Macromolecules 1991, *24*, 1459–1463

Thermal Investigation of the Nematic–Isotropic Biphase in a Thermotropic Main-Chain Polyester

M. Laus, D. Caretti, and A. S. Angeloni

Dipartimento di Chimica Industriale e dei Materiali, Viale Risorgimento 4, 40136 Bologna, Italy

G. Galli and E. Chiellini*

Dipartimento di Chimica e Chimica Industriale, Via Risorgimento 35, 56100 Pisa, Italy

Received March 26, 1990; Revised Manuscript Received July 24, 1990

ABSTRACT: The biphasic behavior at the nematic–isotropic transition for a thermotropic main-chain polyester was studied by differential scanning calorimetry and optical microscopy. The demixing and thermal evolutions of the macroscopically segregated nematic and isotropic components were monitored upon annealing at different temperatures inside the biphasic gap. The equilibrium distribution of the various molecular species at the nematic–isotropic transition and the thermodynamic biphase range were determined. The observed phase segregation is attributed to chain length heterogeneity of the sample, with the longer chain macromolecules tending to selectively segregate into the nematic phase.

Introduction

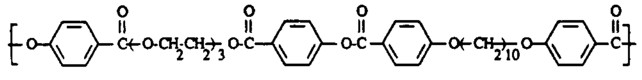
Statistical mechanical theories[1–3] predict that lyotropic solutions consisting of rodlike macromolecules and a nonmesogenic solvent as well as multicomponent mixtures of thermotropic rodlike molecules may show coexisting isotropic and anisotropic liquid phases over a wide range of temperatures. This behavior was recognized[4] in lyotropic solutions of, e.g., aromatic polyamides, polypeptides, polyisocyanates, and degraded DNAs, which exhibited demixing into two coexisting isotropic and nematic phases at equilibrium. The selective retention of the longer molecules in the anisotropic phase is explained in terms of steric effects by the inherent propensity of the rigid and highly anisometric chain molecules to assemble in a high-density anisotropic arrangement. The lattice theory has been more recently adapted to the treatment of solutions of polydisperse rods having diverse distributions,[5–7] mixtures of rods and random coils,[8] and semirigid chains comprising sequences of rigid and flexible units.[9]

Thermotropic systems consisting of rodlike molecules having different axial ratios were studied with respect to their biphasic behavior.[10,11] DSC measurements on binary and ternary mixtures of *p*-oxybenzoate oligomers showed a very small coexistence range of nematic and isotropic phases. In addition, the compositions of the two phases were practically identical. These deviations from theory were explained by considering that the difference between the chemical potentials of the molecules in the two phases, which is the ultimate driving force for the partitioning process, was very small as indicated by the small transition entropies observed.

Various thermotropic copolyesters[12,13] showed broad biphasic regions, and, in addition to the polydispersity of chain lengths, sequence distributions and compositional variations should be accounted for, including also the effects stemming from the incorporation of nonlinear nonmesogenic groups.[14] In this context a comparison has been reported[15–17] of the biphasic behavior at the nematic–isotropic transition for a structurally ordered copolymer and its constitutional isomer containing the same structural units randomly distributed along the main chain.[18] The chemically disordered polymer displayed a very broad biphasic temperature range, whereas the chemically ordered polymer showed a sharp nematic–isotropic transition. The chain flexibility distribution of the chemically disordered polymer was claimed to be primarily responsible for this different behavior.[17]

Detailed information has also been presented[19–22] about the biphase width and the biphasic behavior of thermotropic nematic semiflexible polyesters derived from the condensation of 4,4′-dihydroxy-2,2′-dimethylazoxybenzene and alkanedioic acids. The segregation of the nematic and isotropic phases was studied by several experimental techniques.[20–22] Macroscopic demixing of isotropic and nematic domains accompanied by substantial partitioning of chain lengths was observed, with the longer chains being preferentially retained in the nematic phase. Moreover, the thermal history in the biphase markedly influenced the gross morphology of the solid state.

In view of the fundamental and technological implications connected with the onset of this phenomenon, in the present work a thermal investigation was undertaken of the fractionation process inside the nematic–isotropic biphase of a thermotropic main-chain polymer I having the following structure:



I

The equilibrium distribution of the various species at the nematic–isotropic transition and the thermodynamic biphase width are determined and discussed with reference to the polymer molecular weight.

Experimental Section

Polymer I was synthesized and characterized according to a previous procedure.[23]

Calorimetric analyses were carried out under a dry nitrogen flow with a Perkin-Elmer DSC 7 apparatus equipped with a 3700 data station using Delta standard programs. Polymer samples of 5–10 mg were employed. In all cases the maximum in DSC enthalpic peaks was taken as the phase transition temperature. The temperature scale was calibrated against the melting temperatures of benzoic acid and indium. For the determination of the transition enthalpy indium was used as standard material.

The biphasic behavior was studied by DSC according to the following procedure: a sample of polymer I was heated for 20 min at 433 K in the isotropic phase. Subsequently, the sample

0024-9297/91/2224-1459$02.50/0

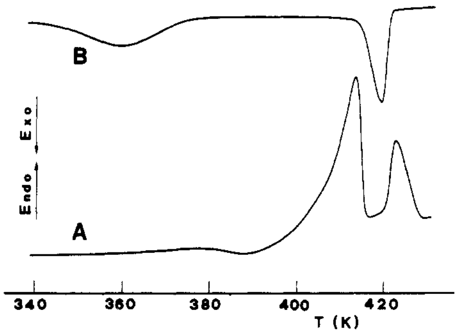


Figure 1. DSC heating (A) and cooling (B) curves (10 K/min) for polyester I after first cooling from the isotropic melt.

was cooled at 2 K/min to a selected temperature in the biphasic region, annealed at this temperature for various times (5–900 min), and then rapidly cooled to room temperature. The sample was finally subjected to several heating/cooling cycles at 10 K/min in the temperature range 298–433 K. In another set of experiments, after annealing in the biphasic region as above, the sample was cooled into the mesophasic region to 405 K far away from incipient crystallization and then heated to complete isotropization. For each annealing temperature a fresh polymer sample was employed. DSC traces were normalized to a 1-mg sample.

A macroscopic fractionation experiment was performed according to the following procedure. A 0.5-g sample of polymer I was introduced under a dry nitrogen atmosphere in a standard 5-mm-diameter NMR tube which was sealed under high vacuum after thorough homogenization of the sample at 453 K. The tube was inserted in a thermostat and slowly cooled to 423 K. After 15 h the isotropic (fraction A) and nematic (fraction B) phases were well separated by a sharp meniscus. The tube was then rapidly cooled to room temperature, and the two phases were physically separated and analyzed. Average molecular weights were measured in chloroform solution by GPC with a 590 Waters chromatograph equipped with a Shodex KF 804 column. Polystyrene standard samples were used for the universal calibration method.[24]

Results and Discussion

Polymer I was synthesized by a polycondensation reaction between 1,8-bis((4-hydroxybenzoyl)oxy)-3,6-dioxaoctane and 1,10-bis((4-chloroformyl)phenoxy)decane under phase-transfer conditions and purified by repeated precipitations from chloroform solutions into methanol.

The number-average molecular weight ($\bar{M}_n$) and the first polydispersity index ($\bar{M}_w/\bar{M}_n$) of polymer sample I as determined by GPC were 10 100 Da and 2.34, respectively. In addition, no traces of oligomeric products were present in the GPC profiles.

The thermal properties of polymer I were taken from the DSC curves on a sample annealed by cooling at 10 K/min from the isotropic melt (Figure 1). In the heating scan, polymer I showed a weak cold-crystallization exotherm at 389 K and two endothermic transitions centered at 414 and 422 K attributed to the crystal melting and to the nematic–isotropic transitions, respectively. The isotropization endotherm extended from 414 to 432 K with an apparent biphasic region of 18 K. On cooling from the isotropic melt, one isotropic–nematic exothermic transition at 420 K and one broad crystallization exotherm at 362 K were observed. The isotropization enthalpy and entropy were 7.6 kJ/mol and 18.0 J/(mol K), respectively. Optical microscopy and X-ray diffraction studies demonstrate that the mesophase is nematic throughout the mesophasic range.

The biphase fractionation process was studied by differential scanning calorimetry by following a procedure analogous to that previously reported.[19-21] Polymer I once heated to 433 K was slowly cooled to the predetermined annealing temperature inside the biphasic gap, maintained at this temperature for 15 h, and then rapidly cooled to either room temperature or inside the nematic range to 405 K. An annealing time of 15 h was found to be optimal to achieve the best separation level without any appreciable chain degradation process.

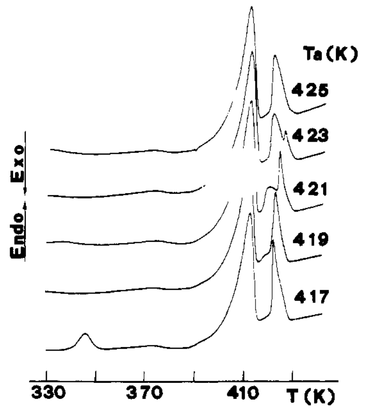


Figure 2. DSC heating curves (10 K/min) following annealing at different temperatures T_a in the biphase (annealing time = 15 h).

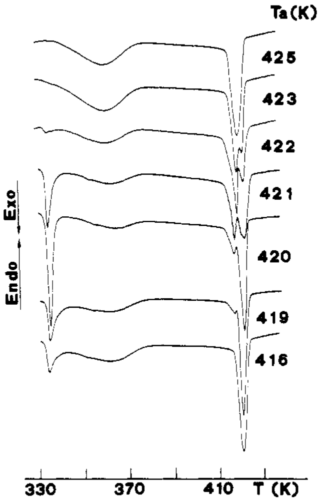


Figure 3. DSC cooling curves (10 K/min) following annealing at different temperatures T_a in the biphase (annealing time = 15 h).

In Figures 2 and 3 are reported the DSC heating and cooling curves in the range 330–433 K of polymer I following annealing at various temperatures. In a parallel set of experiments, the polymer sample was cooled to 405 K to avoid crystallization and heated to complete isotropization to 450 K (Figure 4).

Irrespective of any annealing treatment, polymer I showed, on heating, one melting endotherm preceded by a shallow cold-crystallization exotherm around 390 K (Figure 2). The melting temperature did not change significantly with annealing conditions. In contrast, two distinct nematic–isotropic transition endotherms appeared on heating (Figure 4), and, on cooling, two isotropic–nematic transition exotherms and two crystallization exotherms were clearly detectable in samples annealed between 416 and 422 K (Figure 3). The peak temperatures of both isotropization endotherms in the DSC heating curves regularly increased with annealing temperature (Table I). The area of the lower temperature isotropization endotherm increased with annealing temperature, whereas the area of the higher temperature isotropization endotherm decreased. The thermal behavior of the two isotropic–nematic exotherms in the DSC cooling curves

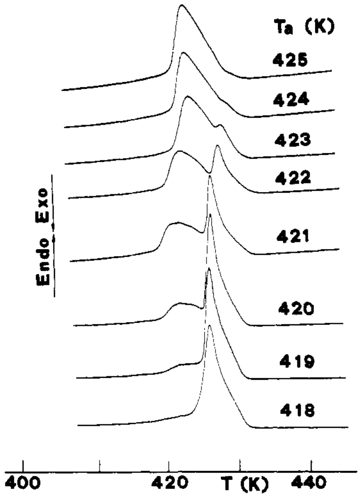


Figure 4. DSC heating curves (10 K/min) relevant to the nematic–isotropic transition following annealing at different temperatures T_a in the biphase.

Table I
Isotropization Thermodynamic Parameters of Components A[a] and B[b] of Polymer I

T_a,[c] K	T_i^A, K	ΔH_i^A, kJ/mol	T_i^B, K	ΔH_i^B, kJ/mol
419	419[d]	0.8[d]	423.7	6.8
420	420[d]	1.8[d]	424.3	5.8
421	420.3	3.0	425.1	4.6
422	420.7	4.8	425.9	2.8
423	421.6	6.0	426.9	1.6
424	422.1	6.9	428[d]	0.7[d]
425	422.3	7.2	429[d]	0.4[d]

[a] A: formerly isotropic component in the biphase. [b] B: formerly nematic component in the biphase. [c] Annealing temperature in the biphasic region (annealing time = 15 h). [d] Indicative values because of strong signal overlap.

closely parallels that of the corresponding endotherms in the DSC heating curves. This dual isotropization behavior was attributed to the occurrence of distinct isotropization processes of the lower and higher molecular weight fractions of the polymer (fractions A and B), which separated during annealing in the biphasic region, the latter segregating into the component with higher transition temperature. This fractionation phenomenon according to molecular weight can also be claimed to be responsible for the origin of two distinct exotherms in the crystallization process. Nevertheless, the two polymer fractions do not show, under the adopted experimental conditions, significant differences in their melting temperatures, resulting in a single melting endotherm.

It is worth noting that the above thermal procedure allowed us to delineate the equilibrium distribution of the volume fractions of the two coexisting phases in the biphasic gap (Figure 5). Accordingly, a thermodynamic width of the biphasic region of 9–10 K was estimated, which was significantly lower than that determined from the width of the relevant DSC enthalpic peak. Indeed thermal relaxation and rounding-off phenomena, which accompany differential scanning calorimetry measurements,[25,26] may concur to enlarge, in a somewhat artificial manner, the width of the enthalpic peaks.

The biphase fractionation process was also studied by DSC following the evolution of the nematic–isotropic transition peak of a polymer sample annealed at 421 K as a function of time. Relevant DSC heating curves are reported in Figure 6. After 15 min of annealing, the peak began to split into two components which emerged progressively better resolved. Beyond 15 h of annealing, the overall peak no longer showed appreciable differences in shape, and the separation process was considered completed from a thermodynamic standpoint, with the two phases coexisting at their compositional equilibrium. The total width of the isotropization peaks of the biphase fractionated sample was significantly larger than that of the initial unfractionated one, particularly toward the lower temperature side. This broadening of the nematic–isotropic transition process in the biphase fractionated samples may be explained[21] by the superimposition of the two biphasic regions corresponding to the respective isotropization processes of the two polymer fractions with different molecular weights. The low end cut of the molecular weight distribution appears to be the major contributing component to the biphase width.

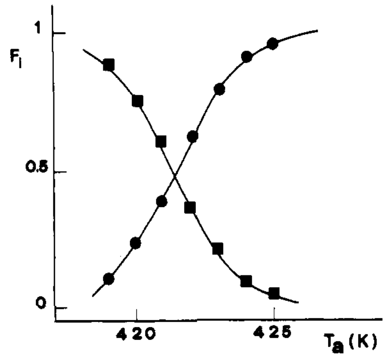


Figure 5. Volume fractions (F_i) of the nematic (■) and isotropic (●) components following demixing (annealing time = 15 h) as a function of annealing temperature T_a.

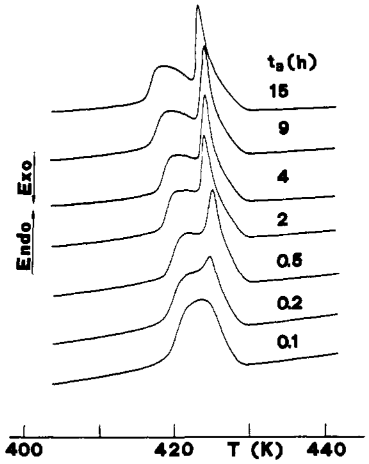


Figure 6. DSC heating curves (10 K/min) relevant to the nematic–isotropic transition following different annealing times (t_a) in the biphase region (T_a = 421 K).

The kinetics of homogenization in the isotropic phase of the sample fractionated at 421 K was also studied by DSC by maintaining the sample at 433 K and following the change in shape of the nematic–isotropic transition trace as a function of time. The relevant DSC heating curves are reported in Figure 7. Although the progressive coalescence of the two peaks indicated the effective remixing of the two polymer fractions in the isotropic phase, the shape of the peak of the original untreated sample was not fully recovered, but some reminiscence of the higher temperature peak was observable even after annealing up to 4 h in the isotropic phase. The low self-diffusion rate of the higher molecular weight polymer fraction in the viscous environment probably prevented the complete homogenization of the sample in the isotropic phase.

To gain a better quantitative insight into the efficiency of the biphase segregation process, a macroscopic frac-

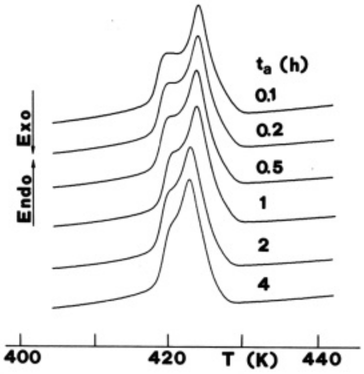


Figure 7. DSC heating curves (10 K/min) relevant to the nematic–isotropic transition following different annealing times (t_a) in the isotropic phase (T_a = 433 K).

Table II
Molecular Weight Characteristics[a] of the Original Polymer I and Fractionated Components[b] (Annealing Temperature 423 K)

	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
original	10100	23600	2.34
fraction A	9500	19700	2.07
fraction B	12300	29500	2.40

[a] By GPC, in chloroform. [b] A: formerly isotropic component in the biphase, B: formerly nematic component in the biphase.

tionation experiment was performed. A polymer sample was heated to 453 K, slowly cooled to 423 K, and maintained at this temperature for several hours. Initially the melt appeared homogeneously cloudy but, over time, better visible isotropic droplets progressively emerged. After 15 h the melt was constituted by a turbid nematic phase (fraction B) and a clear isotropic phase (fraction A) separated by a sharp boundary layer. The sample was kept for an additional 20 h at the selected temperature and then rapidly cooled to room temperature. The two fractions (A and B) were physically divided and analyzed by both ^{13}C NMR and gel permeation chromatography. The ^{13}C NMR spectra of the two separated fractions were superimposable on the corresponding spectrum of the original untreated sample, thus indicating that no side reactions such as transesterification or sequence rearrangements had occured at the annealing temperature within the selected time. On the contrary, the molecular weight characteristics of the two fractions relative to the original sample were significantly different (Table II). The average molecular weight of the polymer fraction recovered in the isotropic phase (A) was lower than that of the polymer fraction in the nematic phase (B), whereas the original sample has an intermediate value. It is apparent that a substantial partitioning of the various molecular species between the two coexisting phases occurred, the higher molecular weight components being preferentially incorporated into the anisotropic phase.

The phase separation process was also followed by visual observation on the hot stage of the polarizing microscope by submitting polymer samples to the same thermal treatments as by DSC. Upon cooling from the isotropic melt, typically the nematic droplets started to nucleate within the continuous isotropic phase. They increased in size with increasing isothermal annealing and coalesced in large domains until demixing was realized. The eventual equilibrium state was established after approximately 15 h, in agreement with DSC measurements, when no more changes in shape and size of demixed domains could be appreciated. The boundary region between the coexisting phases was rather sharp and remained essentially intact during their different and separate thermal evolutions on both heating and cooling. It was, therefore, possible to follow the distinct responses of the demixed components through the nematic–isotropic phase transition. Characteristic textures with their thermal evolution are shown in Figure 8 for the sample annealed in the biphasic region at 419 K. It is clearly seen that isotropization develops progressively and regularly across the sample. This observation suggests that macromolecules with different molecular weights are uniformly distributed within the isotropic and nematic domains, in accordance with previous findings.[20]

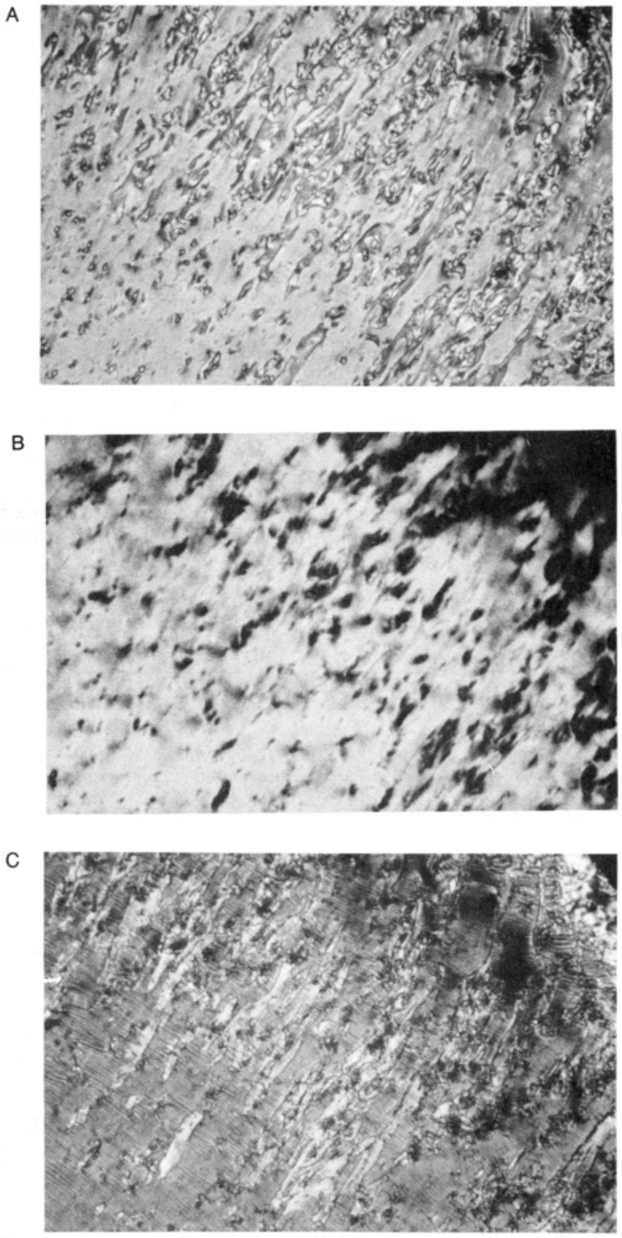


Figure 8. Domain texture (T_a = 419 K) with incipient isotropization (top right corner) at 420 K (A) and progressive isotropization at 424 K (B); after quenching to room temperature from 396 K (C).

From the areas of both regions we could estimate the relative amounts of the two coexisting phases and their dependence on annealing temperature. No particular care was taken to ensure a constant thickness throughout the polymer film, and the volume fraction of the isotropic component was roughly estimated as 10, 35, and 80% upon annealing at 419, 421, and 423 K, respectively. These values are in agreement with DSC results (Figure 5).

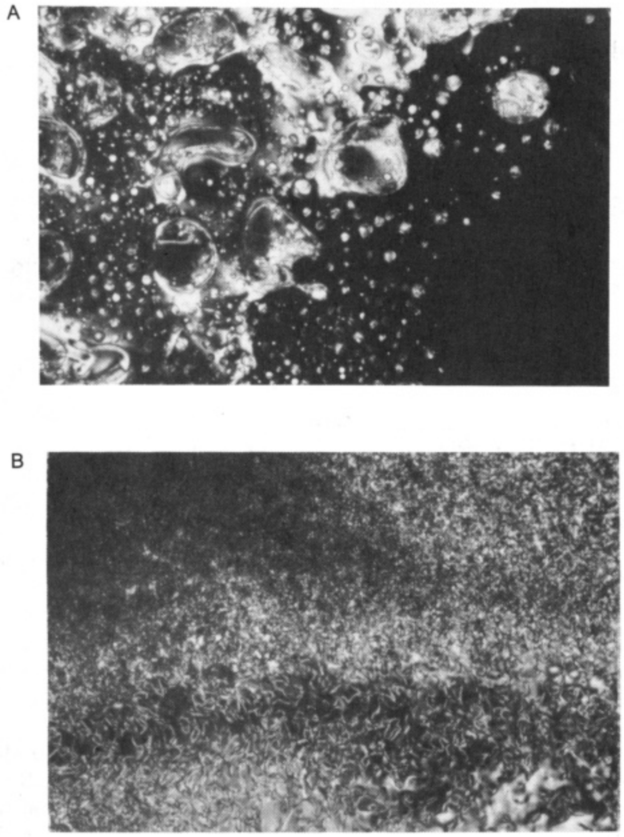


Figure 9. Droplet texture upon incomplete demixing at T_a = 422 K (A); crystal–nematic biphase with the broad boundary region on cooling to 395 K (B).

Smaller nematic and isotropic domains appeared interpenetrated upon incomplete demixing, with a broad interface region connecting the two components (Figure 9). Starting from the formerly isotropic regions, isotropization proceeded through this zone common to both components. Accordingly, there exists an uneven distribution of molar masses, with macromolecules of intermediate chain lengths being accumulated in the boundary regions.

Conclusions

For the semiflexible main-chain polyester sample investigated there exists a biphasic thermal range in which the nematic phase and the isotropic phase coexist at equilibrium. Upon annealing at different temperatures, demixing and thermal evolutions of the two macroscopically segregated components are monitored by DSC and optical microscopy. While there are no indications of the occurrence of chemical rearrangements or degradations, the phase segregation is correlated with the molar mass polydispersity of the sample. The high molecular weight macromolecules are preferentially incorporated into the nematic phase, which shows progressively increasing isotropization temperatures as due to selective enrichment of longer chain macromolecules.

The biphase width is as broad as 10 K, which is however substantially narrower than anticipated from related thermotropic polyesters of comparable molecular weight and molecular weight polydispersity.[21] This suggests that even structural factors can affect the biphasic separation phenomena in semiflexible polyesters connected with different intersegment associations and persistence length distributions,[17,27,28] and, all other things being equal, it seems that the higher is ΔH_{NI} the broader is the biphasic gap.[20] In this respect, we are presently extending our investigations to liquid crystalline polymers of various chemical structures and molar mass distributions, including side-chain thermotropic systems.

Acknowledgment. This work was supported by the "Progretto Finalizzato Chimica Fine II" of the Italian National Council of Researches (CNR).

References and Notes

(1) Flory, P. J. *Proc. R. Soc. London* **1956**, *A234*, 73.
(2) Flory, P. J.; Ronca, G. *Mol. Cryst. Liq. Cryst.* **1979**, *54*, 311.
(3) Flory, P. J. *Adv. Polym. Sci.* **1984**, *59*, 1.
(4) See, for instance, refs 11–29 in ref 3.
(5) Abe, A.; Flory, P. J. *Macromolecules* **1978**, *11*, 112.
(6) Flory, P. J.; Frost, R. S. *Macromolecules* **1978**, *11*, 1126.
(7) Moscicki, J. K.; Williams, G. *Polymer* **1982**, *23*, 558.
(8) Flory, P. J. *Macromolecules* **1978**, *11*, 1138.
(9) Matheson, R. R., Jr.; Flory, P. J. *Macromolecules* **1981**, *14*, 954.
(10) Ballauff, M.; Wu, D.; Flory, P. J.; Barral II, E. M. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 524.
(11) Ballauff, M.; Flory, P. J. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 530.
(12) Lenz, R. W.; Jin, J. I. *Macromolecules* **1981**, *14*, 1405.
(13) Moore, J. S.; Stupp, S. I. *Macromolecules* **1987**, *20*, 273, 282.
(14) Lenz, R. W. *Faraday Discuss. Chem. Soc.* **1985**, *79*, 21.
(15) Moore, J. S.; Stupp, S. I. *Macromolecules* **1988**, *21*, 1217.
(16) Martin, P. G.; Stupp, S. I. *Macromolecules* **1988**, *21*, 1222.
(17) Stupp, S. I.; Moore, J. S.; Martin, P. G. *Macromolecules* **1988**, *21*, 1228.
(18) For the effects of constitutional regularity in thermotropic polyesters, see also: Ober, C. K.; Lenz, R. W.; Galli, G.; Chiellini, E. *Macromolecules* **1983**, *16*, 1034.
(19) D'Allest, J. F.; Wu, P. P.; Blumstein, A.; Blumstein, R. B. *Mol. Cryst. Liq. Cryst. Lett.* **1986**, *3*, 103.
(20) D'Allest, J. F.; Sixou, P.; Blumstein, A.; Blumstein, R. B. *Mol. Cryst. Liq. Cryst.* **1988**, *157*, 229.
(21) Kim, D. Y.; D'Allest, J. F.; Blumstein, A.; Blumstein, R. B. *Mol. Cryst. Liq. Cryst.* **1988**, *157*, 253.
(22) Esnault, P.; Gauthier, M. M.; Volino, F.; D'Allest, J. F.; Blumstein, R. B. *Mol. Cryst. Liq. Cryst.* **1988**, *157*, 273.
(23) Caretti, D.; Angeloni, A. S.; Laus, M.; Chiellini, E.; Galli, G. *Makromol. Chem.* **1989**, *190*, 1655.
(24) Tung, L. H. *Fractionation of Synthetic Polymers*; Marcel Dekker: New York, 1977.
(25) Kasting, G. B.; Garland, C. W.; Lushington, K. J. *J. Phys. (Paris)* **1980**, *41*, 879.
(26) Thoen, J.; Marynissen, H.; Van Dael, W. *Phys. Rev. A* **1982**, *26*, 2886.
(27) Viney, C.; Yoon, D. Y.; Reck, B.; Ringsdorf, H. *Macromolecules* **1989**, *22*, 4088.
(28) Fredrickson, G. H.; Leibler, L. *Macromolecules* **1990**, *23*, 531.

Registry No. I (copolymer), 123467-37-8; I (SRU), 119846-19-4.