Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Formation of a Banded Texture in Solutions of Liquid-Crystalline Polymers 11. Poly(n-Hexylisocyanate) in Toluene

E. Marsano[a]; L. Carpaneto[a]; A. Ciferri[a]; Y. Wut[a]
[a] Istituto Chimica Industriale, University of Genoa, Genoa, Italy

To cite this Article Marsano, E. , Carpaneto, L. , Ciferri, A. and Wut, Y.(1988) 'Formation of a Banded Texture in Solutions of Liquid-Crystalline Polymers 11. Poly(n-Hexylisocyanate) in Toluene', Liquid Crystals, 3: 11, 1561 — 1567

To link to this Article: DOI: 10.1080/02678298808086695

URL: http://dx.doi.org/10.1080/02678298808086695

Liquid Crystals, 1988, Vol. 3, No. 11, 1561-1567

Formation of a banded texture in solutions of liquid-crystalline polymers

II. Poly(*n*-hexylisocyanate) in toluene

by E. MARSANO, L. CARPANETO, A. CIFERRI and Y. WU†
Istituto Chimica Industriale, University of Genoa, I-16132 Genoa, Italy

(*Received 7 January 1988; accepted 12 June 1988*)

The kinetics of band formation has been followed during the relaxation of anisotropic solutions of poly(*n*-hexylisocyanate) in toluene previously subjected to a shear rate, $\dot{\gamma}$, for a time t_s. There is a threshold at low $\dot{\gamma}$, or $\dot{\gamma}t_s$, below which bands do not appear (formation time $t_b \rightarrow \infty$). Past the threshold, t_b decreases with either $\dot{\gamma}$ or t_s, and eventually bands are seen immediately after stopping the flow ($t_b = 0$). However, for still larger $\dot{\gamma}$, particularly for the more viscous solutions and when the flowing solution is well oriented, t_b may increase again. The results are similar to those already reported for hydroxypropylcellulose in water and support a previous suggestion for the origin of the banded texture.

1. Introduction

The occurrence of bands perpendicular to the shear direction in lyotropic or thermotropic liquid crystals has been well characterized with regard to their optical features and the orientation of the chain axes. However, the mechanism responsible for the banded texture is still unknown [1–10]. In a previous communication [11] we have suggested that if a flowing liquid crystal of adequate zero shear viscosity can be well oriented (so as to approach the monodomain described by Asada *et al.* [12]) bands will not appear during flow, but only upon relaxation after a considerable time (t_b) is allowed to elapse. Buckling might cause the observed dispersion of molecular axes preferentially in the shear plane, with angles between 45° and 8° to the direction of shear [2, 6]. Although an out-of-plane component also occurs [4], the dispersion in the shear plane is in accord with the analysis of the Leslie coefficients in polymer nematics put forward by Marrucci [10].

However, if good orientation is not attained (or the zero shear viscosity is too low) the situation is more complicated [11]. In these cases bands may be seen even as $t_b \rightarrow 0$, and it can be argued [7, 11] therefore that they might occur even *during* flow (so far only Kiss and Porter [6] have stated unambiguously that bands occur in flowing solutions of poly (γ-benzyl-L-glutamate) dissolved in m-cresol in the shear rate region where negative normal stress differences occur). In the case where $t_b \rightarrow 0$ it can be argued simply that incomplete orientation or a large concentration of defects or a low viscosity accelerate the relaxation mode. However, particularly in view of the results of Kiss and Porter [6], it is also possible that inhomogeneity promotes flow instability and hence the occurrence of bands even during flow [11]. Marrucci *et al.* [13] recently reported that for hydroxypropylcellulose (HPC) in water the

---

† On leave from Institute of Chemistry, Academia Sinica, Beijing, China.

deformation threshold for observing bands during relaxation at a given shear rate decreases strongly with sample thickness. They suggest that this effect is indicative of an instability possibly occurring during flow. These suggestions are not inconsistent with our own [11].

In this paper we report band formation in tolulene solutions of poly(*n*-hexylisocyanate) (PHIC). We might have expected significant differences between the behaviour of HPC and PHIC since these polymers differ greatly in their chain rigiditiy [4]; the persistence length of HPC in water [15] is 65 Å and that of PHIC in toluene [16] is 310 Å. The results obtained reveal, however, that the behaviour of PHIC is similar to that of HPC thus supporting the concention of a general mechanism which is not directly affected by the polymer type.

2. Experimental

Two samples of poly(*n*-hexylisocyanate) were prepared following the procedure described by Shashoua *et al.* [17]. The intrinsic viscosity was measured in toluene and the corresponding molecular weight was obtained using the relationship $|\eta| = 2{\cdot}48 \times 10^{-5} M_v^{-1{\cdot}05}$ derived by Berger and Tidswell [18]. Anisotropic solutions were prepared as described previously [16] using concentrations, C_p, of 40·0 (±0·1) g/100 g solution for both samples *A* and *B* (see the table). In terms of the phase diagram [16] at these concentrations PHIC in toluene attains a single mesophase; values of the critical concentration C_p' at which the anisotropic phase appears are included in the table. The solutions remain homogeneous upon centrifugation at about 5000 rpm for approximately 12 h confirming the occurrence of a single mesophase. Exploration of still larger values of C_p is precluded by gelation. Band formation was investigated using a Weissenberg rheogoniometer equipped with cone and plate made of highly polished glass. The apparatus and the TV device for observing and recording the texture have been previously described in detail [11]. The thickness of solution observed was 500 μm, and different layers could be observed within that gap (with our apparatus it is not easy to explore the effect of the overall thickness). Beside recording the appearance of the field (extinghished for a well oriented solution under shear, or with bands forming upon relaxation), the time for bands to appear, t_b, was determined using as zero time as that at which rotation was stopped by switching off the power. t_b was determined as a function of the previously applied shear rate, $\dot{\gamma}$, and shear time, t_s. The limits of reproducibility have already been discussed [11]. The texture on cast films was analysed with a Reichert polarizing microscope.

Characteristics of the samples investigated.

Solution code	Solute	$\lvert\eta\rvert$/ dl g^{-1}	M_w	$C_{p'}'$ (per cent)	$C_{p'}$ (per cent)
A-1	PHIC A	2·62	61,000	24·7	40·0
B-1	BHIC B	6·41	131,000	21·9	40·0

3. Results

The plot of the time for band formation versus the time of shear at a constant $\dot{\gamma}$ is given in figure 1 for two PHIC solutions having the characteristics listed in the table. The trend shown by these data appears entirely similar to that previously observed for HPC in water [11]. At a given $\dot{\gamma}$ an increase in the shear time causes a decrease of t_b

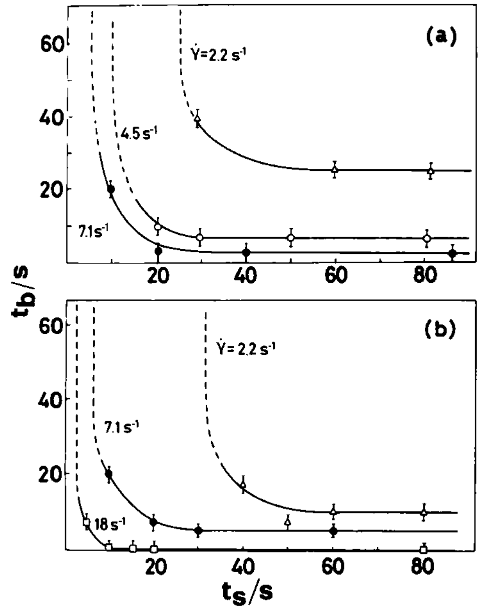

Figure 1. Variation of the time for the appearance of the bands, t_b, with the time of shear, t_s, at the shear rate, $\dot{\gamma}$, indicated. (*a*) Solution A-1 (PHIC A$|\eta|$ = 262 dl/g); (*b*) solution B-1 (PHIC B$|\eta|$ = 6·41 dl/g).

until a plateau value, which is reduced when $\dot{\gamma}$ is increased or when the molecular weight (or viscosity) increases. The shear time needed to reach the plateau value is also considerably shortened when $\dot{\gamma}$ increases, but is not significantly different for the two solutions. The dashed regions of the curves in figure 1 show the lowest values of t_s at which bands do not form at a given $\dot{\gamma}$. Since the experimental evaluation of these threshold times is not easy, we dashed these regions in order to indicate that a certain error must be taken into account.

The plot of t_b versus $\dot{\gamma}$ (see figure 2) illustrates the approach of t_b to zero (bands appear immediately when the flow is stopped) at a value of $\dot{\gamma}$ which decreases the longer the shear time. Since the product $\dot{\gamma}t_s$ characterizes the total deformation, a plot of t_b versus $\dot{\gamma}t_s$ is given in figure 3. For values of the product $\dot{\gamma}t_s$ smaller than about 50, t_b increases dramatically and bands may be assumed not to form. Clearly, band formation requires a threshold of deformation which is still a function of $\dot{\gamma}$. The latter effect is shown better by data obtained by Marrucci *et al.* [13] which cover a wide range of shear rates. Finally, in figure 4 we plot the deformation $\dot{\gamma}t_s$ versus $\dot{\gamma}$ in analogy to the plot given by Marrucci *et al.* [13] which again illustrates the threshold for band formation. Included in figure 4 are data reported by Marrucci *et al.* [13] for HPC in water for a sample thickness comparable to our own. It is difficult to detect significant differences between the behaviour of PHIC and that of HPC reported by us [11] or by Marrucci *et al.* [13].

In the cases discussed here, the observation of the flowing solution under cross-polars reveals that:

for $\dot{\gamma} < 2{\cdot}2\,s^{-1}$: bright areas move along the optical field (see figure 5(*a*));

for $2{\cdot}2 < \dot{\gamma} < 11\,s^{-1}$: incompletely darkened background remains even after 200 s;

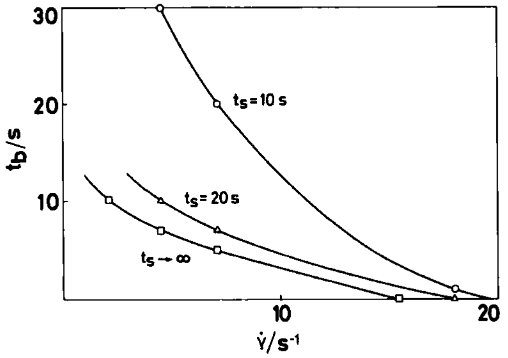

Figure 2. The data given in figure 1 (*b*) for solution B-1 plotted as t_b against $\dot{\gamma}$.

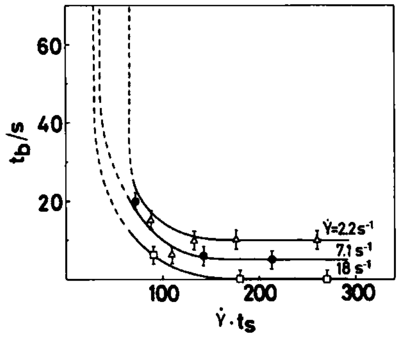

Figure 3. The data appearing in figure 1 (*b*) for solution B-1 plotted at t_b versus $\dot{\gamma}t_s$.

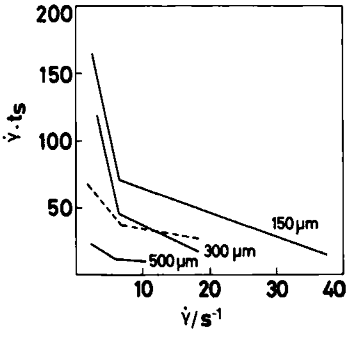

Figure 4. The variation of the deformation $\dot{\gamma}t_s$ with $\dot{\gamma}$ for solution B-1 (dashed line) indicating the threshold for band formation. Full lines indicate the results of Marrucci *et al.* [13] for HPC in water and the indicated sample thickness.

for $\dot{\gamma} > 11\text{–}18\,\mathrm{s}^{-1}$: the field is homogeneously dark as expected for a well oriented solution

The appearance of bands when the field is switched off is illustrated in figures 5 (*b*), (*c*). Figure 5 (*b*) refers to a solution after the field has been switched off while figure 5 (*c*) refers to a film obtained by rapid casting in water of the solution which had just been sheared. The precursor texture which was noticed for HPC is not evident for PHIC. Although in PHIC solutions bands appear to be rather well defined the very moment they appear, they can become slightly sharper in a few seconds, confirming,

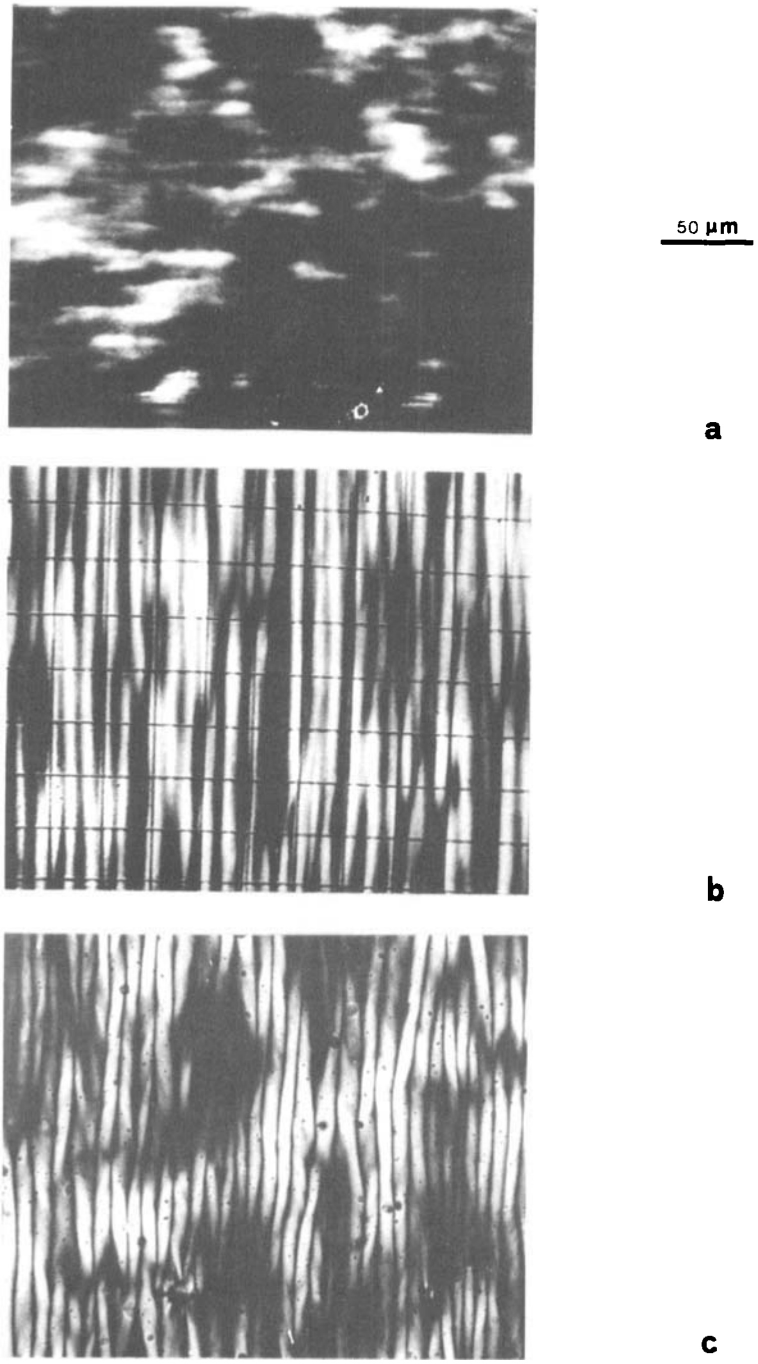

Figure 5. Typical banded texture: (*a*) solution B-1 under shear at $\dot{\gamma}$ of $2{\cdot}2\,s^{-1}$; (*b*) solution B-1 sheared at $\dot{\gamma}$ of $100\,s^{-1}$; (*c*) frozen texture for a film cast from B-1 solution following switch off.

on a faster time scale probably due to lower viscosity, the evolution already reported for HPC [11]. The lower viscosity can also be considered responsible for the faster relaxation of the banded texture of PHIC through the 500 μm layer. The frozen texture appears very regular (see figure 5 (*c*)) and entirely similar (spacing in the order of 7–10 μm) to that reported by investigators who worked on films obtained by cooling thermotropic polyesters. The optical analysis under polarized light of these films, carried out by rotating the sample around the polarization axis, reveals, as already reported by Navard [7], a gradual merging of black bands two by two until a maximum extinction is found alternatively for an angle of $\pm 20°$ between the shear direction and the molecular axis. The projection of the molecular axis on the film plane should consequently follow a sort of soft corner zig-zagging (serpentine) path with an angle of 20° respect to the shear direction.

In analogy with observations reported for HPC [11] if $\dot{\gamma}$ values considerably larger than those reported in figure 1 are used, the more viscous solution (B-1) will maintain its good orientation, as evidenced by a dark background, for a considerable time after the field is switched off. In other words, t_b will remain equal to zero only in a discrete range of $\dot{\gamma}$ (cf. figures 1 and 2), but *will eventually increase again.* Owing to the lower value of C_p and the zero shear viscosity of the present system ($\eta \approx 10^2$ P) with respect to HPC (for the latter $C_p \approx$ 50–54 per cent, $\eta \approx 10^3$ P), values at which the latter effect is observed are considerably larger for PHIC than for HPC, and the corresponding t_b values are lower for PHIC than for HPC. In particular, when $\dot{\gamma} > 2000\,\mathrm{s}^{-1}$, solution B-1 is extremely well oriented and bands appear only 5–10 s after the field is switched off (a comparable effect occurred for high molecular weight HPC [11] already when $\dot{\gamma} > 10\,\mathrm{s}^{-1}$ with t_b up to 60 s).

4. Conclusions

The kinetics of band formation during relaxation for PHIC is similar to that previously observed for HPC; the different flexibility of the two chains does not appear to play a direct role. Residual differences between values of t_b for two different PHIC samples and between PHIC and HPC appear to be related primarily to differences in the bulk viscosity. The latter is controlled by the molecular weight and by the concentration. The concentrations were larger for HPC than for PHIC due to the larger critical concentration of the former, which in turn is a manifestation of the larger flexibility of HPC.

In agreement with Asada *et al.* [12] we find that at sufficiently high $\dot{\gamma}$ ($\approx 2000\,\mathrm{s}^{-1}$) a well oriented (monodomain) sample can be formed. Under such conditions bands certainly do not occur under flow, and appear with a considerable delay when the flow is stopped ($t_b \approx 10$ s). The bands are, therefore, the result of the relaxation of the monodomains. When the sample is less oriented, the bands may not form at all ($t_b \rightarrow \infty$) at low $\dot{\gamma}$ or $\dot{\gamma}t_s$. However, past a threshold value, t_b is finite and decreases to zero with increasing $\dot{\gamma}$ or $\dot{\gamma}t_s$. Should the observation [6] of bands occurring during flow be confirmed, we believe that a flow instability is involved.

We express our appreciation to Professors T. Asada, E. Bianchi and G. Marrucci for useful advice.

References

[1] Shouxi, C., Chenfen, L., and Liying, C., 1981, *Gaofenzi Tongxun*, **6**, 424.
[2] Horio, H., Ishikawa, S., and Oda, K., 1985, *Appl. Polym. Symp.*, **41**, 269 (1983, U.S. Japan Seminar on Polymer Liquid Crystals, Kyoto).

[3] ZACHARIADES, A. E., NAVARD, P., and LOGAN, J. A., 1983, *Molec. Crystals liq. Crystals*, **110**, 93.

[4] VINEY, C., DONALD, A. M., and WINDLE, A. H., 1985, *Polymer*, **26**, 870.

[5] GRAZIANO, D. J., and MACKLEY, M. R., 1984, *Molec. Crystals liq. Crystals*, **106**, 73.

[6] KISS, G., and PORTER, R. S., 1980, *Molec. Crystals liq. Crystals*, **60**, 267.

[7] NAVARD, P., 1986, *J. Polym. Sci. Polym. Phys. Ed.*, **24**, 435.

[8] VINEY, T., and WINDLE, A. H., 1986, *Polymer*, **27**, 1325.

[9] HORIO, H., KANEDA, T., ISHIKAWA, S., and SHIMAMURA, K., 1984, *J. Soc. Text. Cellul. Ind. Japan*, **285**, 40.

[10] MARRUCCI, G., 1985, *Pure appl. Chem.*, **57**, 1535.

[11] MARSANO, E., CARPANETO, L., and CIFERRI, A., 1988, *Molec. Crystals liq. Crystals*, **158**, 267.

[12] ASADA, T., KODA, T., ONOGI, S., 1981, *Molec. Crystals liq. Crystals*, **68**, 231. ONOGI, S., and ASADA, T., 1980, *Rheology*, Vol. I, edited by G. Astarita and G. Marrucci (Plenum).

[13] MARRUCCI, G., GRIZZUTI, N., and BUONARIO, A., 1987, *Molec. Crystals liq. Crystals*, **153**, 263.

[14] CIFERRI, A., 1987, *Developments in Oriented Polymers*, Vol. 2, edited by I. M. Ward (Elsevier).

[15] CONIO, G., BIANCHI, E., CIFERRI, A., TEALDI, A., and ADEN, H., 1983, *Macromolecules*, **16**, 1264.

[16] KRIGBAUM, W. R., HAKEMI, H., CIFERRI, A., and CONIO, G., 1985, *Macromolecules*, **18**, 973.

[17] SHASHOUA, V. E., WEENEY, W. S., and TIEZ, P. F., 1960, *J. Am. chem. Soc.*, **82**, 866.

[18] BERGER, M. N., and TIDSWELL, B. M., 1943, *J. Polym. Sci. Polym. Symp.*, **42**, 2603.