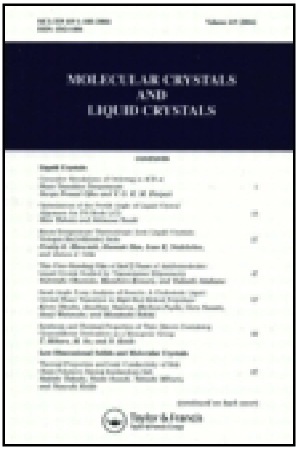

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Investigation of the Nematic-Isotropic Biphase in Thermotropic Main Chain Polymers. Homogeneity of the Pure Isotropic and Nematic Phases. Part III: NMR Study

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INVESTIGATION OF THE NEMATIC-ISOTROPIC BIPHASE IN THERMOTROPIC MAIN CHAIN POLYMERS. HOMOGENEITY OF THE PURE ISOTROPIC AND NEMATIC PHASES.
PART III: NMR STUDY.

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Abstract Nematic fraction f_N and biphase width are measured by combination of broad line PMR and DMR experiments and the data compared with microscopy and DSC results. Time dependence of f_N was monitored isothermally. Preliminary data suggest that:
i) equilibrium distribution of chain lengths between I and N components is established rapidly;
ii) supercooling at the I/N transition is of thermodynamic rather than kinetic origin. The DMR spectrum of PAAd14 is used to probe heterogeneity and isothermal evolution of molecular morphology in the pure N phase (model system of small molecules and polymers). Dynamics of homogenization of the N phase on the molecular level is extremely slow under normal laboratory conditions.

INTRODUCTION

In the two preceding papers, polarizing microscopy[1] and DSC[2] were used to delineate the nematic-isotropic biphase and to follow evolution of the gross morphology of main chain nematic polymers as a function of their thermal history in the precursor biphase. For a given thermal history within the biphase, homogeneity of chain length distribution was also monitored upon isothermal annealing of the sample in either the pure N or pure I phase. Herein, we describe broad line NMR experiments designed to probe on a more molecular level some thermodynamic and kinetic aspects of phase segregation in these polymers.

We have previously used broad line NMR to delineate the N+I biphase in DDA9 polymers[3-4]. The fraction of nematic component f_N at a given temperature was obtained by measuring the relative intensity under the narrow peak of the I component. NMR values of f_N and biphase width are compared here with the corresponding data deduced from microscopy and DSC. NMR is further used to probe molecular morphology in the pure N phase and to observe a pre-transitional range of temperatures within the homogenized I phase. Upon isothermal annealing in the biphase, macroscopic demixing of the I and N components and homogenization of their respective chain length distributions take place, as discussed previously. Microscopy and DSC provide a macroscopic approach to these processes, but offer no answer to the question of compositional equilibration within the biphase (i.e. equilibration of chain length distribution between the I and N components, following the stage of orientational ordering). Here again, NMR is used to provide some elements of answer.

EXPERIMENTAL SECTION

Sample preparation, characterization and definitions of symbols used were as in Part I[1]. Twin model compounds deuterated on the spacer and 2,2'-dimethyl-4,4'-diacetoyloxyazoxybenzene (Ac9Ac, a non mesomorphic analogue of the mesogen) were prepared as described in[5]. In the NMR experiments, the samples (~ 50-100mg of material) were contained in standard 5mm tubes sealed under vaccum. The spectra were obtained using a CXP Bruker Spectrometer working of 90MHz for proton and a Bruker WM250 working at 38.4MHz for deuterium. The values of f_N were deduced by integration of the sharp line of the isotropic component as previously described[3-4].

RESULTS AND DISCUSSION

TEMPERATURE DEPENDENCE AND ISOTHERMAL EVOLUTION OF F_N

In part II, temperature dependence of nematic fraction f_N was deduced from the relative enthalpy change associated with the nematic component and measured isothermally $[(f_N)^{DSC}_{iso}]$ or by means of dynamic scans following complete demixing of the I and N components $[(f_N)^{DSC}_{eq}]$. These results are discussed more fully here in light of a comparison with f_N values measured by NMR. On Fig. 1 are plotted the values of f_N measured for polymer DDA9M5,200 under three different conditions of thermal history. When the sample is cooled from a well homogenized I phase, results are identical within experimental accuracy, with biphase starting at 141°C. The data points plotted on heating a solid sample brutally placed in the middle of the biphase 133°C illustrate the importance of thermal history on the values of f_N. The biphase recorded on heating extends beyond the temperature range on cooling. Similar supercooling was observed by comparing $(f_N)^{DSC}_{iso}$ and $(f_N)^{DSC}_{eq}$ (Table III of ref. 2). Note that such supercooling is observed on cooling well homogenized samples.

Supercooling in well homogenized samples does not appear to be of kinetic origin: area of the isotropic peak recorded on cooling with thermal history cf Fig. 1 was followed isothermally for 24 hours at 141°C (f_N on cooling

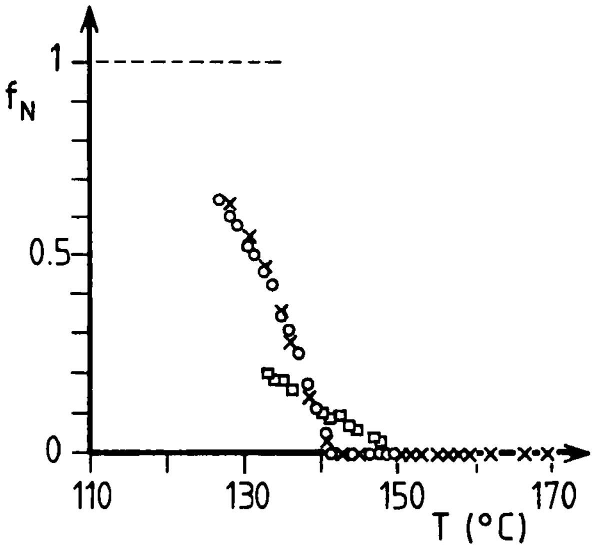

FIGURE 1. $(f_N)_{PMR}$ for sample DDA9M5,200.
○ Isotropization for 3 hours at 150°C, followed by programmed cooling with 500" between points.
× Isotropization for 45' at 170°C followed by the same cooling. □ Solid sample brutally placed in the N+I biphase at 133°C. Equilibration for 6 minutes. Data on heating with 120" between points.

=0)and 138°C (f_N on cooling =0.17) and remained constant over the time of the experiment.

On Fig. 2 are plotted the values of $(f_N)_{PMR}$ and $(f_N)_{DMR}$ measured on a 90/10(w/w) mixture of polymer DDA9M5,200 and twin model 9DDA9-d20 (deuterated on the spacer). Nematic fraction values were measured independently by PMR and DMR on cooling from a well isotropized I phase, as described in[4] . Kinetics of phase separation and reproducibility of points were checked by PMR (polymer) and DMR (model

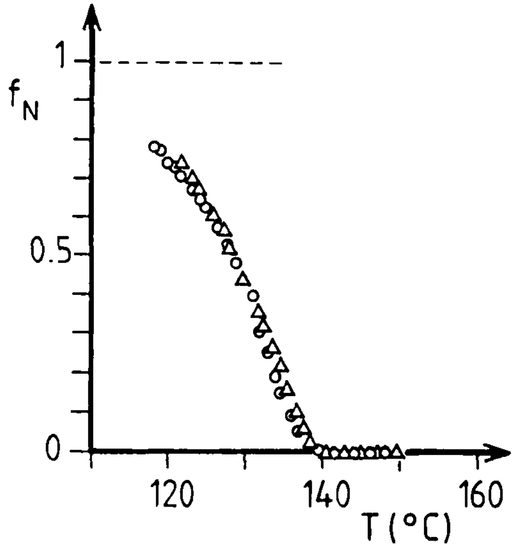

FIGURE 2. $(F_N)_{PMR}$ (○)and $(f_N)_{DMR}$ (△) for a 90/10 (w/w) mixture of DDA9M5,200 and model 9DDA9-d20. Same thermal history in both PMR and DMR runs: istropization for 3 hours at 150°C; 500" between points.

compound) as follows: i. DMR. Following equilibration in the I phase, the sample was cooled in less than a minute to 130°C and f_N followed isothermally for 24 hours with 200" between points. Value of f_N stabilized within one minute at the value measured on cooling with thermal history of fig. 1 ($f_N \approx 0.44$) and did not change subsequently with time. ii. PMR Starting from 125°C ($f_N \approx 0.63$), the sample was rapidly heated to 136°C ($f_N \approx 0.25$) and again followed isothermally for 24 hours, with 20" between spectra. The value $f_N = 0.25$ was recovered after 2' and remained unchanged. Note that agreement between f_N value on heating and cooling in this specific instance may be due to the limited range of

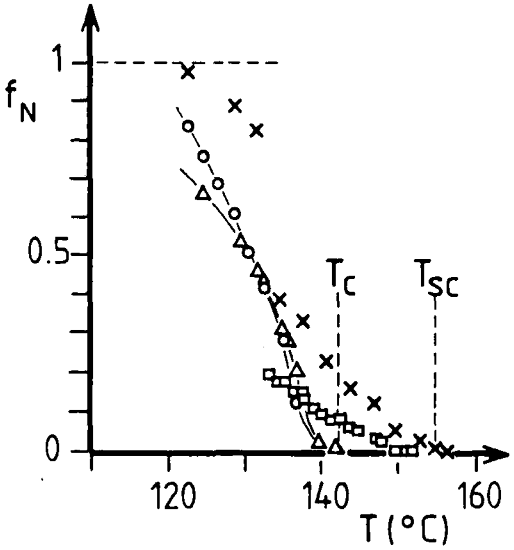

FIGURE 3. Comparison of f_N values (DDA9M5,200) derived from isothermal DSC (○), dynamic DSC (✕) and PMR (cooling (△) or heating (□) as on fig. 1).

thermal cycling within the biphase (f_N=0.63-0.25). However, all isothermal runs clearly show that compositional equilibration (i.e. equilibrium distribution of chain lengths between the I and N components of the biphase) appears to occur in less than 1-2 minutes, which is the time required for stabilization of instrument response.

On fig. 3 are collected the values for temperature dependence of $(f_N)_{PMR}$, $(f_N)^{DSC}_{iso}$ and $(f_N)^{DSC}_{eq}$ for DDA9M5,200, the last two measured as shown in the previous paper. Both $(f_N)_{PMR}$ and $(f_N)^{DSC}_{iso}$ were measured on cooling from a well isotropized I phase, whereas $(f_N)^{DSC}_{eq}$ was obtained from cooling scans immediately following heating the demixed solid phase (see Table III in ref. 2). Note that sample

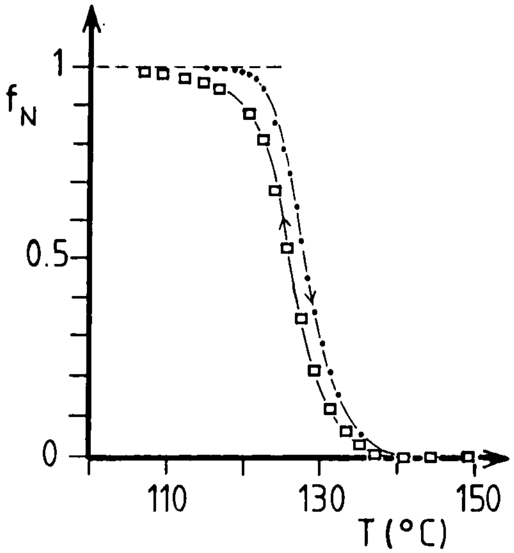

FIGURE 4. Comparison of f_N measured on heating and cooling through the biphase (DDA9M2,600). □; Cooling from a well isotropized I phase (1620" between points; ●; followed by heating from 105° (1000" between points).

DDA9M5,200 displays a biphase by microscopy until T_{sc}. To further illustrate influence of thermal history, sample DDA9M2,600 was isotropized at 150°C then cooled at 25°/min to 115°C, at the lower limit of the biphase. Following overnight annealing at 115°C, f_N was measured on heating. The values of f_N on heating were slightly shifted relative to f_N measured on cooling as shown on fig. 4.

Discrepancies between f_N on heating and f_N on cooling (from a well isotropized state) can be easily understood by considering molecular segregation processes. On heating, the longest molecules progressively concentrate in the remaining N phase and isotropize near their equilibrium

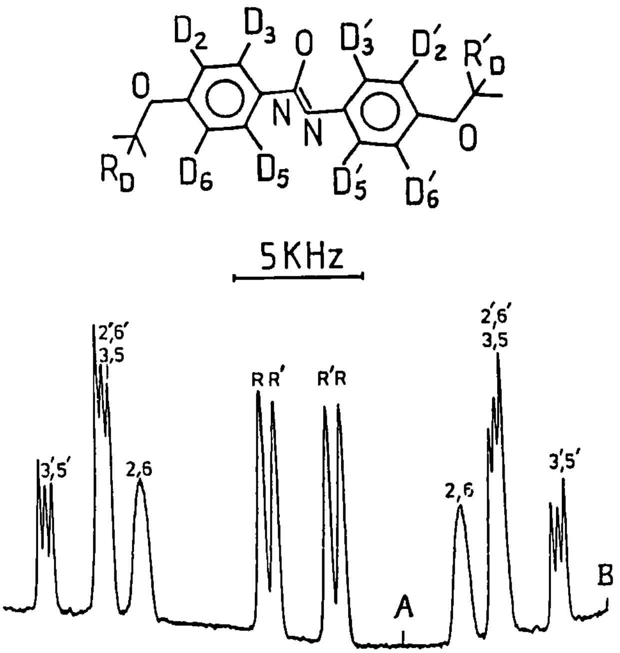

FIGURE 5. Typical DMR spectrum of neat PAAd14 in the N phase (peak assignments as [15]). The high field portion of the spectrum between A and B is used to probe homogeneity of the mixtures.

N/I transition temperature. On cooling (from a well isotropized I phase), the longest molecules are more molecularly dispersed and diluted with short chains. It is interesting to observe that f_N measured on cooling under such conditions does not change with time (over a span of 24 hours), as mentioned above. This might mean that supercooling, as illustrated on fig. 7 of ref.[2], is inherent to the nature of the I/N transition in these systems. The temperature range T_c-T_{sc} (Fig. 3) can thus be considered as a pretransitional region where fluctuations of chain

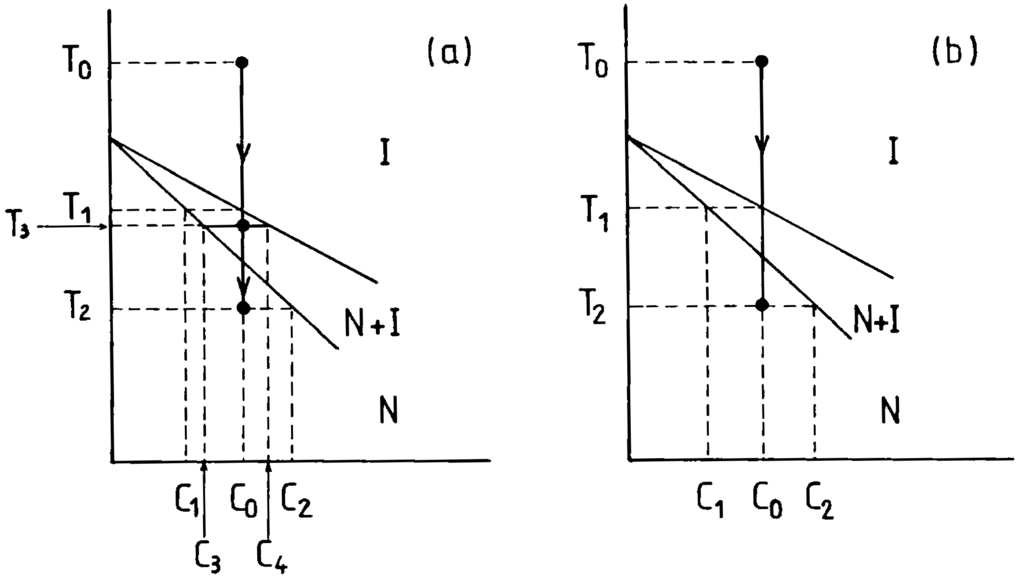

FIGURE 6. Thermal history of 85/15 (w/w) mixtures of PAAd14-Ac9Ac shown on the phase diagram; a) Isotropization at T_o=152°C for 10 minutes. Annealing for 24 hours at T_3=111°C, roughly in the middle of the biphase. Cooling to T_2=103°C, in the pure N phase; b) Cooling from T_o to T_2 at 25°C/min.

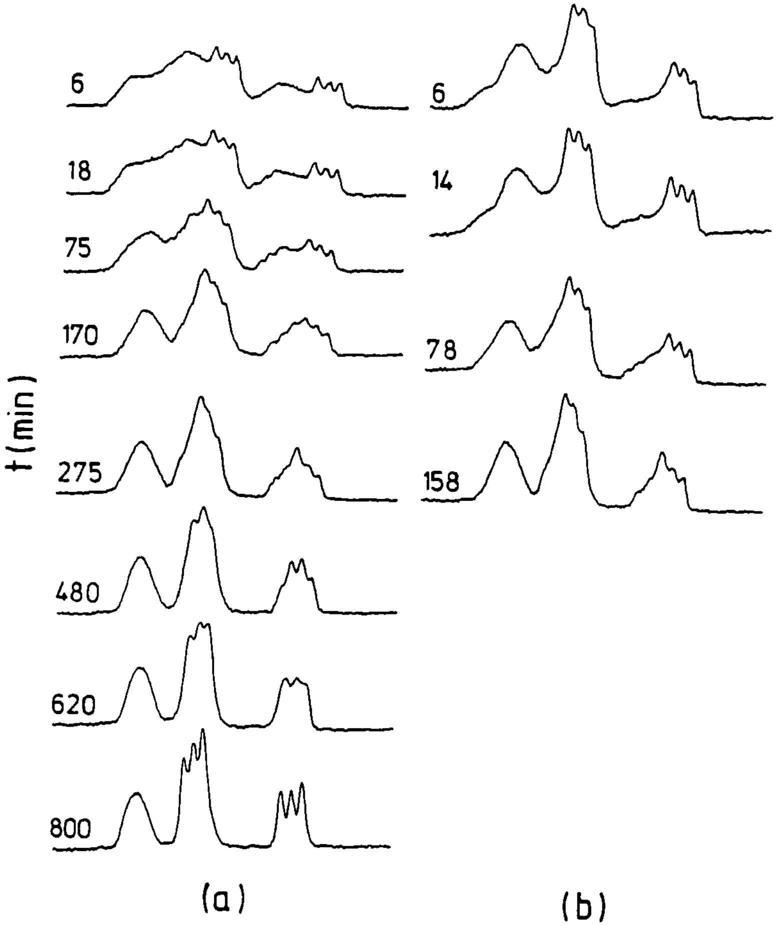

FIGURE 7a and b. Time dependence of the high field part of the DMR spectrum of PAAd14 in 85/15 (w/w) mixtures of PAAd14-Ac9Ac at 103°C. Time in minutes, thermal history corresponding to fig. 6a and b.

length distribution alone are unable to nucleate a nematic phase, starting from a reasonably homogeneous medium.

Our experiments provide no information concerning the dynamics of phase separation during the stage of

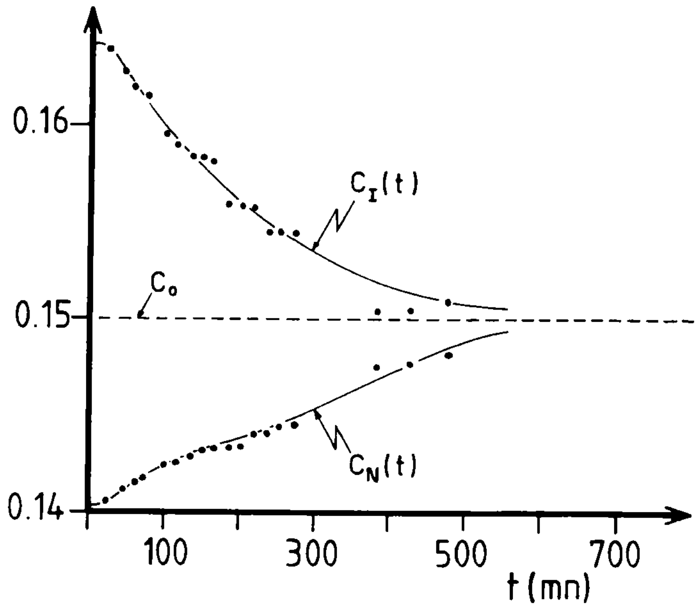

FIGURE 8. Time dependence of the mean concentrations $c_N(t)$ and $c_I(t)$ of Ac9Ac in FN and FI components homogenizing at temperature T_2=103°C (thermal history as in 6a).

orientational and conformational ordering, such as would be obtainable from time-resolved SALS scans, for example. But they do illustrate the absence of appreciable net migration of chains across I/N boundaries following initial ordering. Macroscopic demixing between the I and N components occurs without measurable change in the value of f_N.

HOMOGENEITY OF THE NEMATIC PHASE: ISOTHERMAL EVOLUTION OF MOLECULAR MORPHOLOGY

Below T_c, nematic droplets grow through a process of molecular segregation. As a result, inhomogeneity in chain length distribution will necessarily follow as the remaining I phase is progressively depleted of the longest chains. During isothermal annealing in the biphase, chain length distribution will homogenize within the demixed I and N components via a process of diffusion. This homogenization is reflected in the progressive disappearance of the boundary region of intermediate chain lengths observed by microscopy upon demixing[1] and of the intermediate isotropization peak observed by DSC[2]. In order to follow this homogenization process on a more molecular level, we have carried out NMR experiments on a model system of low mass molecules and on various polymer samples.

Model System

Binary mixtures of nematic perdeuterated p-azoxyanisole (PAAd14) and 2,2'-dimethyl-4,4'-diacetoyloxyazoxybenzene (Ac9Ac, a potentially nematic molecule comprising the mesogenic core of the polymer)were previously investigated[6]. The phase diagram was established. Order parameters of both components were measured independently through combination of DMR and PMR. In the present study, the DMR spectrum of PAAd14 was used as a probe and is illustrated on fig. 5. Note the well resolved and well separated lines. Triplet 3'5' was used to follow the distribution of concentration within the sample. Indeed, in[6] it was shown that, for each concentration and temperature, the position of this triplet is perfectly determined. Conversely, observation of distribution of positions at a fixed temperature necessarily reflects inhomogeneity of concentration.

Figures 6 and 7 schematize the experiments performed on a 85/15 (w/w) mixture of PAAd14-Ac9Ac. Experimental details are outlined in [6]. Thermal history of the samples is summarized on figures 6a and b. On figures 7a and b is shown the time dependence of the high field part of the DMR spectrum of PAAd14 in the pure N phase at 103°C, with thermal history corresponding to 6a and b, respectively. Initial spectrum 7b is observed as the superposition of a reasonably well resolved triplet and a broad peak centered at lower frequencies. Initial spectrum 7a is similar but the lower frequency peak is significantly broader.

Initial spectra 7a and b can be explained as follows. At temperature $T=T_1$ nematic droplets are nucleated with an average concentration c_1. The homogenization time of these droplets is diffusion controlled and proportional to their radius R(t), with

$$\tau_{\text{hom}}(t) = \frac{R^2(t)}{6D} \tag{1}$$

(D=Self diffusion coefficient).

As cooling proceeds along pathway 6b, these droplets grow from an isotropic phase that becomes progressively depleted in PAA. As long as $\tau^{-1}(t)$ remains inferior to the cooling rate the droplets homogenize and the resulting portion of the N phase appears as a relatively well resolved triplet. The broad distribution of frequencies, then, corresponds to the remaining portion of the N phase and is centered at lower frequencies, as its average concentration in PAA is lower.

Along 6a, cooling starts from a macroscopically demixed N+I biphase in which the concentrations of the two components have been homogenized, with concentrations c_3 and c_4 for components N and I respectively. Cooling to point T_2 in the pure N phase results in a triplet corresponding to the FN component (concentration c_3) and a relatively broad distribution of frequencies (compared to case b) corresponding to FI.

Figures 7a and b roughly illustrate a metastable nematic N_1+N_2 biphase. The dynamics of its isothermal evolution provide a model for rationalization of phenomena observed in the case of polymers. On figure 8 is shown the time dependence of the mean concentration of Ac9Ac in FN and FI components during homogenization at temperature $T_2=103°C$, following the evolution illustrated on figure 6a. The two concentrations tend toward their common equilibrium value in nearly exponential fashion. A mean homogenization time $\tau_{1/2}$ may be defined as the time at which the deviation from equilibrium concentration is divided by two ($\frac{1}{2}\,[c(o)-c_o]$). This time is of the order of 200 minutes and is compatible with a diffusion controlled homogenization of a macroscopically demixed system. Applying eq.1 with $R \sim 3.5$mm (average radius of the sample in the NMR tube) leads to a diffusion coefficient $D \sim 2\times10^{-6}\,cm^2sec^{-1}$, in agreement with literature value of the self diffusion coefficient in nematic PAA at 103°C[7].

Remixing of components and homogenization of concentration are slow even after a rapid cooling (figure 7b): compare spectrum at 275min in figure 7a with spectrum obtained at 158min. in fig. 7b. Clearly, such molecular homogenization will be orders of magnitude slower in the case of polymers. Since $D \propto \gamma^{-1}$ (where γ is an average viscosity) and $\tau_{\frac{1}{2}} \propto D^{-1}$, homogenization times are expected to be proportional to the average viscosity of the medium. In the case of our polymer this viscosity is about 5 to 8 orders of magnitude higher than in PAA[8-13].

Polymers

Save for kinetics of homogenization, polymers are treated by exact analogy with the model system, provided the concentration gradient formed upon crossing the phase diagram is replaced with a gradient of chain length distribution. Due to molecular segregation, nematic droplets of polymer will grow by successive addition of roughly concentric shells of shorter and shorter average chain length. As a biphasic region must inevitably be crossed to reach a pure N phase, on heating or cooling, the nematic phase must inevitably segregate into metastable domains. Morphology of the N phase, and of the resulting solid, will depend on thermal history. Progressive homogenization of chain length distribution may be revealed as a time dependent rheological behavior upon isothermal aging of the mesophase. Evolution of optical textures from dense disclination lines to loosely threaded textures has been reported by several authors[14] and may perhaps be the result of such a homogenization.

Molecular homogeneity and dynamics of remixing in the pure N phase of polymer were tracked by following the DMR spectrum of PAAd14 dissolved at low concentration in AZA9 or DDA9, and acting as a probe. On fig. 9a and b is shown the time evolution of the spectrum of PAAd14 in AZA9 polymer, following thermal history corresponding to 6a and 6b. Two fractions ($\frac{\overline{Mw}}{\overline{Mn}} \leq 1.1$) of mass 7,300 and 3,100 were mixed with PAAd14 in ratios 45/45/10 (w/w). Initial peak 9a, roughly a superposition of two peaks corresponding to FN and FI components, is slightly narrower after 3 hours, but the system is far from homogeneity. Initial spectrum 9b represents a more homogeneous morphology which evolves slowly, as illustrated by the progressive appearance of a triplet. This triplet is still far from being well resolved after 60 hours.

By comparing time scale of homogenization and viscosity of polymer (fig. 9b) and model system (fig. 7b), one can estimate an order of magnitude for the dimensional scale of heterogeneity in this system. Taking a ratio of $\sim 10^6$ between viscosities and ~ 30 between time scales an average value $\rho \sim 20\mu$ is estimated.

On fig. 10 is shown the spectrum of PAAD14 in DDA9M4,000 (10/90 mixture) as the sample is heated from 118°C (pure N phase) to 146°C in the pure I phase. Thermal history corresponds to fig. 6a. The spectrum at 118°C appears as a superposition of a triplet corresponding to the FN component and a broad peak corresponding to the FI component. Peak separation is more pronounced than in AZA9 since concentration gradients are larger, due to an intrinsically larger biphasic gap, as discussed in[1].

No evolution was observed at 118°C (over a period of 24 hours). Evolution of the spectrum during isotropization accurately reflects previous microscopic observation, namely sequential isotropization of the peaks corresponding to FI and FN components. The area corresponding to the triplet of the FN component remains constant between 118 and 127°C, i.e. until disappearance of the broad FI peak.

SUMMARY

The nematic phase of main chain PLCs is composed of metastable domains that result from molecular segregation by chain length, on heating and cooling. Thermal history in the precursor N+I biphase determines the initial morphology of the resulting I or N phase. Dynamics of

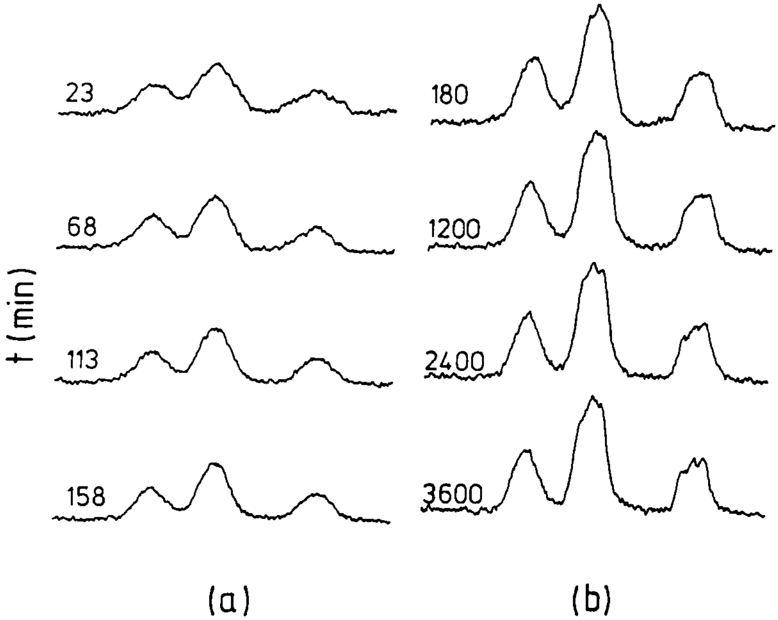

FIGURE 9. Time dependence of the high field portion of the DMR spectrum of PAAd14 in AZA9. Thermal history: a) Isotropization at 151°C for 3 hours; annealing 4.5 hours at 133°C, roughly in the middle of the biphase; cooling to 115°C in 2 min. b) Isotropization at 151°C followed by cooling to 115°C in 2 min.

homogenization of the N phase on the molecular level is extremely slow on the time scale of normal laboratory conditions.

Juxtaposition of microscopy, DSC and NMR experiments provides a reasonable correlation between macroscopic and molecular interpretation of data. Save for time scale of events, kinetics of homogenization can be treated by exact analogy with a model system of small molecules in which

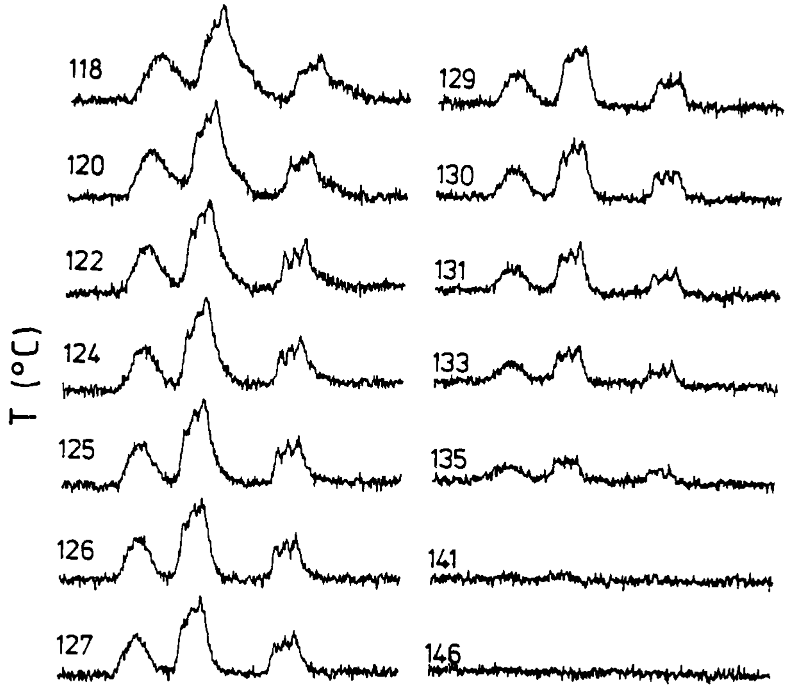

FIGURE 10. Evolution of the DMR spectrum of PAAd14 in DDA9M4,000 (10/90) during isotropization. Thermal history: isotropization at 150°C for 1.5 hours; annealing 14 hours at 131.5°C, roughly in the middle of the biphase; cooling to 118°C in the pure N phase, followed by heating to 146°C, with 100 min. between spectra.

the phase diagram and molecular morphology were investigated by combination of DMR and PMR spectroscopy.

ACKNOWLEDGEMENT

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