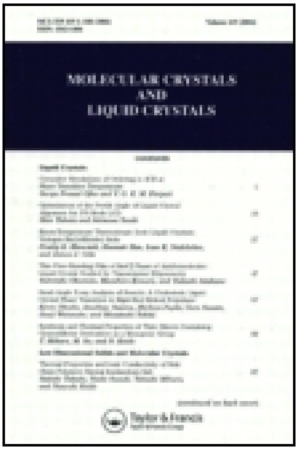

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Investigation of the Nematic-Isotropic Biphase in Thermotropic Main Chain Polymers. Homogeneity of the Pure Nematic and Isotropic Phases. Part II: Study by dsc

D. Y. Kim [a], J. F. D'allesty [b], A. Blumstein [a] & R. B. Blumstein [a]

[a] Polymer Science Program, Department of Chemistry, University of Lowell, Lowell, MA, 01854

[b] Laboratoire de Physique de la Matière Condensée, Nice, Cedex, U.A. C.N.R.S. 190, Faculté des Sciences-Parc Valrose, 06034, (France)

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INVESTIGATION OF THE NEMATIC -ISOTROPIC BIPHASE IN THERMOTROPIC MAIN CHAIN POLYMERS. HOMOGENEITY OF THE PURE NEMATIC AND ISOTROPIC PHASES.

PART II: STUDY BY DSC

D.Y. KIM, J.F.d'ALLEST,* A. BLUMSTEIN AND
R. B. BLUMSTEIN
Polymer Science Program, Department of Chemistry
University of Lowell, Lowell, MA 01854
*Present Address: Laboratoire de Physique de la
Matière Condensée, U.A. C.N.R.S. 190, Faculté
des Sciences-Parc Valrose, 06034 Nice Cedex (France)

Abstract The fraction f_N of nematic component is measured by means of isothermal scans or by means of dynamic scans following complete demixing of the I and N components. The method is applicable regardless of chain length and spacer parity. Evolution of the system in the demixing-homogenization stage can be monitored by following splitting of cold crystallization, melting and isotropization peaks. Pure I and N phases retain a lasting memory of demixed domain morphology.

INTRODUCTION

This is the second of this series of papers devoted to thermodynamic and kinetic aspects of behavior in the nematic-isotropic biphase and their relationship to molecular morphology of the isotropic, nematic and solid phases in thermotropic main chain polyesters. In the first paper, polarizing microscopy was used to monitor demixing between the isotropic and anisotropic components[1]. The longest chains are preferentially transferred into the N phase. The morphology induced by this segregation is retained upon cooling to the solid state, and upon subsequent melting and reisotropization of the formerly nematic (FN) and formerly isotropic (FI) components. "Equilibrium" demixing in the biphase is reflected in the solid state as a macrodomain morphology with sharply defined FN/FI boundaries that remain virtually intact upon subsequent isotropization. Following incomplete demixing, on the other hand, intermediate chain lengths are accumulated in a broad boundary region.

Upon cooling from the I phase, phase separation occurs via orientational and conformational ordering of the N component. Isothermal annealing in the biphase subsequently leads to macroscopic demixing of the I and N components, concomittant with homogenization of their respective chain length distributions. In the present study, we use DSC to separate, albeit somewhat arbitrarily, the stage of orientational ordering from the demixing-homogenization stage. This is achieved through combination of isothermal and dynamic scans, the latter following isothermal annealing within the biphase.

EXPERIMENTAL SECTION

Samples are prepared and characterized as in the previous paper[1]. Nomenclature and symbols used are also the same. DSC experiments are run on a Perkin-Elmer 2C instrument with data station.

Isothermal Scans

A typical isothermal run is illustrated on Fig. 1. The dashed line provides the "baseline", that is a scan of the sample in a range of temperatures where no phase transition is observed. Isothermal data for the I/N transition are recorded on the full line. Subtraction of the baseline provides the corrected signal of the sample. The nematic fraction f_N at a given temperature is the ratio of the heat measured isothermally to the total heat of isotropization measured by means of dynamic scanning.

Dynamic Scans Following Isothermal Annealing

As in the previous paper, an "untreated" sample is a specimen that has not been isothermally treated in the biphase, regardless of the remainder of its thermal history. Typically, a virgin sample is homogenized in the I phase for about 15 minutes, kept at the segregation temperature T_s for a time t_s, then rapidly cooled to 0°C. This quenches the biphase morphology. The sample is then cycled at 20 K/min between 0°C and 15°C past complete isotropization. Unless otherwise specified, the data shown here refer to first heating and cooling scans.

The isotropization peak following complete demixing is split into FN and FI components, defined as in the previous paper. Their relative peak areas and, hence, the nematic fraction f_N are determined by peak deconvolution (assuming superposition of two gaussians). Three or more gaussian peaks can be deconvoluted (see below). Unsymmetric peaks are treated by conventional deconvolution methods used in chromatography[2].

RESULTS AND DISCUSSION

Isothermal Scans

Selected isotherms recorded at several temperatures within the biphase are shown on figures 2 and 3. Isothermally measured values of f_N are listed in Table I and plotted on fig. 4 for AZA9M15,000 and DDA9M14,500. Comparison of figures 2 and 3 shows significant kinetic control of the N/I transition in the case of DDA9, whereas in AZA9 the thermal event is completed in less than 0.5 min even at the highest temperatures. Table I and fig. 4 show that

TABLE I Isothermally measured values of f_N

	AZA9M15,000			DDA9M14,500	
T(K)	Heating	Cooling	T(K)	Heating	Cooling
412	0.79	0.87	418	0.99	1.00
413	0.73	0.77	420	0.97	0.96
414	0.63	0.66	422	0.94	0.89
415	0.41	0.47	424	0.86	0.78
416	0.33	0.29	426	0.73	0.57
416.5	-	0.13	428	0.56	0.19
417	0.17	0.04	430	0.35	0.0
			432	0.18	-
			434	0.12	-

TABLE II Equilibrium nematic fraction in DDA9M4,600

	Heating		Cooling	
T_s(K)	ΔH_{NI} (cal/g)	f_N	$-\Delta H_{IN}$ (cal/g)	f_N
408	3.50	0.82	3.46	0.82
410	3.49	0.79	3.48	0.79
411	3.47	0.76	3.47	0.74
412	3.42	0.76	3.45	0.73
413	3.43	0.75	3.44	0.67
415	3.42	0.47	3.50	0.49
416	3.42	0.37	3.39	0.43
417	3.40	0.32	3.43	0.44
418	3.43	0.23	3.52	0.23
419	3.27	0.06	3.42	0.10

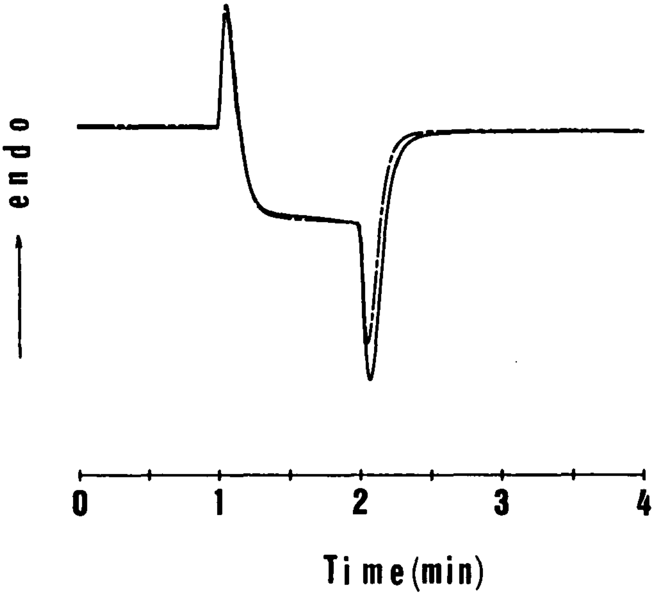

FIGURE 1. Typical isothermal DSC measurement for the baseline and I/N transition peak. Sample AZA9M15,000. Temperature program sequence: isothermal 1 min - cooling 1 min (20K/min) - isothermal 2 min. Dashed line: baseline; cooling from 450 to 430K (entirely within the I phase). Full line: I/N transition; cooling from 436 to 416K (through part of biphase).

hysteresis is more pronounced in the case of DDA9. This is in agreement with previous reports of the influence of spacer parity on extent of supercooling at the I/N transition[3-4].

Dynamic Scans Following Isothermal Annealing

Kinetics of the demixing-homogenization stage is governed

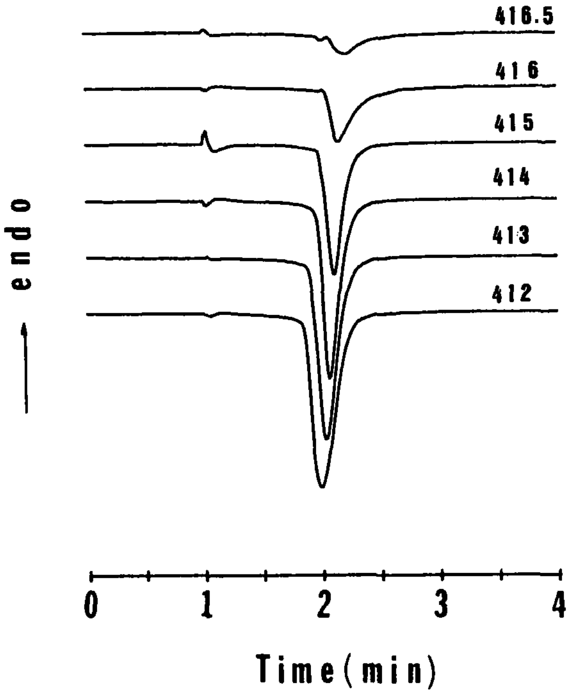

FIGURE 2. Corrected isotherms for AZA9M15,000 at several temperatures within the N+I biphase. Temperature program sequence: isothermal 1 min - cooling 1 min (20K/min) -- isothermal 2 min. Baseline: cooling in the I phase (from 440 to 420K, 20K/min).

by factors such as interfacial and diffusional properties of the system. It can be followed by DSC if the demixed domains are large enough to appear as separate entities under conditions of dynamic scanning. Isothermal evolution of the N/I peak with annealing time t_s is illustrated on fig. 5 for DDA9M4,600. After approximately 10 minutes, the inital peak splits into three, with a

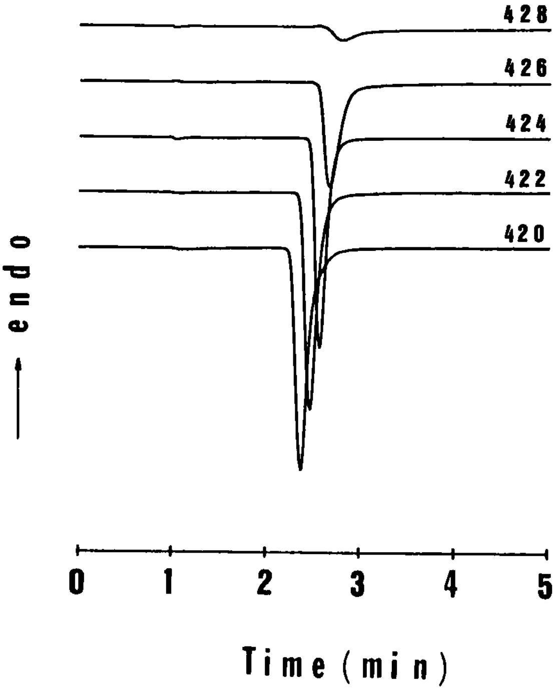

FIGURE 3. Corrected isotherms for DDA9M14,500 at several temperatures within the biphase. Temperature program: isothermal 1 min -- cooling 1.5 min -- isothermal 4.5 min. Baseline: cooling in the I phase (from 470 to 440K, 20K/min).

central peak corresponding to the broad boundary region of intermediate chain lengths illustrated of fig. 4 of reference[1]. Deconvolution shows superposition of three gaussian peaks. Isothermal evolution of their respective areas and widths at half height provides a means to follow homogenization of chain length distribution in the I and N domains. Upon homogenization, "equilibrium" demixing is

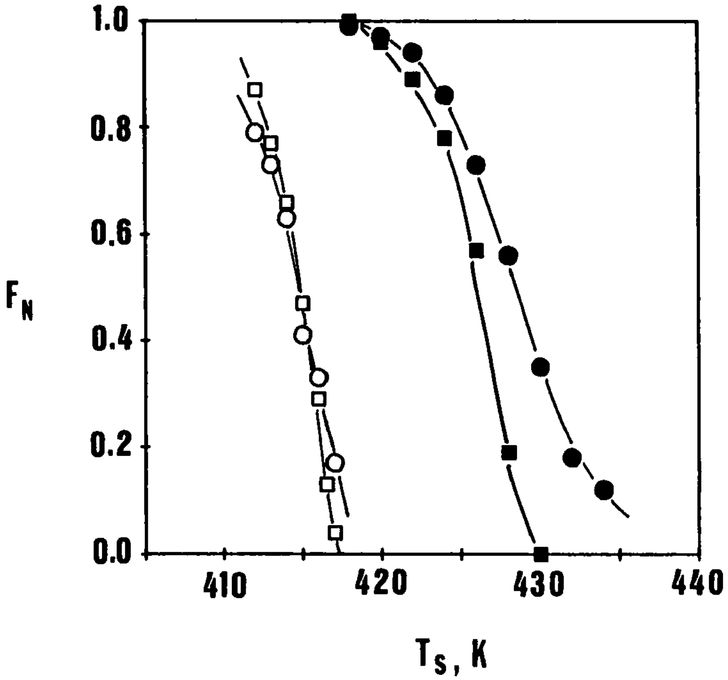

FIGURE 4. Values of f_N measured isothermally. ● DDA9M14,500 N/I transition; ■ DDA9M14,500 I/N transition; ○ AZA9M15,000 N/I transition; □ AZA9M15,000 I/N transition

reflected in a two peak morphology with the broad low temperature peak corresponding to the FI component. Note that the equilibrium biphase width delineated by the total width of the N/I peak following complete demixing is much broader than ΔT for the untreated polymer, especially at the low temperature end of the biphase

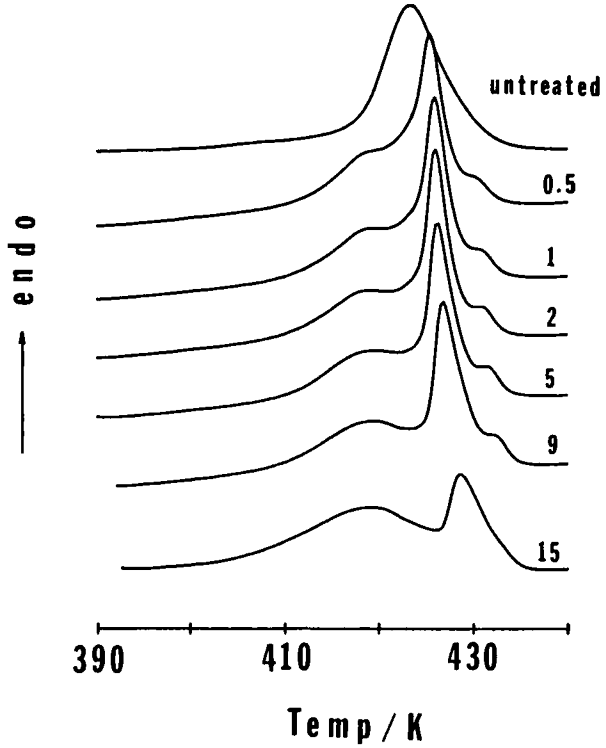

FIGURE 5. Isothermal evolution of the N/I peaks with annealing time t_s (in hours). DDA9M4,600; (T_s=419K).

(see preceding paper for a discussion of this point).

Deconvolution of peaks following complete demixing yields "equilibrium" values of f_N as listed in Table II for various annealing temperatures T_s. The total enthalpy of isotropization is constant and equal to ΔH of the untreated sample.

Data similar to fig. 5 and Table II are shown on fig. 6 and Table III for DDA9M5,200. Characteristics of the two samples are listed in Table IV. The two polymers differ mainly by the nature of their end groups, DDA9M4,600 being predominantly mesogen terminated and DDA9M5,200 predominantly spacer terminated. Dominance of aromatic end-groups is reflected in the higher values of isotropization enthalpies and temperatures[5]. Untreated DDA9M5,200 displays a broad isotropization peak which overlaps with the melting peak on heating and splits into three upon annealing, before evolving into the two peak morphology of complete demixing. For DDA9M4,600, equilibrium f_N values on heating and cooling are identical. This is not suprising, since the memory of complete demixing is so strong that a cooling scan immediately following a heating scan (as described in the experimental section) is simply its predecessor's mirror image. The same applies to DDA9M5,200. The differences observed between heating and cooling in this case are likely due to overlap of K/N and N/I peaks on heating, which necessitated simultaneous deconvolution of four peaks (see fig. 6).

On figure 7 are plotted peak maxima and minima for isotropization of FN and FI components following 15 hours of demixing at various values of T_s. Molecular segregation is reflected in the steady increase of all peak temperatures with increasing T_s. Supercooling at T_{NI} is roughly 10°, except for the lowest chain lengths. This explains why the shape of cooling peaks is generally unsymmetric, as illustrated on fig. 8, for example.

Heating and cooling scans following complete demixing in DDA9M5,200 at various values of T_s are collected on figure 8. Here again, molecular segregation is apparent in the splitting of melting and isotropization peaks.

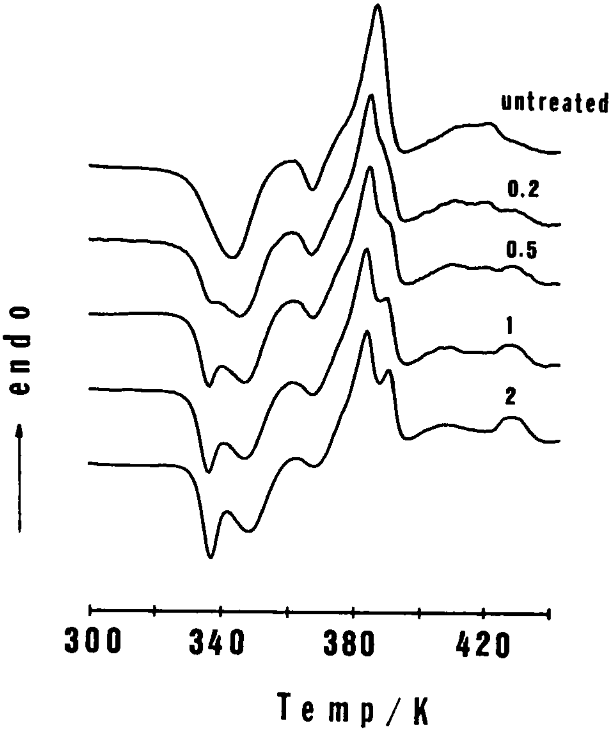

FIGURE 6. Heating scans for DDA9M5,200 following annealing in the biphase (T_s=411K; t_s as indicated, in hours).

In Table III, "equilibrium" values of f_N are listed alongside values obtained isothermally, the latter being identical to the values mesured by NMR within experimental error. "Equilibrium" values, on the other hand, are in agreement with microscopic observation, which reveals a biphase below 428K (see part III for a discussion of this point).

Fig. 9 shows evolution of the N/I peak with annealing

TABLE III Nematic fraction in sample DDA9M5,200

T_s(K)	Equilibrium f_N heating	Equilibrium f_N cooling	Isothermal f_N cooling
396	1.00	0.97	0.83
402	1.00	0.88	0.60
405	0.82	0.81	0.45
408	0.72	0.38	0.28
411	0.34	0.32	0.08
414	0.27	0.23	0
417	0.18	0.16	-
420	0.11	0.12	-
423	0.03	0.05	-
426	-	0.03	-

TABLE IV Characterization of samples DDA9M4,600 and DDA9M5,200

	$\overline{M}_w/\overline{M}_n$	fraction of aromatic end groups	ΔH_{IN}(cal/g)	T_{IN}(K)
DDA9M5200	1.5	0.2	-3.24	406.4
DDA9M4600	1.4	0.8	-3.46	412.5

time for AZA9M15,000 at T_s=416K (isothermal f_N=0.3). Since the biphase is inherently narrower in AZA9 than in DDA9[1], it is not suprising to see a smaller peak separation in the latter. Molecular segregation, however, is clearly illustrated by microscopy[1] and by the evolution of FN and FI peak maxima with T_s illustrated in Table V. Deconvolution is hindered by the unsymmetric shape of the peaks.

TABLE V Evolution of T_{NI} and T_{IN} peaks with annealing temperature T_s (AZA9M8,000;t_s=5 hours)

	T_{NI}(K)	T_{IN}(K)
untreated	415.3	411.2
T_s=413	412.7 and 417	410.4 and 412.4
T_s=415	414.5 adn 418.5	410.8 and 414.7
remixed*	415.7	411.6

* remixed by holding 12 hours in the pure N phase at 380K (following demixing at 415K).

Homogeneity of the Pure I and N Phases

Fig. 10 shows evolution of the I/N peak of DDA9M3,000 as a function of annealing time in the pure I phase (at 15° past $(T_2)_N$). The sample had been previously kept for 60 min. approximately in the middle of the biphase (incomplete demixing). Progressive homogenization of the I phase is apparent, but the "untreated" peak is not recovered, although molecular mass was low and demixing deliberately incomplete. If one assumes that self diffusion coefficients in the pure I phase vary as M^{-2}, one must expect homogenization of higher masses to be considerably slower[6].

The shear thinning in the I phase that is reported in

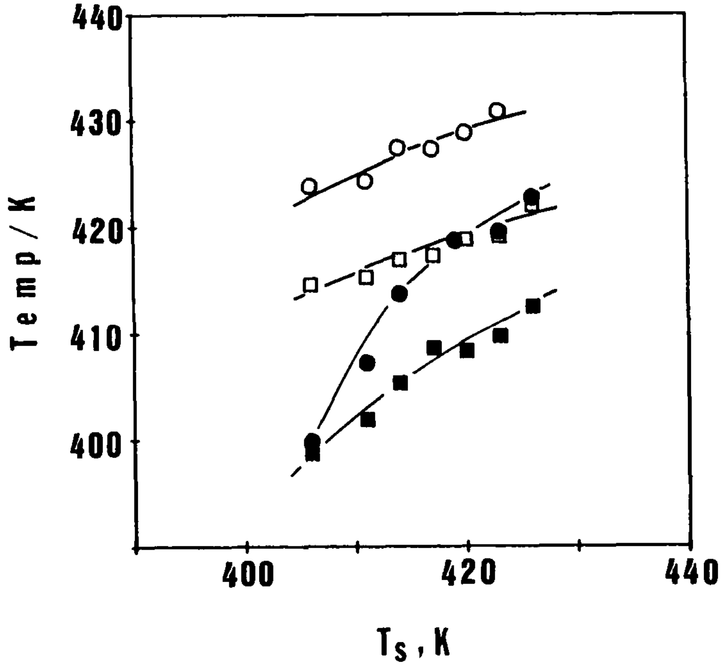

FIGURE 7. Peak maxima (circles) and minima (squares) for isotropization of FN and FI components in DDA9M4,600 following demixing (t_s=15 hours), as a function of T_s.

rheological studies of main chain PLCs[7-8] may perhaps be explained by the memory of domain segregation illustrated here.

Figure 11 shows evolution of heating scans of DDA9M5,200 with remixing time in the pure N phase following demixing at f_N=0.32. A three N/I peak morphology appears as the

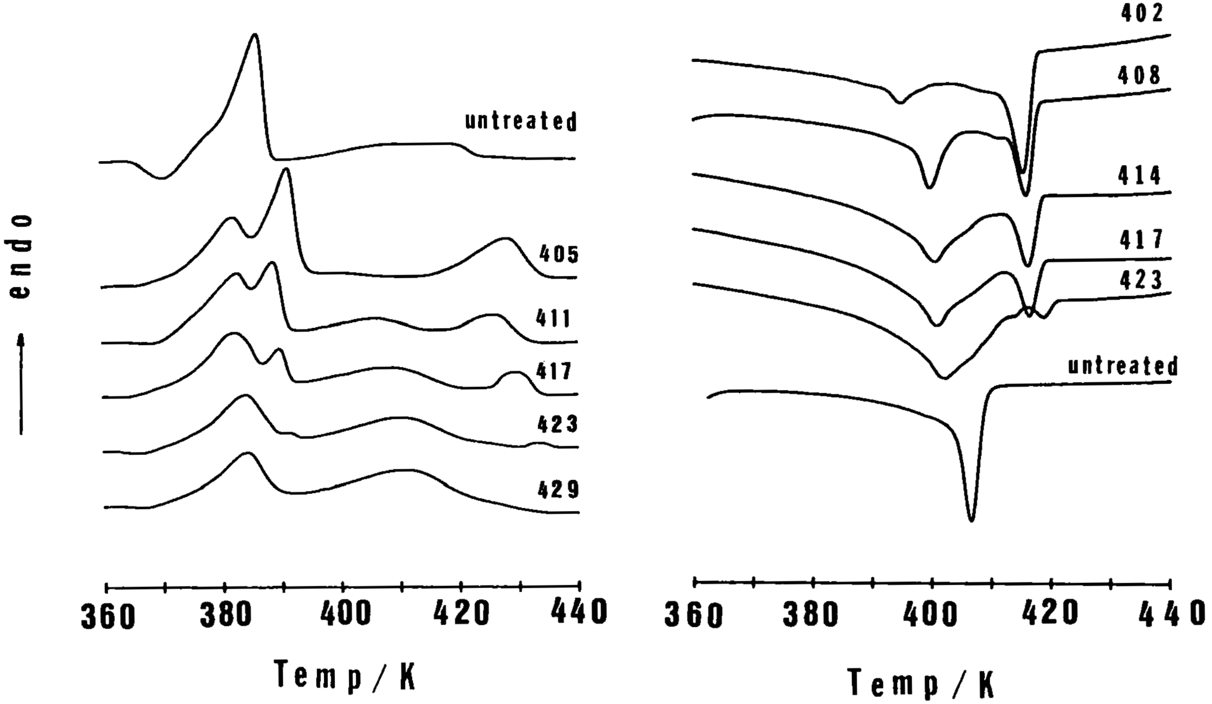

FIGURE 8. Heating and Cooling Scans. DDA9M5,200 following annealing in the biphase (t_s=15 hours; T_s in K, as indicated).

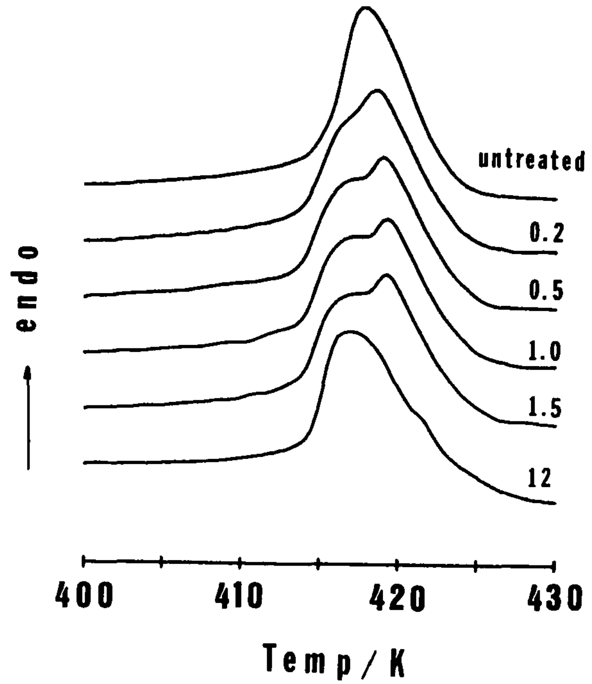

FIGURE 9. N/I transition of AZA9M15,000 (T_s=416K; t_s in hours, as indicated).

hallmark of partial remixing, just as it did in partial demixing. A symmetrical single peak appears after 43 hours and is well separated from the melting peak. Note the overlap between K/N and N/I peaks in the "untreated" sample. This suggests that the "untreated" sample (which was obtained by precipitation of the polymer from solution) is not homogeneous. Phase demixing from solution upon film casting or precipitation has not been investigated, but the above preliminary data suggest that homogeneity of chain length distribution in "untreated' or "as received" samples should not be taken for granted.

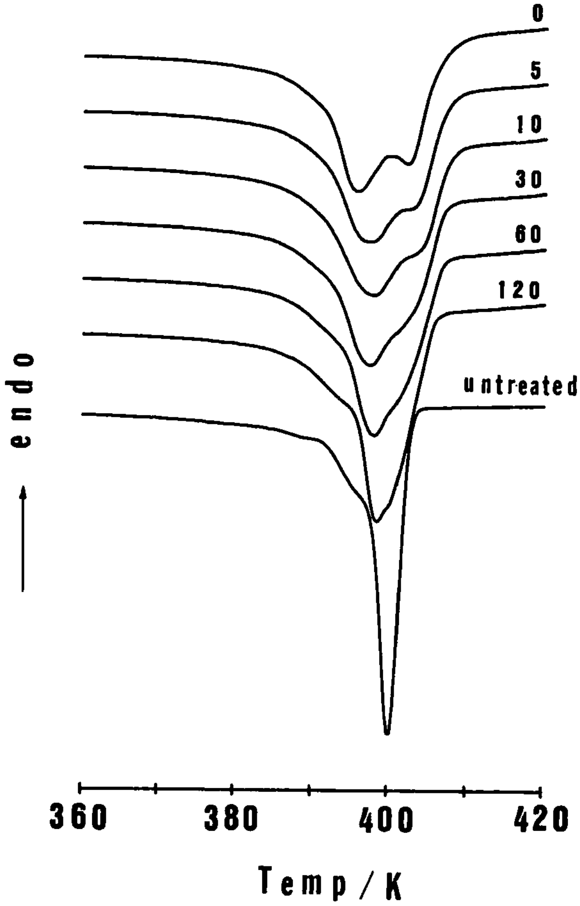

FIGURE 10. Homogenization of DDA9M3,000 in the pure I phase as a function of time (in minutes), following demixing in the biphase (T_s=403K; t_s=60 min).

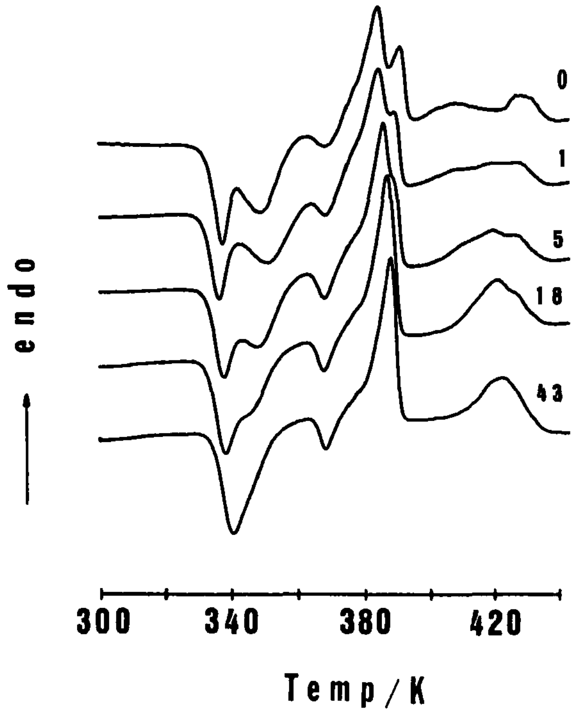

FIGURE 11. Homogenization of DDA9M5,200 in the pure N phase (at 393K) as a function of time (in hours), following demixing in the biphase (T_s=411K; t_s=2 hours).

The potential implications of the phenomena just described on morphology, textures, mechanical and rheological behavior of PLCs have already been alluded to[1]. Crystallization and melting behavior as a function of thermal history will be dicussed elsewhere. An investigation of isothermal evolution of molecular morphology in the pure N phase will be presented in Part III (see next paper).

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