Crystallization-induced band formation in nematic polyethers

M. Hoff*, A. Keller and J. A. Odell
H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK

and V. Percec
Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106-2699, USA
(Received 7 September 1992)

The effect of the nematic-solid phase transition on the texture of both crystallizable and amorphous nematic polymers is studied using polarizing and electron microscopy and light scattering. We found that crystallization, unlike vitrification, can lead under certain conditions to the formation of banding, which has so far been reported only as having been induced by external flow. To achieve banding on crystallization, nematic domains must acquire a sufficient size through previous annealing. Crystallization brings about directionally non-uniform volume changes and corresponding excess free-volume energy to which we attribute the presently observed effect.

(Keywords: liquid crystalline polymer; banded texture; crystallization; annealing; domain growth)

INTRODUCTION

In the past decade, close attention has been paid to banded textures formed in liquid crystalline nematic polymers during the relaxation of chains previously oriented by external flow[1-4]. Although the precise mechanism of band formation has not yet been satisfactorily explained, it is generally believed that the bands, a periodical arrangement of the molecular director, form to minimize the excess elastic energy of the system[2,5-8]. There are two principle sources of the elastic energy that could drive the effect[9]: the molecular elasticity due to a distortion of molecules from their equilibrium arrangement; and the elasticity of the texture (particularly splay). We recently observed that the equivalent banding effect was due to localized orientation in strain fields which can arise unintentionally during the course of normal sample manipulation[10]. The same work also indicated a connection between the banding and the intrinsic nematic domains in the unoriented state, hence the influence of texture in addition to purely molecular features.

In this study we show how banding can arise spontaneously in nematic polymers without previous orientational treatment, when passing through the nematic-crystal transition, and suggest another possible mechanism that leads to its formation.

EXPERIMENTAL

The polymers used in this study were random aromatic copolyethers of mesogenic α-methyl stilbene and flexible alkyl spacers with 5 and 7 methylene groups in the 1:1 ratio (PHMS 5/7) and random copolyethers of mesogenic 1-(4-hydroxy-4′-bisphenyl)-2-(4-hydroxy phenyl butane) with spacers containing either 10 (TPB 10) or 14 (TPB 14) methylene units. The TPB 10 grade is amorphous, i.e. it exhibits during heating only glass-nematic (T_g) and nematic-isotropic (T_{NI}) transitions, whereas PHMS 5/7 and TPB 14 are crystallizable, exhibiting also a crystalline-nematic transition (T_{CN}). Chemical formulae of the polymers are shown in *Figure 1*, d.s.c. heating traces obtained on the Perkin–Elmer DSC 7 instrument in *Figure 2*, and their molecular weights are listed in *Table 1*. All the polymers used show pronounced shear-induced banding effect.

Thin films (10–20 μm) solvent-cast onto a coverslip were placed in the Linkam TMS 91 hot stage, annealed in the nematic state in an inert atmosphere, and subsequently cooled to either the crystalline or the glassy state. *In situ* microscopic observations were carried out with a Zeiss Ultraphot polarizing microscope, and light scattering patterns were obtained by inserting a Bertrand lens into the optical path.

To prepare samples for transmission electron microscopy (TEM), we used two-stage replication from the polymer surface etched in a permanganic etchant[11]. The Pt–Pd replicas were studied in a Philips EM 301 microscope.

RESULTS

In situ observations during annealing of the polymers in the nematic state have confirmed what has already been reported elsewhere; the nematic domains grow with time up to a certain maximum size[12]. An increase in the orientation correlation length was confirmed by simultaneous recording of light scattering; the maxima

---

* To whom correspondence should be addressed. Permanent address: Institute of Macromolecular Chemistry, Czechoslovak Academy of Science, 162 06 Prague 6, Czechoslovakia

0032-3861/93/091800-06

in typical four-quadrant V_H patterns shifted towards smaller scattering angles, as shown in *Figure 3*. The maximum domain size was found to be affected by the annealing temperature, higher temperatures, i.e. closer to T_{NI}, leading to larger maximum-sized domains. This is shown in *Figure 4* by a plot of the angle of the maximum scattering intensity against annealing time for TPB 10 and TPB 14. Up to this point, no substantial differences were found in the behaviour of the polymers which were crystallizable (on appropriate cooling) and those which were not.

On cooling, the crystallizable polymers were found to change their textures dramatically after passing through the nematic-crystalline transition; apparently spontaneous pronounced banding appeared within the, by now, enlarged domains. This was accompanied by the appearance of wide-angle light scattering maxima due to a much smaller band spacing (*Figure 5*). No spontaneous flow could be detected either during the annealing or the cooling stages. To achieve the banding effect, domains

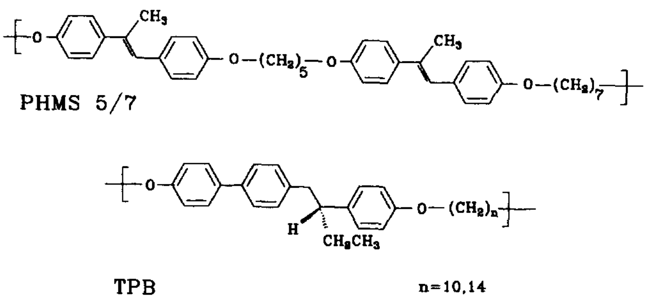

Figure 1 Chemical formulae of the polymers used

Table 1 Molecular weights of the polymers TPB 10, TPB 14 and PHMS 5/7 as determined by g.p.c.

Grade	M_w	M_n
TPB 10	62 600	31 600
TPB 14	84 000	40 800
PHMS 5/7	30 200	14 500

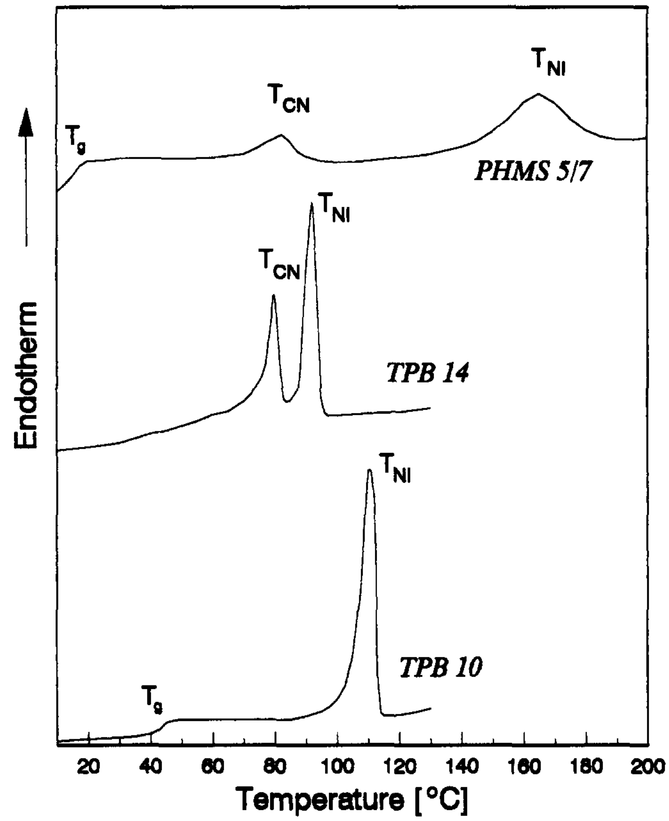

Figure 2 D.s.c. heating traces of the polymers used. T_g, T_{CN} and T_{NI} are the glass–nematic, crystalline–nematic and nematic–isotropic transitions, respectively

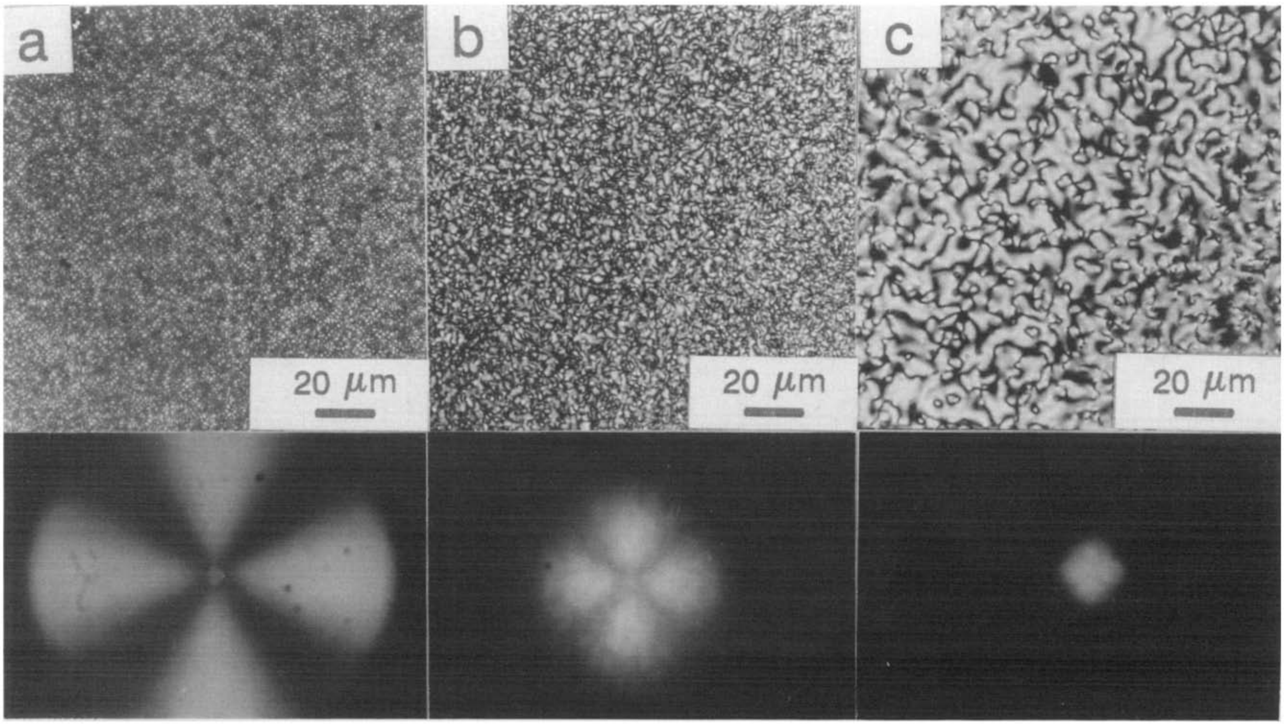

Figure 3 Effect of annealing in the nematic state on the texture and light scattering of TPB 14. Polymer (a) just heated up to 90°C and annealed for (b) 220 min, (c) 2550 min, crossed polars

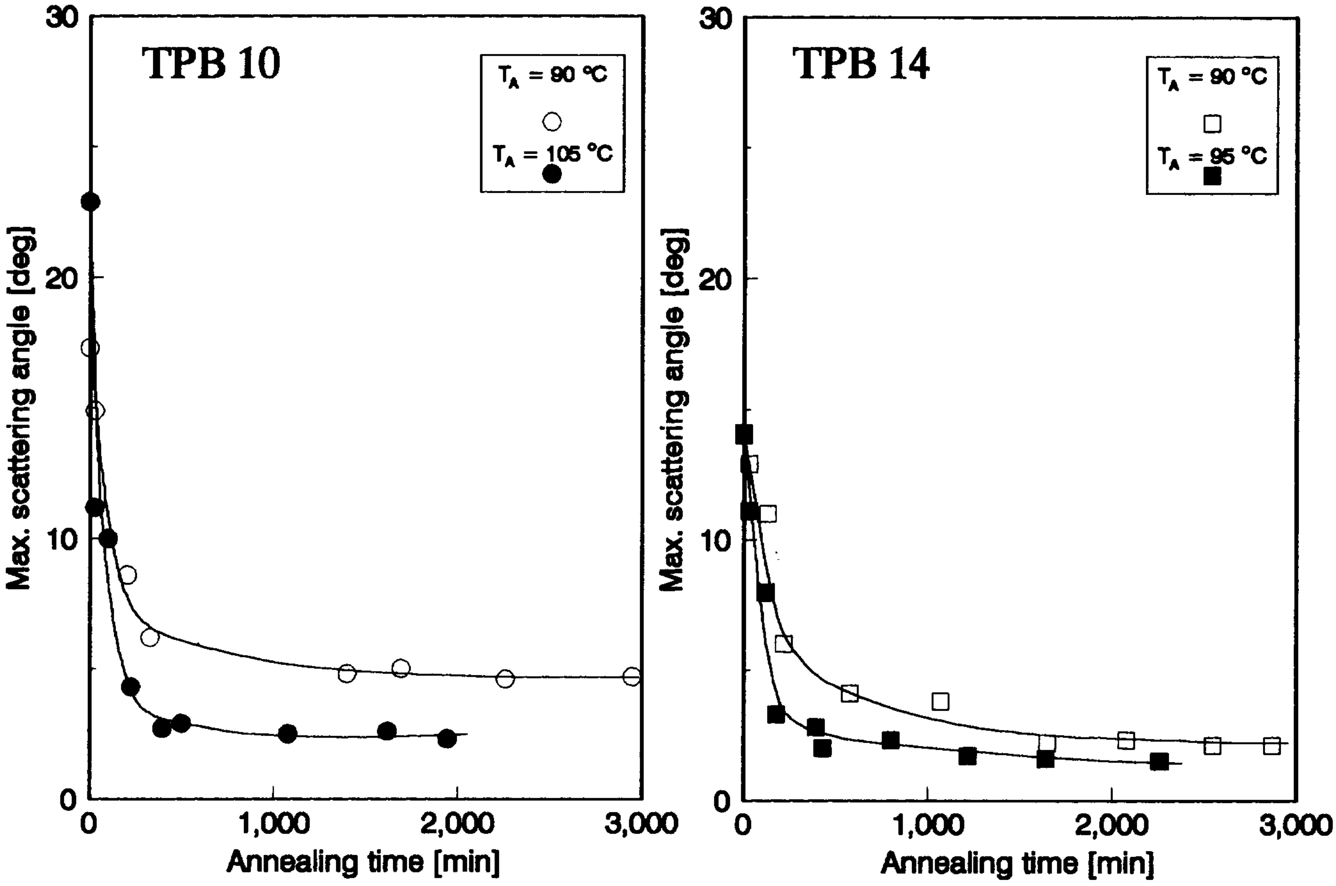

Figure 4 Decrease in the maximum light scattering angle during annealing, showing kinetics of domain growth for different annealing temperatures

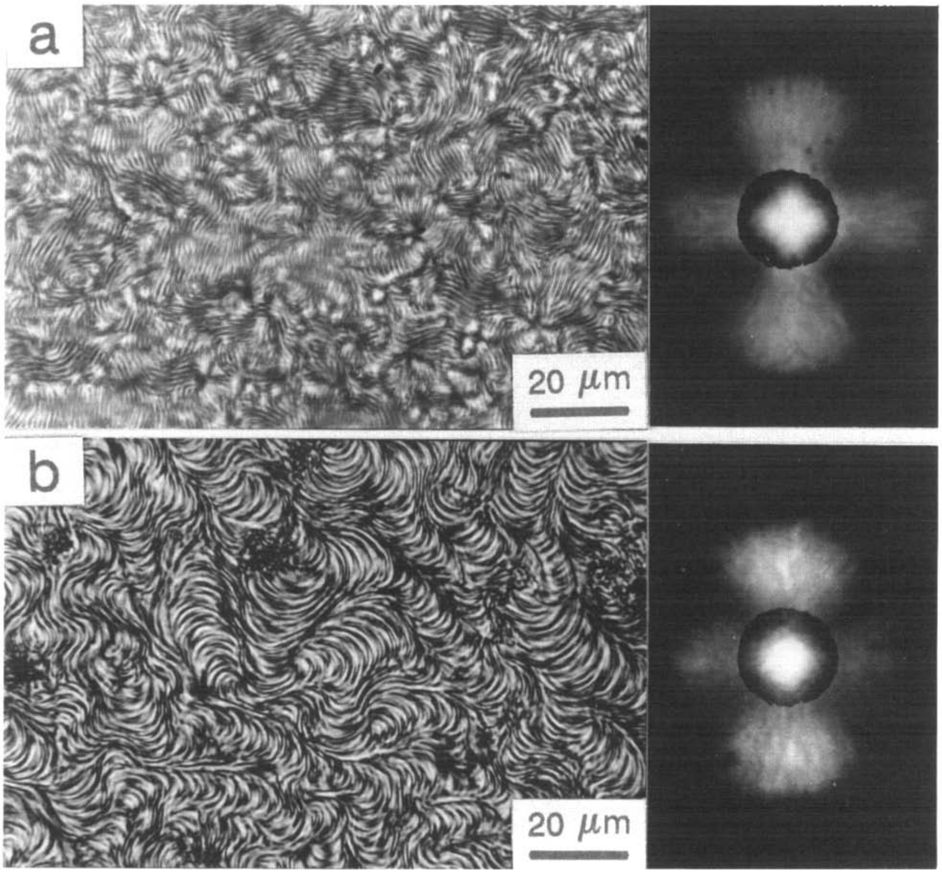

Figure 5 Optical micrographs and V_H light scattering patterns of the crystallizable polymers quenched after annealing (3000 min) close to T_{NI} below their crystallization temperatures. (a) TPB 14; (b) PHMS 5/7, crossed polars. The centres of the prints were exposed longer to envisage more intense scattering at the small-angle areas

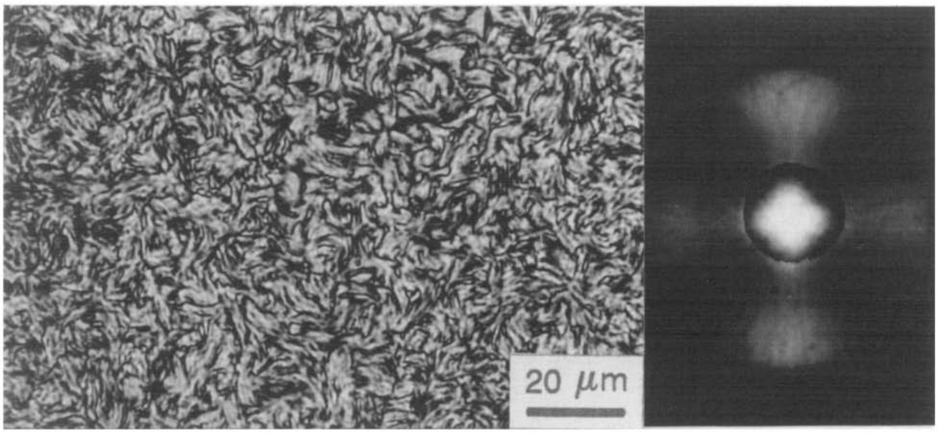

Figure 6 Optical micrograph and V_H light scattering pattern of TPB 14 annealed at 90°C for 2260 min and cooled to room temperature by the rate 0.01°C min^{-1}. The centre of the print was exposed longer to envisage more intense scattering at the small-angle areas

had to be sufficiently enlarged; smaller domains (shorter annealing times or lower temperatures) led to less pronounced banding and, finally, below a certain domain size the bands did not form at all. The same procedure applied to the amorphous TPB 10, here cooled to well below T_g (42°C), did not lead to band formation; there were no changes in texture or light scattering pattern in comparison with those observed before cooling, regardless of the domain size.

The cooling rate was observed to have only a minimal effect on band formation, but has not yet been fully evaluated. At present, we can only say that banding appears at any cooling rate investigated, i.e. in the range between quenching and 0.01° min^{-1}. The banding which arises at very low cooling rates does, however, look somewhat less pronounced (*Figure 6*).

The annealing temperature had an effect through its influence on the domain size; the lower the annealing temperature (increasing difference T_{NI}-T) the smaller is the domain size which is reached at a comparable annealing time (see *Figure 4*), and correspondingly less pronounced is the banding.

The alternation of narrow extinction lines and broader light bands (straighter in TPB 14 than in PHMS 5/7, *Figure 5*) indicates the same kind of periodic variation in director orientation as with sheared polymeric nematics[1]. For PHMS 5/7, TEM micrographs of etched samples revealed that there were two levels of supermolecular structure. In *Figure 7a*, the overall topology is shown at a lower magnification, corresponding to the optical texture from *Figure 5b*; column-like domains containing smoothly packed curved structural elements (corresponding to curved bands in *Figure 5b*) are separated by corrugated boundaries. Higher magnification revealed a zigzag morphology within individual bands (*Figure 7b*, magnified area denoted in *Figure 7a*).

The banding itself was conspicuously revealed by electron micrographs also of the TPB 14 polymer (*Figures 8a,b*), where the boundaries are seen to protrude from the surface. However, the permanganic etchant employed proved inadequate for revealing any fine structure in TPB 14 (etched and unetched samples did not show any difference in TEM). Analogously processed amorphous TPB 10 displayed no banding, exhibiting only a more or less smooth topology (*Figure 8c*).

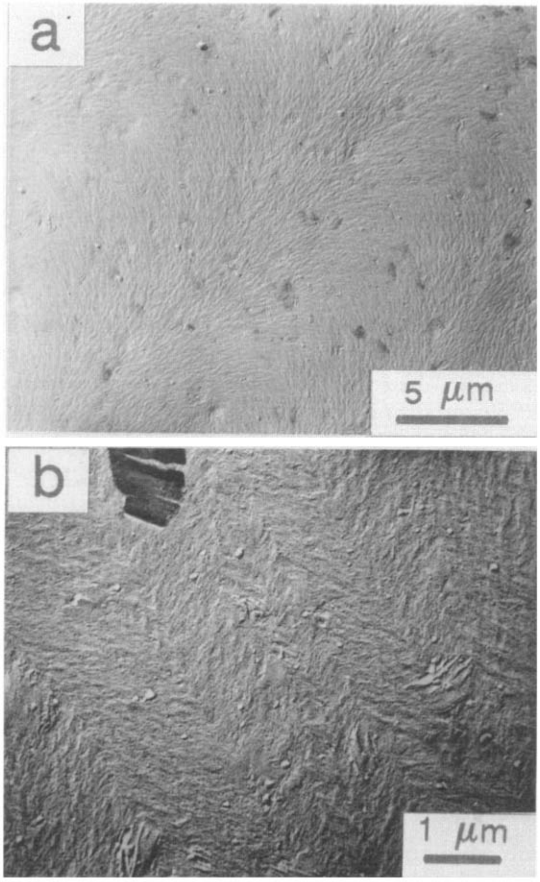

Figure 7 Banded morphology of PHMS 5/7 annealed close to T_{NI} and quenched into the crystalline state. TEM, Pt–Pd replica at low (a) and high (b) magnification

DISCUSSION

The salient feature in the present observations is the appearance of a banded structure, similar to that seen in flowing or deformed systems after removal of the external orienting influence, but in this case arising apparently spontaneously, without external interference to the system. It is clear that the effect sets in only when sufficiently enlarged domains are allowed to crystallize.

It is further evident that vitrification does not lead to the same effect as crystallization. The nematic-

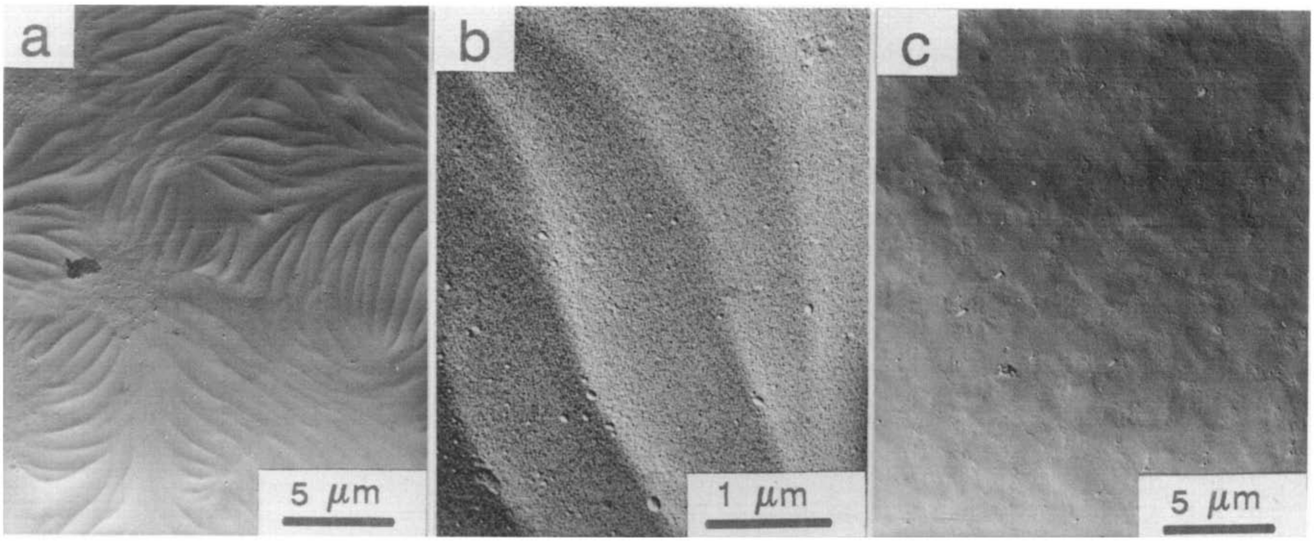

Figure 8 Morphology of TPB polymers annealed close to T_{NI} and quenched to the crystalline or glassy state. (a), (b) Banding in crystalline TPB 14; (c) smooth surface of glassy TPB 10. TEM, Pt–Pd replica

crystal transformation, as a thermodynamic first order transition, is accompanied (unlike vitrification) by a decrease in volume. In separate domains with local anisotropy in molecular orientation, one would expect the volume change to be highly anisotropic as well. In fact, as the chains acquire closer lateral packing and better alignment in crystals, the domain will contract perpendicular to the chain direction and expand along it. As adjacent domains have different orientations within an overall randomly-oriented sample, expansion will be frustrated, a situation which can then lead to periodic buckling which could be manifested as banding. Convincing precedents of such buckling under essentially equivalent circumstances have been found in polyethylene shish-kebab crystals expanding on further crystallization while embedded in a matrix[13], and in macroscopic nylon fibres surrounded by a contracting medium[14].

On a more general basis, volume changes will produce an excess free-volume energy contributing to the energies due to texture elasticity (splay, bend, twist). In the nematic continuum, the latter is localized in disclinations, the concentration of which decreases with increasing domain size[15]. In the early stages of annealing, the concentration of the disclinations will be sufficient to also localize the excess free volume created by crystallization. Distances between neighbouring disclinations are small, so the net longitudinal expansion of the crystallizing chains per domain will be small, and thus insufficient to cause buckling. Domain growth causes the disclination-to-disclination distance to increase, and the net expansion per domain will then be accompanied by band formation. The free volume relieved, and thus the respective excess free-volume energy, will then remain localized at the band boundaries. As can be seen from *Figure 8b*, protruding material between the bands indeed indicates an excess volume (hence lower interior density), which then squeezes out material to above the ambient sample plain, as seen here in a periodic manner.

It is not obvious whether factors such as those discussed above could play any part in the more usual band formation in oriented systems, such as are seen to arise in the nematic state without the intervention of crystallization. Nevertheless, when crystallization is known to occur, the present new phenomena will certainly need to be taken into account.

Recently, after completion of the present work, similar observations (of band formation on domain growth without an external orienting influence) have come to our notice from another source using different liquid crystal forming polymers[16,17]. Hence, the effect seems general. We have no information as to any attribution of this effect to crystallization (as done here by ourselves) in this parallel work.

CONCLUSIONS

A new source of banding has been discovered which does not involve external flow. This arises on crystallization of sufficiently enlarged domains. We propose that the effect is connected with non-uniform volume changes within the crystallizing material which may cause buckling of the directionally constrained polymer. In general, this draws attention to the role of volume changes, and to that of excess free volume in particular as a source or contributing factor to band formation in the nematic polymers.

ACKNOWLEDGEMENT

Sponsorship by the US Army European Office, London (grant No. DAJA 45–89–0–0021) is gratefully acknowledged.

REFERENCES

1 Donald, A. M., Viney, C. and Windle, A. H. *Polymer* 1983, **24**, 155
2 Horio, M., Ishikawa, S. and Oda, K. *J. Appl. Polym. Sci. Appl. Polym. Symp.* 1985, **41**, 269
3 Marruci, G., Grizutti, N. and Buonaurio, A. *Mol. Cryst. Liq. Cryst.* 1987, **153**, 263
4 Wang, J., Bhattacharaya, S. and Labes, M. M. *Macromolecules* 1991, **24**, 4942
5 Zachariades, A. E., Navard, P. and Logan, J. P. *Mol. Cryst. Liq. Cryst.* 1984, **110**, 93
6 Nishio, Y., Yamane, T. and Takahashi, T. *J. Polym. Sci., Polym. Phys. Edn* 1985, **23**, 1053
7 Ernst, B. and Navard, P. *Macromolecules* 1989, **22**, 1419

8 Maffettone, P. L., Grizutti, N. and Marruci, G. *Liq. Cryst.* 1989, **4**, 385
9 Gleeson, J. T., Larson, R. G., Mead, D. W., Kiss, G. and Cladis, P. E. *Liq. Crystals* 1992, **11**, 341
10 Hoff, M., Keller, A., Odell, J. A. and Percec, V. *Mol. Cryst. Liq. Cryst.* (to appear)
11 Olley, R. H. and Bassett, D. C. *Polym. Commun.* 1982, **23**, 1707
12 Feijoo, J. L., Ungar, G., Owen, A. J., Keller, A. and Percec, V. *Mol. Cryst. Liq. Cryst.* 1988, **155**, 187
13 Grubb, D. T. and Keller, A. *Colloid. Polym. Sci.* 1978, **256**, 218
14 Dale, W. C. and Baer, E. *J. Mater. Sci.* 1974, **9**, 369
15 Shiwaku, T., Nakai, A., Hasegawa, H. and Hashimoto, T. *Polym. Commun.* 1987, **28**, 174
16 Chen, S. and Qian, R. *China–UK Bilateral Conf. Polymer Sci.* April 1992, Beijing, China, Abstracts, p. 18
17 Qian, R. and Chen, S. *Makromol. Chem. Macromol. Symp.* 1992, **53**, 345