments which regularly alternate along the polymer chain was recently studied[15]

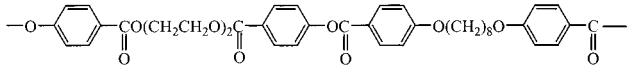

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Table 1. Molecular and Thermal Characterization Data[a]

sample	M_n	M_w/M_n	T_g (°C)	$T_{S_A-S_B}$ (°C)	$\Delta H_{S_A-S_B}$ (J·g^{-1})	T_{S_B-N} (°C)	ΔH_{S_A-N} (J·g^{-1})	T_{N-I} (°C)	ΔH_{N-I} (J·g^{-1})
unfractioned polymer **I**	18 000	1.76	39	136.8	4.0	155.5	3.5	186.5	5.6
fraction 1	23 000	1.44	40	141.3	4.1	159.2	3.8	187.6	5.7
fraction 2	16 300	1.62	40	138.6	4.1	156.5	3.8	186.9	5.7
fraction 3	11 200	1.86	39	134.8	3.5	152.9	3.0	185.6	5.5

[a] The thermal properties are obtained after rapid cooling from the isotropic phase.

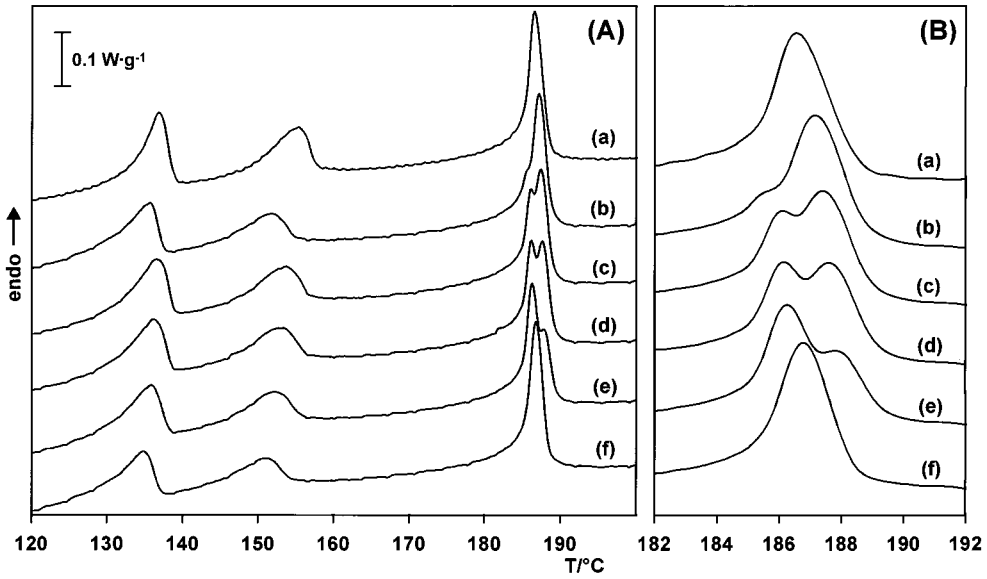

Figure 2. (A) DSC heating curves (10 °C/min) for polymer **I** after annealing for 15 h (annealing temperatures: (b) 184.3, (c) 185, (d) 185.3, (e) 185.7, and (f) 187 °C) and successive cooling to 50 °C. Curve a is obtained after rapid cooling from the isotropic phase. (B) Enlargement of the DSC scans in the temperature range 182−192 °C.

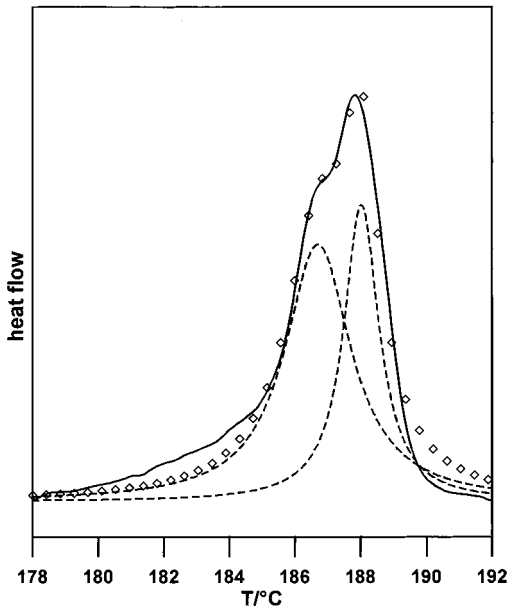

Figure 3. Example of the nonlinear fitting for the DSC curve portion associated with the N−I transition: (solid line) experimental curve; (dashed lines) resolved curves; (□) sum of the resolved curves.

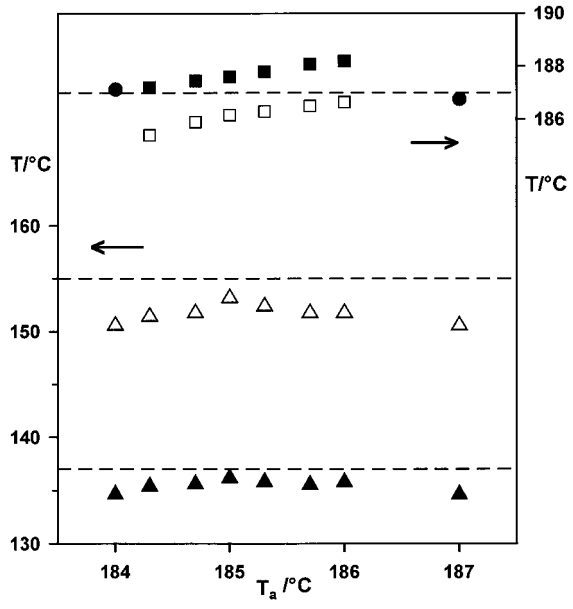

Figure 4. Temperatures of the transitions S_B-S_A (▲), S_A-N (△), and N−I (●, nonsplit peaks; □ and ■, resolved split peaks) as a function of the annealing temperature T_a. For the sake of comparison, the temperature of the nonannealed peaks is also shown (dashed lines).

by annealing the sample in chosen biphasic ranges. Although the overall phenomenology of the biphasic behavior of this polymesomorphic polymer was quite complex, there were some features that deserve particular interest. When the sample was annealed at a temperature in the nematic−isotropic biphasic region, only the N−I transition was found to be split into two well-resolved endothermic peaks. The S_B-S_A and S_A-N processes were not affected by the demixing that occurred during the annealing in the N−I biphasic region thus indicating that the smectic mesophases are insensitive to the molar mass features which produce two distinct N−I transitions. In contrast, when the sample was annealed at a temperature in the biphasic regions involving a smectic phase, both the S_A-N and S_B-S_A

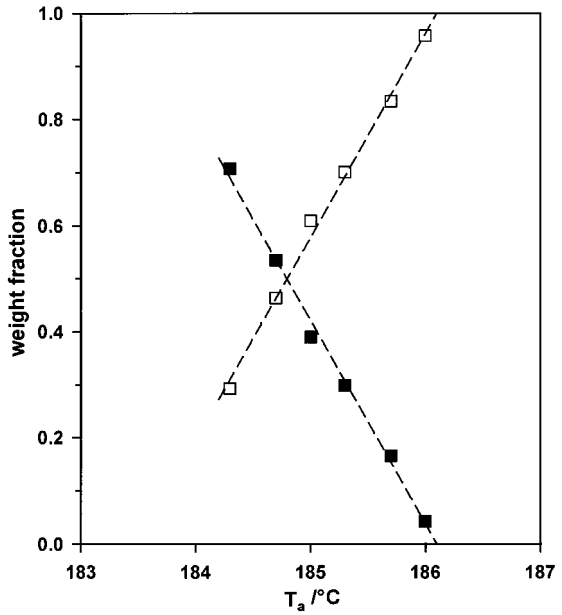

Figure 5. Weight fraction of the two resolved N−I transition components as a function of the annealing temperature T_a: low-temperature peak (□) and high-temperature peak (■). The lines are guides for the eyes.

processes appeared separated into two components whereas the N−I transition process was found little affected by the thermal treatment.

To better delineate the biphase demixing phenomenology of the above polymesomorphic sample, in the present study, we describe the temperature evolution of biphase segregation at the N−I as well as the S_A−N and S_B−S_A transitions of polymer **I**.

Experimental Section

Polymer **I** was prepared by a condensation reaction at room temperature under phase transfer conditions, according to the procedure previously reported,[16] and purified by precipitations from chloroform solution into methanol. The mild synthetic conditions were proved to afford polyesters with regular structure in which the polymethylene and polyoxyethylene spacers alternate along the polymer chain.[17] Polymer **I** was separated into three fraction by fractional precipitation with chloroform/methanol as solvent/nonsolvent pair. A diluted solution of 1.0 g of polymer **I** in 100 mL of chloroform was poured into a 500 mL fractionation vessel at 30 °C. Methanol (100 mL) was added dropwise to the solution under vigorous stirring. The vessel was then heated at 50 °C, and after homogeneity was reached, stirring was stopped. The system was cooled slowly to the initial temperature and allowed to settle for 24 h. The polymer-rich phase was separated and evaporated under vacuum. The fractionation cycle was continued by addition of successive fresh portions of methanol. Fractions of 0.2−0.3 g were typically recovered. Average molar masses were determined by SEC of THF solutions with a 590 Waters chromatograph equipped with refractive index and ultraviolet detectors, using PLgel 10^3, 10^4, and 10^5 Å columns calibrated with appropriate polyester samples.

The molar mass parameters for the unfractioned polymer and its three fractions are collected in Table 1 together with thermal data.

Differential scanning calorimetry (DSC) was carried out using a Perkin-Elmer DSC 7 apparatus. Samples of about 5 mg were employed. The instrument was calibrated with high purity standards (indium, naphthalene, benzoic acid, cyclohexane) at 10 °C min^{-1}. Dry nitrogen was used as purge gas. A preliminary characterization of polymer **I** was performed in the temperature range between −30 and 200 °C. Afterward, the temperature evolution of biphasic segregation was studied according to the following procedure. Samples of polymer **I** were heated to 200 °C and kept at this temperature for 20 min in order to cancel the previous thermal history. Subsequently, they were cooled at a nominal rate of 200 °C min^{-1} to a selected temperature T_a, chosen in the region associated with the mesophase transitions. After annealing at this temperature for 15 h, the samples were cooled to 50 °C. The samples were finally subjected to a heating run up to 200 °C at a rate of 10 °C min^{-1} and the corresponding DSC curves analyzed. The annealing time was chosen in order to achieve the best separation without simultaneous chain degradation or structural scrambling.[16−17] In fact, no structural rearrangements were observed by ^{13}C NMR in samples annealed at 200 °C in the isotropic phase for 20 h. In addition, the phase transition parameters of the polyester, including peak temperature, area, and shape, were identical after annealing in the isotropic phase for different times.

The transition temperatures were determined as peak values of the endothermic processes.

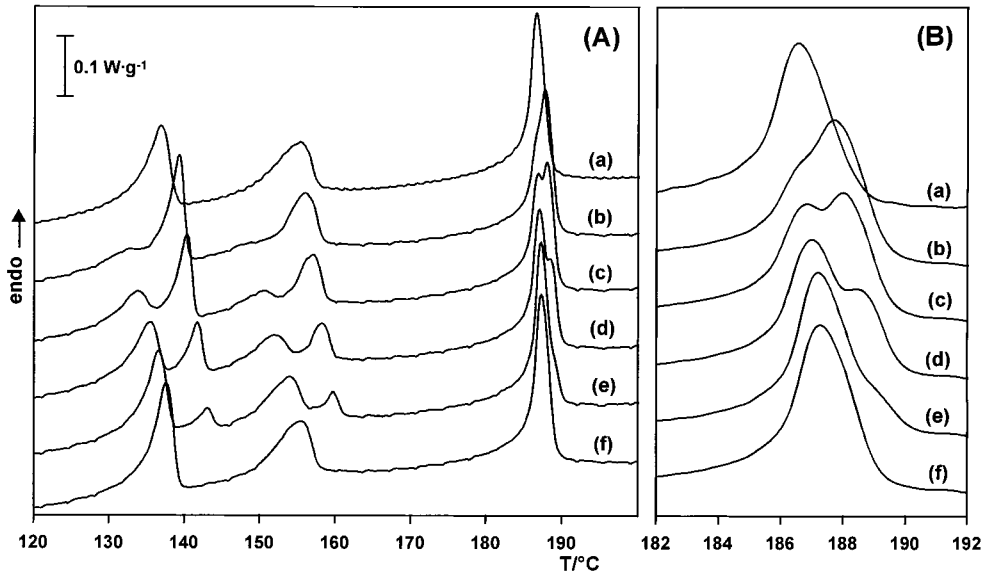

Figure 6. (A) DSC heating curves (10 °C/min) for polymer **I** after annealing for 15 h (annealing temperatures: (b) 149, (c) 151, (d) 153, (e) 155, and (f) 156 °C) and successive cooling to 50 °C. Curve a is obtained after rapid cooling from the isotropic phase. (B) Enlargement of the DSC scans in the temperature range 182−192 °C.

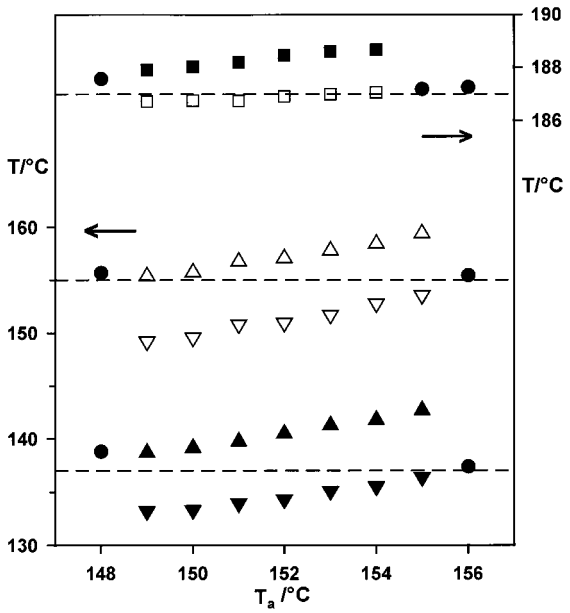

Figure 7. Temperatures of the transitions S_B-S_A (●, nonsplit peaks; ▼ and ▲, resolved split peaks), S_A-N (●, nonsplit peaks; ▽ and △, resolved split peaks) and N−I (●, nonsplit peaks; □ and ■, resolved split peaks) as a function of the annealing temperature T_a. For the sake of comparison, the temperature of the nonannealed peaks is also shown (dashed lines).

Results and Discussion

Figure 1 gives the DSC heating trace of polymer **I** after thermal treatment at 60 °C for 24 h. A well-defined step due to the glass transition is observed at about 40 °C, followed by four sharp endothermic transitions at 79.0, 136.8, 155.5, and 186.5 °C, respectively. Combined thermal optical analysis (TOA) and X-ray diffraction analysis showed that the endothermic process observed at the lowest temperature corresponds to the melting (crystal−S_B) whereas the three endothermic peaks at higher temperatures correspond to smectic B−smectic A, smectic A−nematic, and nematic−isotropic transitions, respectively.

The biphasic behavior of polymer **I** was delineated for each mesomorphic transition by differential scanning calorimetry according to the procedure described in the experimental part.

For each mesophase transition, the annealing temperature T_a was selected to cover the whole range of the relevant DSC endothermic peak. The glass transition process was always found to be unaffected by the annealing treatment. The temperature evolution of the biphasic segregation processes at the three mesomorphic transitions is described separately below. In addition, the biphasic behavior of the three fractions of polyester I is also shortly discussed.

A. Biphasic Segregation at the N—I Transition. Figure 2 illustrates some DSC heating curves after annealing at different temperatures inside the N−I biphasic region and fast cooling to 50 °C. The N−I peak is split into components whose peak temperatures and relative magnitudes depend on the annealing temperature. In contrast, the endothermic peaks associated with the S_B-S_A and S_A-N transitions do not appear to be affected by the above thermal treatment. To separate the two overlapping peaks in the N−I region, a nonlinear curve fitting was performed with multiple Lorentzian peaks. Figure 3 reports an example of the fit. The sum of the two resolved endotherms does not reproduce perfectly the experimental curve in the low and in the high-temperature regions of the N−I endotherm. Nevertheless, the error introduced in the determination of the relative percentage of the two components is estimated to be less than 10%. Moreover, because of the broadening that is observed in the low-temperature side of the N−I transition, the area of the low temperature component is always found, by the fitting procedure, to be higher than that of the high temperature component. The peak temperature trend of the nematic−isotropic endothermic components as a function of the annealing temperature is illustrated in Figure 4. The peak temperatures of both the nematic−isotropic components increase regularly with increasing annealing temperature from T_a = 184.3 to 186 °C. The relative percentages,

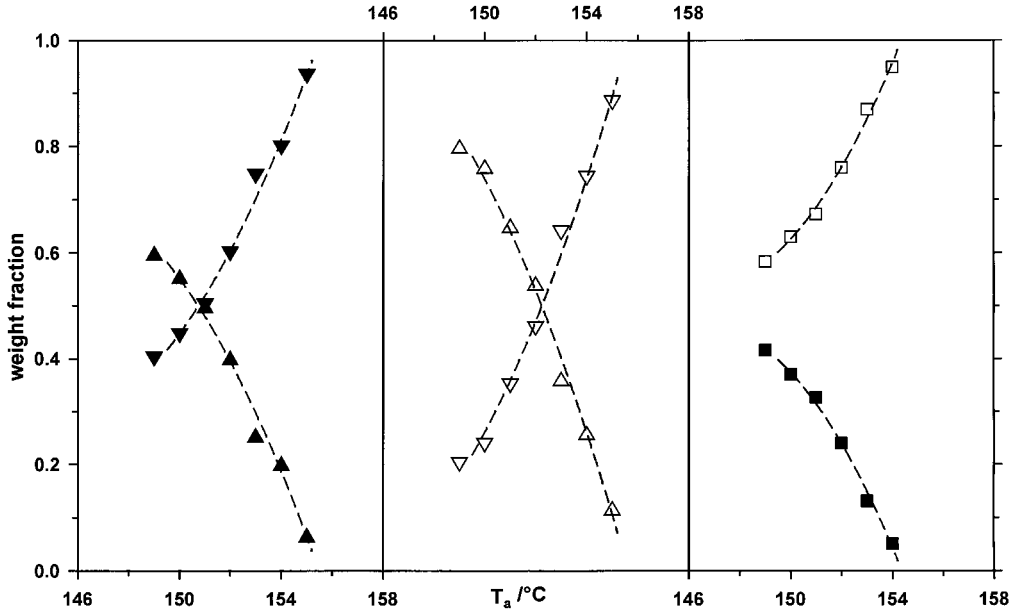

Figure 8. Weight fraction of the resolved S_B-S_A (▼, low-temperature peak; ▲, high-temperature peak), S_A-N (▽, low-temperature peak; △, high-temperature peak), and N−I (□, low-temperature peak; ■, high-temperature peak) transition components as a function of the annealing temperature. The lines are guides for the eyes.

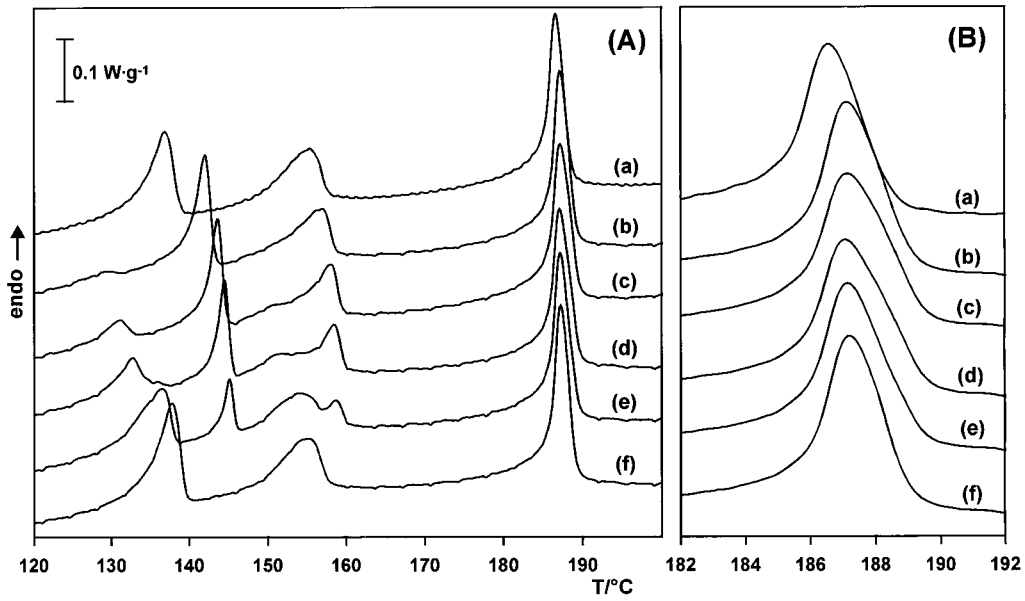

Figure 9. (A) DSC heating curves (10 °C/min) for polymer **I** after annealing for 15 h (annealing temperatures: (b) 132, (c) 134, (d) 135, (e) 135.8, and (f) 138 °C) and successive cooling to 50 °C. Curve a is obtained after rapid cooling from the isotropic phase. (B) Enlargement of the DSC scans in the temperature range 182−192 °C.

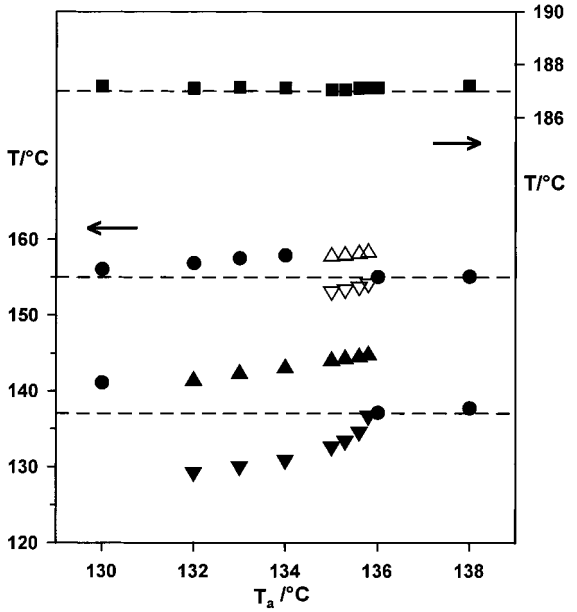

Figure 10. Temperatures of the transitions S_B-S_A (●, nonsplit peaks; ▼ and ▲, resolved split peaks), S_A-N (●, nonsplit peaks; ▽ and △, resolved split peaks), and N−I (■) as a function of the annealing temperature T_a. For the sake of comparison, the temperature of the nonannealed peaks is also shown (dashed lines).

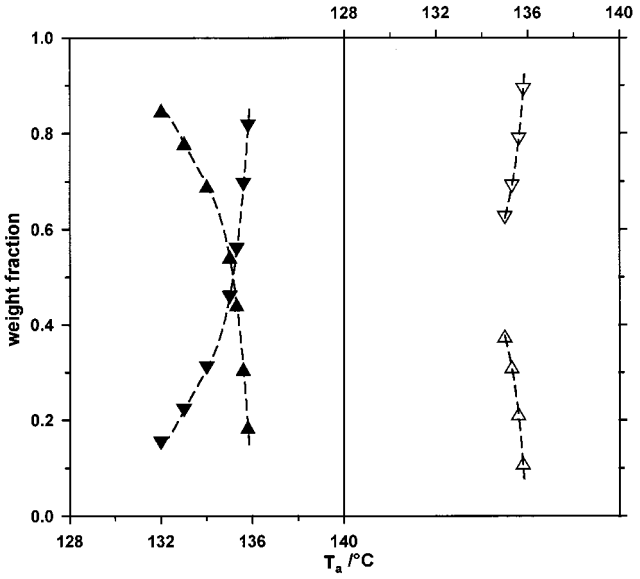

Figure 11. Weight fraction of the resolved S_B-S_A (▼, low-temperature peak; ▲, high-temperature peak) and S_A-N (▽, low-temperature peak; △, high-temperature peak) transition components as a function of the annealing temperature. The lines are guides for the eyes.

obtained from the two resolved areas, are reported in Figure 5 as a function of annealing temperature. The fractional area of the high temperature peak decreases with temperature whereas the mirroring trend is obviously observed for the low-temperature peak. The dual behavior at the nematic−isotropic transition is attributed to distinct transition processes of polymer **I** fractions with different average molar mass which phase segregate during annealing at temperatures inside the nematic−isotropic biphasic region.[13,14] The thermodynamic width of the biphasic region corresponding to the nematic−isotropic transition is about 2 °C, which is significantly lower than the width of the relevant DSC enthalpic peak. In addition, the average separation between the two segregated components is observed to be about 2 °C.

It is interesting to note that the peak temperature of the lower temperature component is always lower than the temperature of the original untreated sample. In contrast, the peak temperature of the higher temperature component is always higher than the temperature of the original sample. The peak temperatures of the smectic−nematic and smectic−smectic transitions are lower than the temperatures of the corresponding transitions in the original thermally untreated sample. In addition, the total transition enthalpies associated with the S_B-S_A and N−I endotherms after the biphasic segregation are equal to those of the original nonannealed peaks whereas the enthalpy associated with the smectic−nematic transition is found to be appreciably

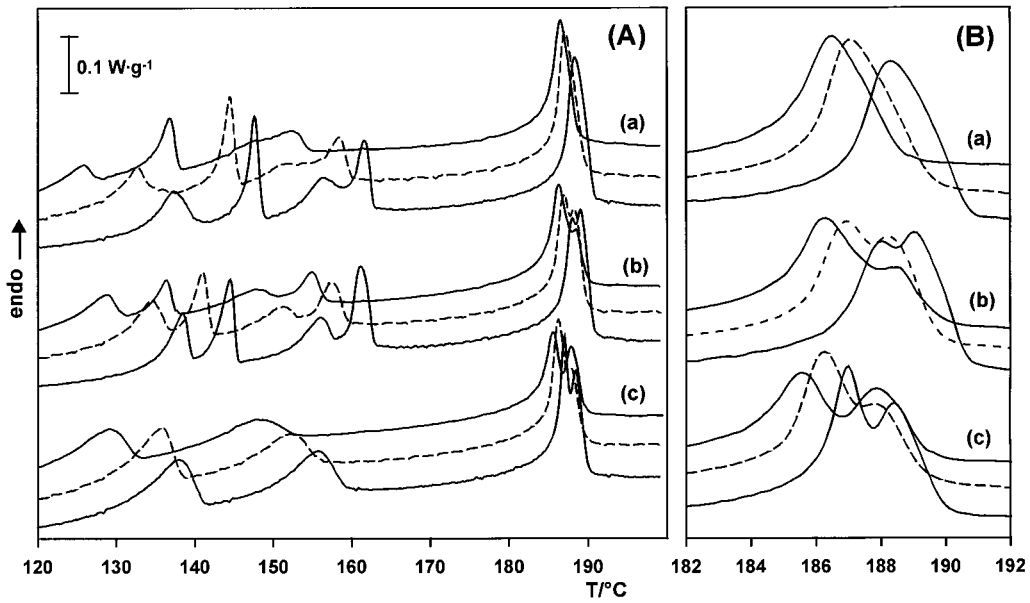

Figure 12. (A) DSC heating curves (10 °C/min) for unfractioned polymer **I** (dashed line), fraction 1 (solid line below the dashed line), and fraction 3 (solid line above the dashed line) after annealing for 15 h at the following temperatures: (a) 128.5, 135, and 139 °C, (b) 150, 152, and 157 °C, and (c) 185.2, 185.9, and 187 °C, respectively. (B): Enlargement of the DSC scans in the temperature range 182−192 °C.

lower than that of the original peak (about 10% on average).

B. Biphasic Segregation at the S_A—N Transition. Figure 6 illustrates some DSC heating curves after annealing at various temperatures in the S_A−N biphasic region. Under these conditions also the S_B−S_A and N−I transition processes appear structured into two well-resolved components whose peak temperature evolves parallel to that of the S_A−N transition.

Using the above-described fit procedure, the peak temperatures and relative percentage of the two components were evaluated for the S_A−N, S_B−S_A, and N−I transition processes after annealing in the S_A−N biphasic region. The results are shown in Figures 7 and 8, respectively. Also in this case, the various transition components are observed at temperatures higher and lower than the temperature of the corresponding thermally untreated peak (Figure 7). In addition, the fractional areas of the low- and high-temperature peaks increase and decrease with temperature, respectively. The thermodynamic width of the biphasic region corresponding to S_A−N transition is about 6 °C. Also the average separation between the two segregated components at the S_A−N is about 6 °C.

The width of the S_B−S_A transition process, after demixing, is significantly larger than that obtained after rapid cooling from the isotopic phase.

As far as the enthalpy change is concerned, it is interesting to note that the total enthalpy associated with the S_B−S_A and the N−I transitions after the biphasic separation is equal to that measured for the relevant nonannealed peaks. In contrast, the enthalpy change for the S_A−N transition is found to be lower (4% on average) than that of the original peak.

C. Biphasic Segregation at the S_B—S_A Transition. Figure 9 shows some DSC heating curves after annealing at temperatures inside the S_B−S_A biphasic gap. The temperature evolution of the S_B−S_A and S_A−N processes is similar. In contrast, the DSC peak associated with the N−I transition is not split but is only slightly broadened by the thermal treatment in the S_B−S_A biphasic region.

Figures 10 and 11 illustrate the peak temperatures and the relative percentage of the S_B−S_A and S_A−N components segregated in the S_B−S_A biphasic region.

The width of the S_B−S_A biphasic region is about 4 °C whereas the average separation of the segregated S_B−S_A components is about 12 °C, confirming that, after demixing, the width of the overall S_B−S_A transition process is significantly larger than that obtained after rapid cooling from the isotropic phase.

Also in this case, the various transition components are observed at temperatures higher and lower than those of the corresponding original peaks (Figure 10). In a similar fashion, the total enthalpy associated with the S_B−S_A and the N−I transitions after the biphasic separation is equal to that measured for the relevant nonannealed peaks. In contrast, the enthalpy change for the S_A−N transition is found to be appreciably lower (15%) than that of the original peak.

D. Biphasic Segregation of Polyester I Fractions. To get a better understanding of the molecular factors that control the biphase segregation behavior, three fractions of polyester I were analyzed. Table 1 collects the molar mass characteristics and the transition temperatures for these fractions. As expected, the transition temperatures increase with increasing the molar mass. To get information concerning the molar mass dependence of the biphasic segregation behavior, fractions 1 and 3, which present the most different molar masses, were subjected to the same annealing treament of the original unfractionated sample. Although the complete description of the biphasic phenomenology of fractions 1 and 3 is outside the scope of this paper, Figure 12 reports the DSC curves obtained after annealing for 15 h at annealing temperatures inside the S_B−S_A, S_A−N, and N−I transition regions. The annealing temperatures were selected in order to obtain, for the two fractions and the original sample, comparable weight fractions of the demixed components. Although the overall biphase segregation phenomenol-

ogy is qualitatively similar for the three samples, it is apparent that the peak location moves to higher temperatures as the average molar mass increases. In addition, the width of the biphase segregation process for the three transitions is wider for the sample with the widest molar mass distribution, thus clearly indicating that the molar mass parameters are key factors in determining the overall biphase segregation phenomenology.

Concluding Remarks

The temperature evolution of the biphase segregation at the N−I as well as S_A−N and S_B−S_A transitions of a main chain polyester was studied by annealing the sample inside the relevant biphasic gaps. When the sample is annealed at a temperature in the nematic−isotropic biphasic region, a splitting of the N−I transition process is observed. In contrast, S_B−S_A and S_A−N processes are not affected by the annealing in the N−I biphasic region. In contrast, when the sample is annealed at a temperature in the biphasic regions involving a smectic phase, both the S_A−N and S_B−S_A processes appear to be separated into two components. As regards the N−I process, when the segregation is performed in the S_A−N transition region, the N−I transition is found to be split into well-resolved components. In contrast, a little broadening of the N−I peak is observed when the thermal treatment is carried out in the S_B−S_A mesophasic gap. The thermodynamic width of the mesophasic transitions resulted 2 °C for the N−I transition and 6 and 4 °C for the S_A−N and S_B−S_A transitions, respectively. In addition, the average separation of the demixed components was found to be 2 °C for the N−I transition, 6 °C for the S_A−N, and 12 °C for the S_B−S_A transition. The maximum efficiency of the biphase demixing, in terms of peak resolution, was found for the transitions at which the demixing was performed. This indicates that the system lowers its free energy by selective redistribution of species of different molar mass between two different phases according to the distinct steric packing features relevant to the various mesophases.

In samples with different molar mass and molar mass distribution, the biphase segregation behavior was found to be qualitatively similar with the peak location moving to higher temperatures as the average molar mass increases.

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