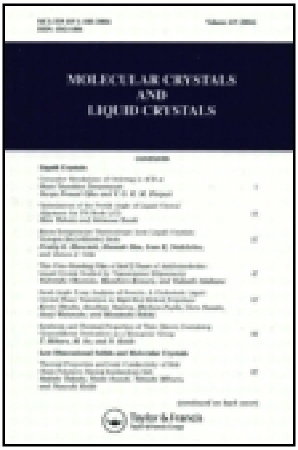

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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E. Marsano [a], L Carpaneto [a] & A. Ciferri [a]

[a] Istituto di Chimica Industrials, University of Genoa, 1-16132, Genoa, Italy

To cite this article: E. Marsano , L Carpaneto & A. Ciferri (1989): Formation of a Banded Texture in Solutions of Liquid Crystalline Polymers: III. Poly(ρ-Benzamide) in N,N Dimethylacetamide/Lithium Chloride, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 177:1, 93-99

To link to this article: http://dx.doi.org/10.1080/00268948908047773

Mol. Cryst. Liq. Cryst., 1989, Vol. 177, pp. 93–99
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Printed in the United States of America

Formation of a Banded Texture in Solutions of Liquid Crystalline Polymers: III. Poly(*p*-Benzamide) in *N*,*N* Dimethylacetamide/Lithium Chloride

E. MARSANO, L. CARPANETO and A. CIFERRI
Istituto di Chimica Industriale, University of Genoa, I-16132 Genoa, Italy

(*Received February 2, 1989; in final form June 24, 1989*)

We present new data on the kinetics of band formation during the relaxation of anisotropic solutions of poly(*p*-benzamide) in dimethyl acetamide + LiCl. The new data, along with previous reports for hydroxypropylcellulose and poly(*n*-hexylisocianate) solutions, reveal that the band formation time t_b decreases with solution viscosity at low shear rates $\dot{\gamma}$. The occurrence of a new effect is manifested by a minimum in the t_b vs $\dot{\gamma}$ dependence. A description in terms of current theoretical concepts is presented.

INTRODUCTION

The kinetics of formation of a banded texture during the relaxation of anisotropic solutions of hydroxypropylcellulose (HPC) in H_2O, and of poly(n-hexylisocyanate) (PHIC) in toluene, has been reported in parts I and II of this series.[1,2] The kinetic parameter considered, t_b, was the time necessary for the detection, under polarized light, of black and bright lines perpendicular to the shear direction starting from the moment at which the field (gradient $\dot{\gamma}$ and deformation $\dot{\gamma}\ t_s$) was switched off.

For both HPC and PHIC, the variation of t_b upon increasing shear time t_s, $\dot{\gamma}$ or $\dot{\gamma}t_s$ consists of three distinct regions: a threshold below which bands do not form ($t_b \rightarrow \infty$); a region where t_b decreases with t_s, $\dot{\gamma}$ or $\dot{\gamma}t_s$ until eventually t_b = 0 (bands seen immediately after stopping flow); a region, at still larger gradients, in which t_b increases again.

Detailed studies of the optical features and of the orientation of chain axes within the bands have been reported by others for both lyotropic and thermotropic liquid crystals.[3-8] In particular, molecular axes are dispersed in the shear plane following a serpentine pattern with angles between 45° and 8° to shear direction. This orientation is often retained during solidification.

Theoretical descriptions[9,10] of the experimental findings cited above have met with only limited success. In the most recent work, Marrucci and coworkers[10] suggest an analogy between the bands considered here and those observed by Meyer and coworkers[11] in connection with Freederickzs transitions at high magnetic field for low molecular weight liquid crystals. In the latter case it was shown, on the basis of irreversible thermodynamics considerations,[11] that bands are dinamically favoured as a route to the equilibrium, uniform distribution. Marrucci and coworkers[10] further suggested that the line tension (Frank elasticity) resulting from the deformation of disinclinations during shear is an (internal) force component transverse to the preferred alignment playing an analogous role to that of the magnetic field in Meyer's experiments.[11]

In the present work we extend the kinetic measurements cited above for HPC and PHIC to the case of poly(*p*-benzamide) PBA dissolved in dimethylacetamide (DMAc) containing 3% LiCl. These data fulfil our expectation that the comparison of the behavior of several polymers would reveal new significant features of the mechanism of band formation.

EXPERIMENTAL

A PBA sample was kindly supplied by the China Textile University.[12]

Intrinsic viscosity measured at 25°C in H_2SO_4 96% was $|\eta| = 2.35$ dl/g corresponding to a molecular weight $\overline{M}_v = 14.000$ in terms of the relationship given by Schaefgen and coworkers.[13] Concentrated solutions in DMAc + 3% LiCl were prepared by gradually adding polymer to a diluted solution and stirring at low speed for at least two weeks.[12] The critical concentration at which the anisotropic phase first appear was $C_p' = 5.2$ g/100 g solution. This value was determined by optical microscopy.[14] For the present study, a fully anisotropic solution having $C_p = 8.3\%$ was obtained by isolating the anisotropic portion of a centrifugated biphasic solution having an overall $C_p = 7.2\%$ and a volume fraction of isotropic phase $\Phi \approx 0.4$. The intrinsic viscosity of the polymer in the anisotropic phase was $|\eta| = 2.45$ dL/g corresponding to a molecular weight $\overline{M}_v = 14.500$. The viscosity of concentrated solutions was determined in a range of shear stresses using a Weissenberg viscometer.[14,15] Alternatively, a Brookfield viscometer operated at rather low $\dot{\gamma}$ was used. These measurements were performed for the PBA solutions, as well as for the HPC and PHIC solutions used in previous investigation of the kinetics of band formation. Band formation was followed using a modified Weissenberg rheogoniometer with cone and plate made of highly polished glass. Details of the instrument, of the TV camera used for observing and recording the texture, of the determination of t_b as a function of shear time t_s at a given gradient $\dot{\gamma}$, are similar to those previously described.[1,2]

Experimental indeterminatios which affect t_b have been previously pointed out.[1]

RESULTS AND DISCUSSION

Figure 1 illustrates typical flow curves. The extrapolation to $\dot{\gamma} = 0$ is complicated by a yield stress effect which is a distinctive feature of lyotropic liquid crystals.[16] Data obtained at a small, but finite $\dot{\gamma}$ value (0.066 $\sec^{-1}$) are included in Table

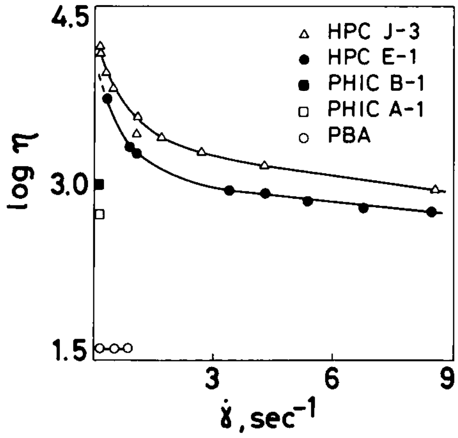

FIGURE 1 Flow curves for HPC/H_2O solutions E-1 and J-3 and viscosity at low $\dot{\gamma}$ for PBA/DMAc + 3% LiCl, and for PHIC/toluene solutions A-1 and B-1.

I. Although the non-newtonian behavior precludes a strict comparison of data at constant $\dot{\gamma}$, there is no doubt that η attains large values for HPC, intermediate ones for PHIC, and rather small values of PBA.

Figure 2 illustrates the variation of the time for band formation with shear time at a constant $\dot{\gamma}$ value. At $t_s > \sim 20$ sec a plateau value of t_b is observed at each $\dot{\gamma}$. The plateau value strongly decreases with $\dot{\gamma}$. Qualitatively, the trend observed is similar to that already reported for HPC[1] and PHIC[2]. The present data do not show a region at low t_s where t_b decreases with t_s. However, the occurrence of the threshold, approximately indicated by the dashed lines, was definitively evident even in the present case (measurements have not been carried out in the region where a decrease of t_b and t_s occur). More significantly, the present data show values of t_b consistently *larger*, at a given $\dot{\gamma}$, than those reported for HPC[1] and PHIC[2]. This effect is evidenced in Figure 3 in which we collect the variation of the plateau, or steady-state value of t_b (at large t_s) with shear rate for the present PBA solution and for the HPC and PHIC solutions previously investigated. Two samples differing in molecular weight were studied for both HPC and PHIC.

The significant variation of t_b (at given $\dot{\gamma}$) for the five samples in Figure 3 stands in satisfactory correlation with the trend of the viscosity data collected in Table I.

TABLE I

Viscosity data at $\dot{\gamma} = 0.066$ sec^{-1} for the present and previously investigated solutions.

Solution	Ref.	C_p%	M_v	$\eta_{20°}$ (poise)
HPC, E-1	1	50.0	60,000	10,000
HPC, J-3	1	50.0	100,000	16,000
PHIC, A-1	2	24.7	61,000	600
PHIC, B-1	2	21.9	131,000	1,000
PBA	This work	8.3	14.500	40

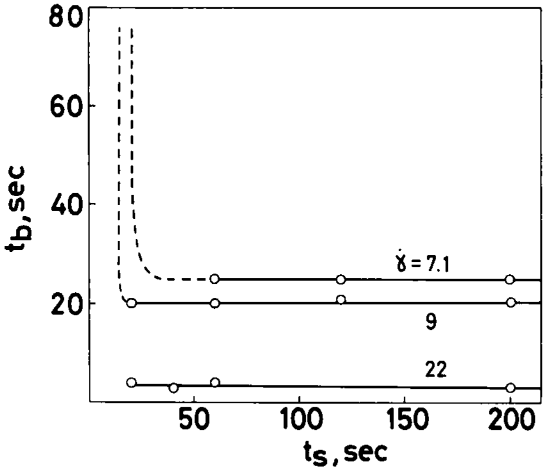

FIGURE 2 Variation of the time for the appearance of bands, t_b, with shear time, t_s, at the indicated values of shear rate, $\dot{\gamma}$ for a PBA solution in DMAc + 3% LiCl (M_v = 14,500; C_p = 8.3%).

A decrease of t_b appears correlated to an increase in η. The role of bulk viscosity was not overlooked in our previous work.[1,2] Yet it is the consideration of the whole body of data so far obtained which is definitively revealing the primary importance of this parameter on band formation.

Figure 4 is a plot of t_b *vs* $\dot{\gamma}$ similar to that in Figure 3, but includes the region of very large $\dot{\gamma}$. For clarity, only the data for HPC J-3 and PHIC B-1 are included. As recalled in the Introduction, we observed[1] that, particularly for HPC J-3, the

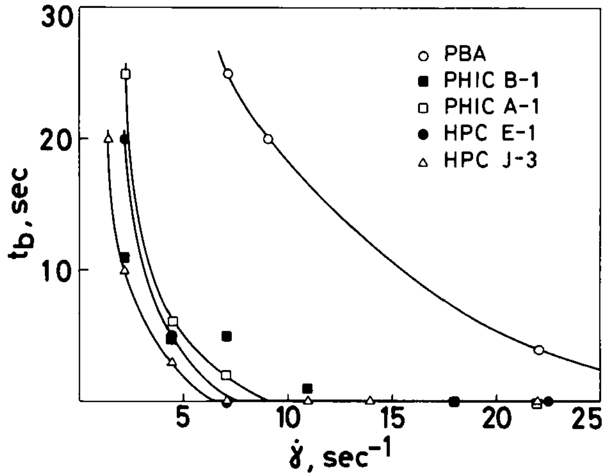

FIGURE 3 Plateau values of t_b plotted *vs* $\dot{\gamma}$ for the PBA solution characterized in Figure 1. Also shown are previously reported data for two HPC/H_2O solutiosn[1] (E-1: M_v = 60,000, C_p = 50.0%; J-3: M_v = 100,000, C_p = 50.0% and two PHIC/toluene solutions[2] (A-1; M_v = 61,000, C_p = 24.7%, B-1: M_v = 131,000, C_p = 21.9%).

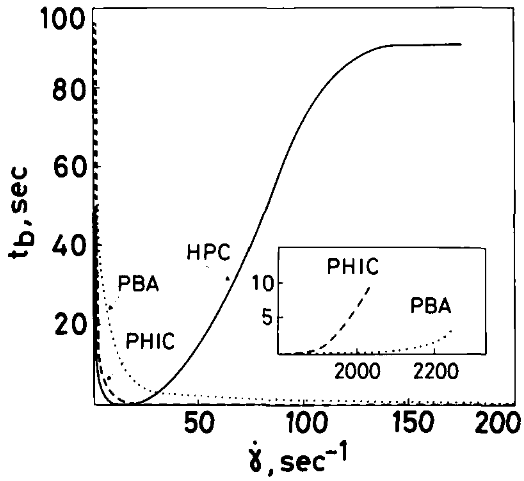

FIGURE 4 Same data of Figure 3, but with the inclusion of data to much larger $\dot{\gamma}$ values. HPC solution E-1, and PHIC solution A-1 have been omitted for clarity.

t_b value, which had decreased to zero on increasing $\dot{\gamma}$ (up to $\sim$ 8 sec^{-1}), started to increase again upon further increase of $\dot{\gamma}$. A more detailed representation of this effect is now shown in Figure 4. The reincrease of the time for band formation is quite a large one, t_b attains values of ~80 sec already at $\dot{\gamma}$ ~100 sec^{-1}. We did not observe a similar behavior with HPC E-1 (which has a lower bulk viscosity that of HPC J-3) but at the time of our first study we did not extend the observations at $\dot{\gamma}$ larger than 230 sec^{-1}.

By the time of our second study[2] in which PHIC was used (having a much lower bulk viscosity than PHIC), we decided to investigate the occurrence of an upturn on the t_b *vs* $\dot{\gamma}$ diagram in a rather large $\dot{\gamma}$ range. As shown by the data now included in Figure 4, even PHIC B-1 shows an upturn: t_b remains equal to zero when $\dot{\gamma}$ is between ~50 and ~1900 sec^{-1}, but increases to ~10 sec at $\dot{\gamma}$ ~2000 sec^{-1}. Again, we did not explore the occurrence of an upturn at still larger $\dot{\gamma}$ with the less viscous PHIC A-1 sample.

Finally, the PBA solution presently investigated—which has an extremely low viscosity—attains $t_b \approx 0$ at a larger $\dot{\gamma}$ (~200 sec^{-1}) than for HPC and PHIC. t_b remains negligibly small until $\dot{\gamma}$ ~2200, but definite evidence for an upturn is manifested at $\dot{\gamma}$ ~2250 sec^{-1}.

It should be pointed out that for the present PBA solution, and for the cases previously investigated,[1,2] the occurrence of an upturn is manifested by solutions which are extremely well oriented during flow, as evidenced by a fully darkened background under cross polars. It also appears that the upturn appears at lower $\dot{\gamma}$ and it is less pronounced the lower is the sample viscosity. Thus we arrive to the conclusion that viscosity has opposite effects in the pre-upturn and the upturn region. *Lower* viscosity corresponds to larger t_b when $\dot{\gamma} < \dot{\gamma}$ upturn. On the other hand, the reincrease of t_b at $\dot{\gamma} > \dot{\gamma}$ upturn is facilitated by *larger* viscosity.

CONCLUDING REMARKS

We emphasize the experimental finding of a correlation of the time for band formation with viscosity such that, in the low $\dot{\gamma}$ region, t_b decreases when η increases. We also emphasize the observation that t_b appears to go through a minimum with $\dot{\gamma}$, the effect being more conspicuous the larger the viscosity.

The interpretation of the above effects is not simple, and a theory which accounts for them does not exist. At the best, we can attempt to discuss if the experimental findings can be brought into qualitative agreement with current ideas concerning the mechanism of band formation. As mentioned in the introduction, the flow-induced distortion of disinclinations is believed to play an essential role in band formation.[10] In terms of this picture, we might assume that Frank elasticity is larger for HPC which shows instantaneous band formation ($t_b = 0$) at a smaller $\dot{\gamma}$ than PHIC and PBA. For the latter, fewer defects would imply that the intensity of Frank elasticity needed to produce $t_b = 0$ can only be reached at relatively larger $\dot{\gamma}$. The newly discovered correlation between t_b and η would then suggest that the more viscous system has a larger defect concentration, or it allows a slower dissipation of stored elasticity, particularly at low $\dot{\gamma}$. These conjectures are not inconsistent with the fact that the critical concentration C_p^* increases in the order PBA < PHIC < HPC (Table I), which is just the order of increasing chain flexibility (persistence lengths are, respectively, in the order of 700[12], 300[17] and 100[18]). Thus, the larger concentration and viscosity of HPC are merely a reflection of its larger flexibility. More frequent director variation (i.e. more defects) would in fact be expected for the more flexible mesogen. On the other hand, the larger viscosity would hinder the dissipation of stored elasticity.

The above picture would be in line with experimental behavior at low $\dot{\gamma}$, but fails to justify the behavior observed at large $\dot{\gamma}$ in the upturn region. To retain consistency with the scheme just described, one might suggest that at large $\dot{\gamma}$ defects could actually *decrease*. In other words, viscous forces might prevail over Frank elasticity causing a reduction of defects. The system would then evolve toward a monodomain, a tendency which has already been anticipated to occur at large $\dot{\gamma}$ by Onogi and coworkers.[16] The evolution of the system toward a monodomain is possible only for large $\dot{\gamma}$, for small $\dot{\gamma}$ the tumbling of the molecules does not allow them to align perfectly even for large t_s.[10] However, as long as t_b retains small or finite values, as shown by all our data, an elastic recovery component is still effective. Thus, some defects might in fact never be eliminated. They would provide a network with a memory of the initial defect topology, as suggested some time ago by Marrucci.[19]

Acknowledgment

We express our appreciation to Professors E. Bianchi and G. Marrucci for interest in this work and to China Textile University for supplying the PBA sample.

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