Polymer, 1991, Vol. 32, 34–38

Solid-state deformation of *trans*-1,4-polybutadiene

N. A. J. M. van Aerle and P. J. Lemstra
Department of Polymer Technology, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

T. Kanamoto
Department of Applied Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-Ku, Tokyo 162, Japan

and C. W. M. Bastiaansen*
DSM Research, PO Box 18, 6160 MD Geleen, The Netherlands

(Received 11 October 1989; accepted 10 January 1990)

The uniaxial deformation behaviour of *trans*-1,4-polybutadiene was investigated. *Trans*-1,4-polybutadiene exhibits a solid–solid phase transition to a mobile pseudo-hexagonal, conformational disordered (condis), crystal structure at a temperature of approximately 65°C. *Trans*-1,4-polybutadiene cannot be deformed to high draw ratios via tensile drawing in the pseudo-hexagonal condis phase. Using coextrusion, *trans*-1,4-polybutadiene can be deformed, in the pseudo-hexagonal condis phase, to high (extrusion) draw ratios. Structures possessing a high degree of chain orientation in the extrusion direction and a strongly enhanced Young's modulus and tensile strength can be produced.

(Keywords: tensile drawing; solid-state extrusion; *trans*-1,4-polybutadiene; hexagonal phase; modulus; strength)

INTRODUCTION

High-strength and high-modulus polyethylene fibres can be produced using a variety of techniques comprising solution-spinning/drawing[1–3], melt-spinning/drawing[4–6] and solid-state deformation processes[7–9]. In these techniques a high degree of chain orientation/extension in one dimension is generated in linear polyethylenes by uniaxial deformation in the solid state. The mechanical properties of these highly oriented polyethylene structures are impressive, especially with respect to short-term modulus and tensile strength[1–9].

In previous studies, attempts have been reported to reduce the long-term creep of oriented polyethylene fibres by introducing chemical crosslinks in the fibres[10]. It was shown that crosslinking of polyethylene fibres after ultra-drawing is rather difficult to achieve. In most cases, mainly chain scission occurred, which resulted in a reduced tensile strength. Crosslinking before ultra-drawing, for example via electron beam irradiation, was used to improve the balance between crosslinking and chain scission[11]. However, the maximum attainable draw ratio and hence the modulus and tensile strength decrease with increasing crosslink density. Consequently one has to compromise between short-term (modulus, strength) and long-term (creep) properties[11].

We started to investigate the deformation behaviour of polyalkenamers to produce crosslinked high-strength and high-modulus structures based on unsaturated polymers. In this study some preliminary results concerning the deformation behaviour of *trans*-1,4-polybutadiene are presented.

EXPERIMENTAL

Trans-1,4-polybutadiene was synthesized at room temperature by polymerization of 1,3-butadiene using a $VCl_3/Al(C_2H_5)_3$ catalyst system[12]. The yield of the reaction was about 60%. The viscosity-average molecular weight of the polymer is approximately 75 kg mol^{-1} (ref. 13). Infra-red analysis and ^{13}C n.m.r. indicated that the vinyl content of the polymer was approximately 0.9–1.2%. No detectable amount of *cis* isomer could be observed.

Trans-1,4-polybutadiene (*trans*-1,4-PB) was dissolved in toluene, at a nominal polymer concentration of 0.2 wt%, under N_2 atmosphere at 90°C. Prior to the dissolution procedure 2 wt% di-t-butyl-*p*-cresol was added to the polymer. After complete dissolution occurred, the solution was slowly cooled to 10°C and kept at this temperature for at least 12 h. Single crystal mats were obtained by filtering the suspension of crystals, followed by drying *in vacuo* at 30°C.

Melt-crystallized *trans*-1,4-polybutadiene films were prepared by compression moulding of single crystal mats at 160°C for 15 min.

Melt-crystallized high-density polyethylene (HDPE) films were prepared by compression moulding of pellets at 180°C for 30 min.

Tensile drawing at elevated temperature was performed on a Frank 81565 tensile tester equipped with an air oven. Dumbbell-shaped samples with an original length of 20 mm were drawn at a constant crosshead speed of 20 mm min^{-1}.

HDPE billets with a diameter of 1 cm were prepared by compression moulding at 160°C. The HDPE grades used were Alathon 7050 (DuPont, $M_w = 58$ kg mol^{-1}) and JX-20 (Mitsubishi Petrochemical Co., $M_w = 67$ kg mol^{-1}).

---

* To whom correspondence should be addressed

0032-3861/91/010034-05

The billets were split longitudinally into two halves. Strips, with a width of 1–2 mm, were cut from the *trans*-1,4-PB single crystal mats and subsequently sandwiched in the centre of a split billet and coextruded, at various temperatures, through conical brass dies with an entrance angle of 20° to nominal extrusion draw ratios (*EDR*s) ranging from 2 to 36. The coextrusions were performed at a constant pressure of 10–150 MPa. The extrudates could be split easily into two halves again and a coextruded strip of *trans*-1,4-PB was obtained. The *EDR* of the samples was determined from the displacement of ink marks on the strips.

The Young's modulus and tensile strength of coextruded strips were determined on an RTM 100 Tensilon tensile tester at room temperature at a strain rate of $10^{-2}\,s^{-1}$. To avoid sample fracture at the clamps, tapes were glued between fine grained sandpaper strips before mounting in the tensile tester. The cross-sectional area of the samples was calculated from the sample length and weight, using a density of $0.97\,g\,cm^{-3}$.

Thermally induced shrinkage measurements were performed on (coextruded) samples with a length of 20 mm. The samples were immersed in a pre-heated silicone oil bath ($T = 180°C$) for approximately 10 s. The molecular draw ratio (*MDR*) was calculated from the measurements using equation (1):

$$MDR = (L_t - L_s)/L_0 + 1 \qquad (1)$$

In equation (1) L_0 is the original length prior to extrusion, L_t is the sample length after extrusion and L_s is the shrunken length.

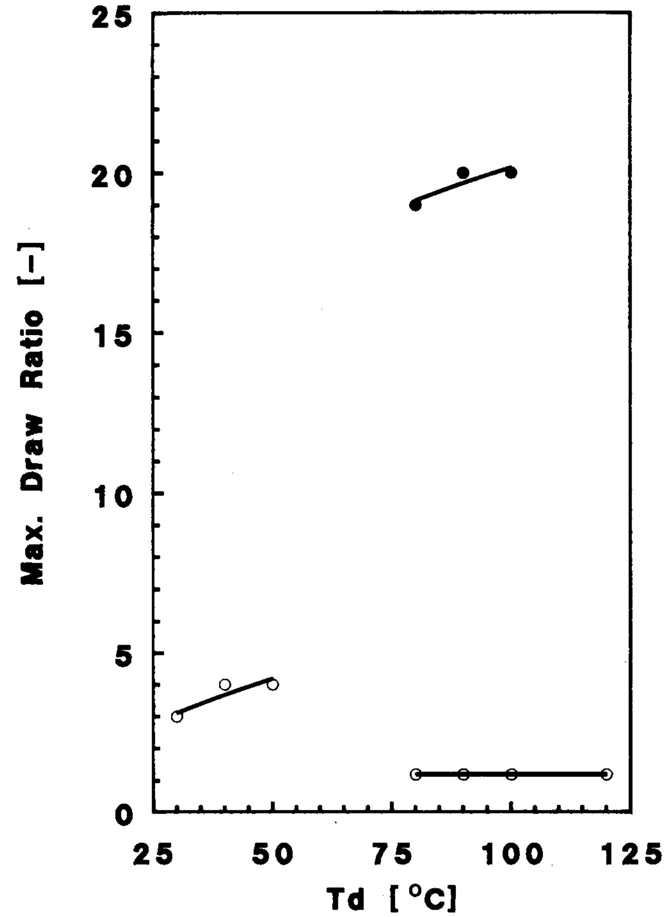

Figure 1 Maximum attainable draw ratio of melt-crystallized *trans*-1,4-PB (○) and HDPE (●) as a function of drawing temperature (T_d)

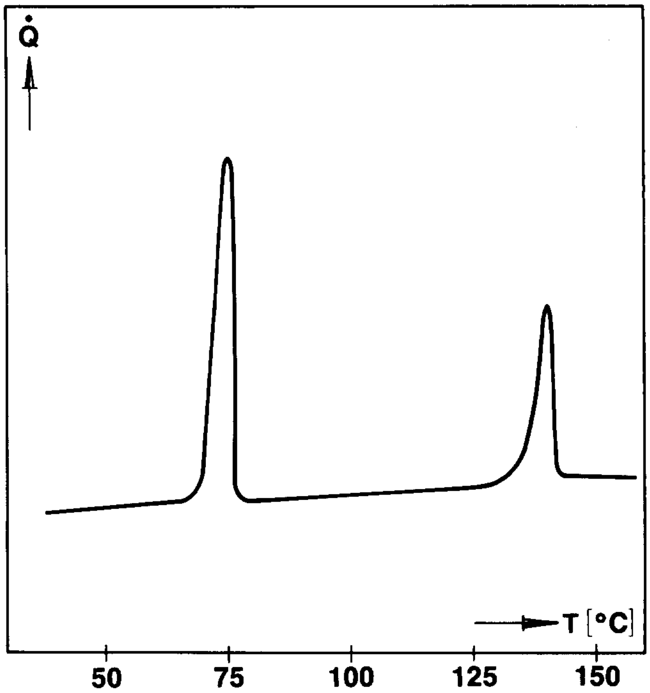

Figure 2 D.s.c. thermogram of melt-crystallized *trans*-1,4-PB

D.s.c. measurements were performed using a Seiko-Denshi DSC-10 differential scanning calorimeter at a constant heating rate of $5°C\,min^{-1}$.

Wide-angle X-ray patterns were recorded with a flat-plate camera. WAXS patterns at elevated temperature were recorded using a Statton camera equipped with an oven. In both cases Ni-filtered Cu Kα radiation was used.

RESULTS

Tensile drawing behaviour of trans-*1,4-polybutadiene in the solid state*

The maximum attainable draw ratio of melt-crystallized *trans*-1,4-PB is plotted in *Figure 1* as a function of tensile drawing temperature. The maximum attainable draw ratio of melt-crystallized *trans*-1,4-PB is rather low especially in the temperature region from 70 to 140°C ($\lambda_{max} = 1$–2). At first sight this behaviour seems unusual, especially if the experimental results on *trans*-1,4-PB are compared with data of melt-crystallized HDPE possessing a similar molecular weight (*Figure 1*).

In *Figure 2*, a d.s.c. thermogram of melt-crystallized *trans*-1,4-PB is shown. A large endotherm is observed at approximately 65°C, which in general is related to a first-order solid–solid phase transition to a hexagonal crystal phase[14,15].

It was shown that high maximum attainable draw ratios cannot be obtained by tensile drawing of *trans*-1,4-PB. Therefore we turned to solid-state coextrusion in order to produce highly oriented structures.

Solid-state coextrusion of trans-*1,4-polybutadiene single crystal mats*

The maximum attainable extrusion draw ratio (EDR_{max}) of coextruded *trans*-1,4-PB single crystal mats is plotted in *Figure 3* as a function of extrusion temperature. This figure shows that high (extrusion) draw ratios can be

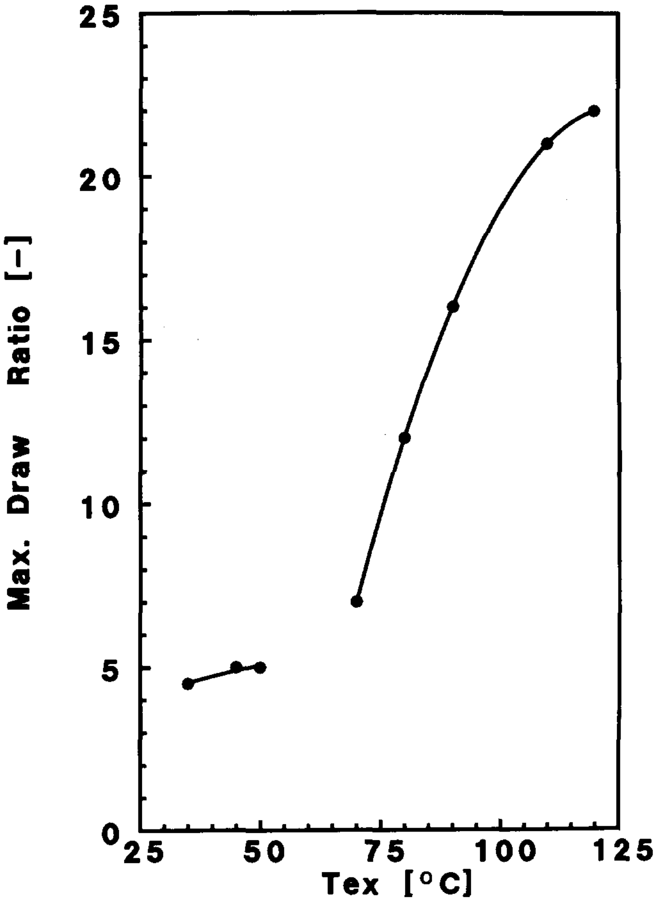

Figure 3 Maximum attainable draw ratio of *trans*-1,4-PB as a function of extrusion temperature (T_{ex})

obtained by coextrusion of *trans*-1,4-PB in the temperature region from 70 to 140°C (compare with *Figure 1*).

The Young's modulus and tensile strength of coextruded *trans*-1,4-PB are plotted in *Figures 4* and *5* as functions of draw ratio. These figures show that structures with a modulus and tensile strength of respectively ~20 GPa and ~0.4 GPa can be obtained.

Experimental results of elastic recovery measurements are shown in *Figure 6*. The macroscopic extrusion draw ratio is compared with the molecular draw ratio as deduced from shrinkage measurements (see 'Experimental' section). *Figure 6* indicates that coextrusion of *trans*-1,4-PB in the conformational disordered (condis) phase is highly effective in generating chain orientation/extension.

In *Figure* 7 WAXS patterns, recorded at 20 and 100°C, of coextruded *trans*-1,4-PB are shown. The WAXS patterns indicate that the samples are highly oriented in the extrusion direction and that the solid-state phase transition to the hexagonal phase is still present after coextrusion.

Post-drawing of coextruded trans-*1,4-polybutadiene*

In *Figure 8* experimental results are shown of post-drawing experiments of *trans*-1,4-PB that was coextruded at 110°C to an extrusion draw ratio of 6. This figure shows that the coextruded *trans*-1,4-PB single crystal mats cannot be post-drawn ($\lambda_{max} < 1.2$) in the temperature region from 70 to 140°C. Again, it is observed that it is impossible to draw *trans*-1,4-PB in the hexagonal crystal phase.

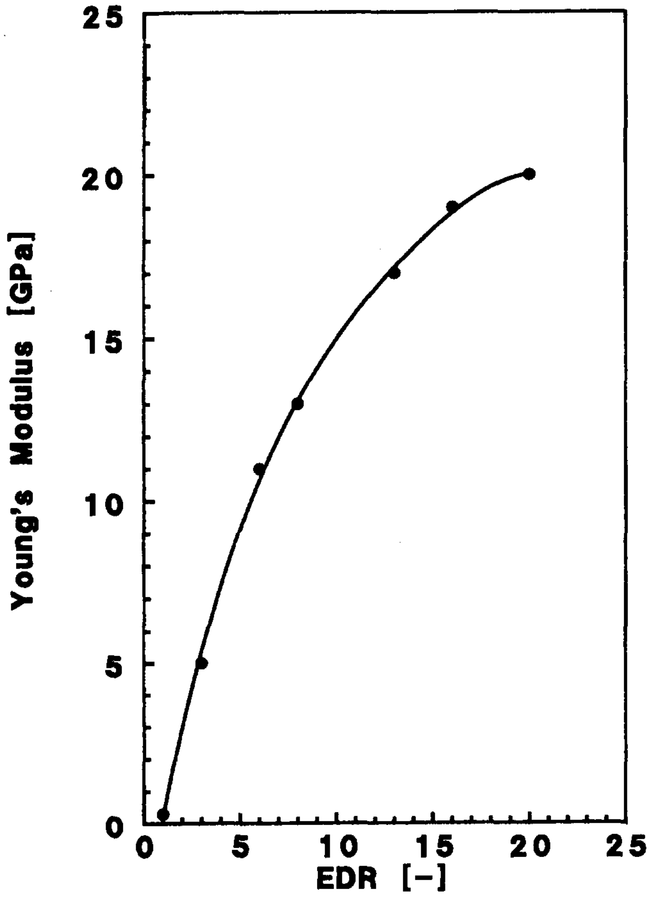

Figure 4 Young's modulus of coextruded *trans*-1,4-PB (T_{ex} = 110°C) as a function of extrusion draw ratio (*EDR*)

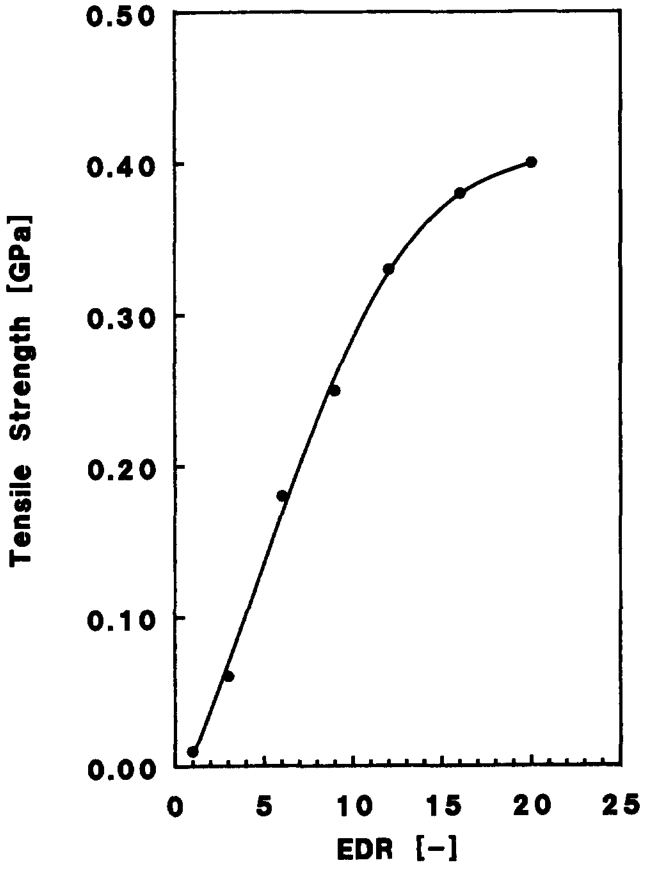

Figure 5 Tensile strength of coextruded *trans*-1,4-PB (T_{ex} = 110°C) as a function of extrusion draw ratio (*EDR*)

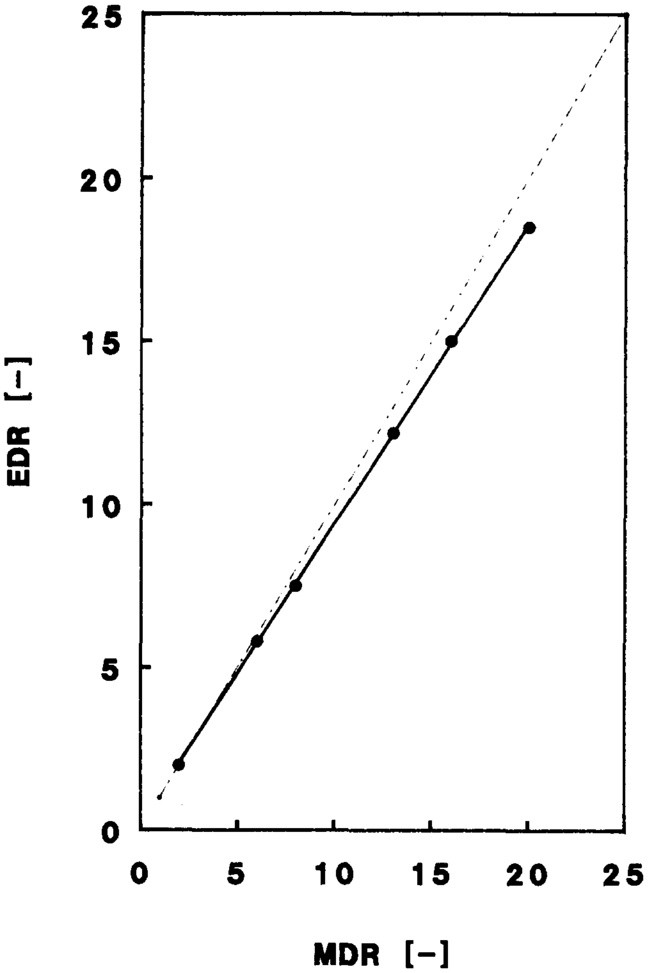

Figure 6 Molecular draw ratio (*MDR*) of coextruded *trans*-1,4-PB (T_{ex} = 110°C) as a function of extrusion draw ratio (*EDR*)

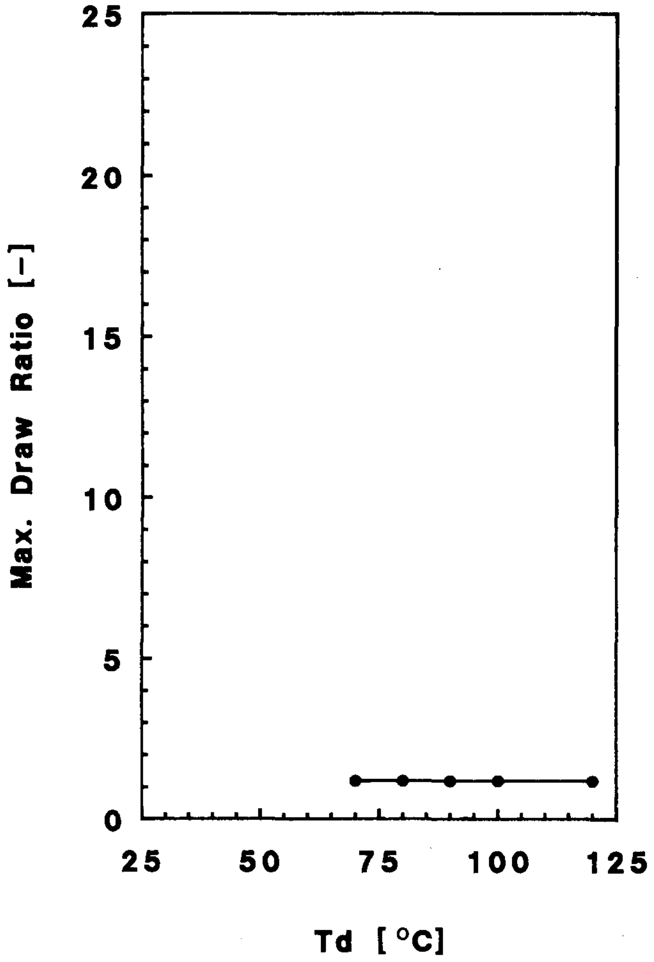

Figure 8 Maximum attainable draw ratio of coextruded *trans*-1,4-PB (*EDR* = 6) as a function of drawing temperature (T_d)

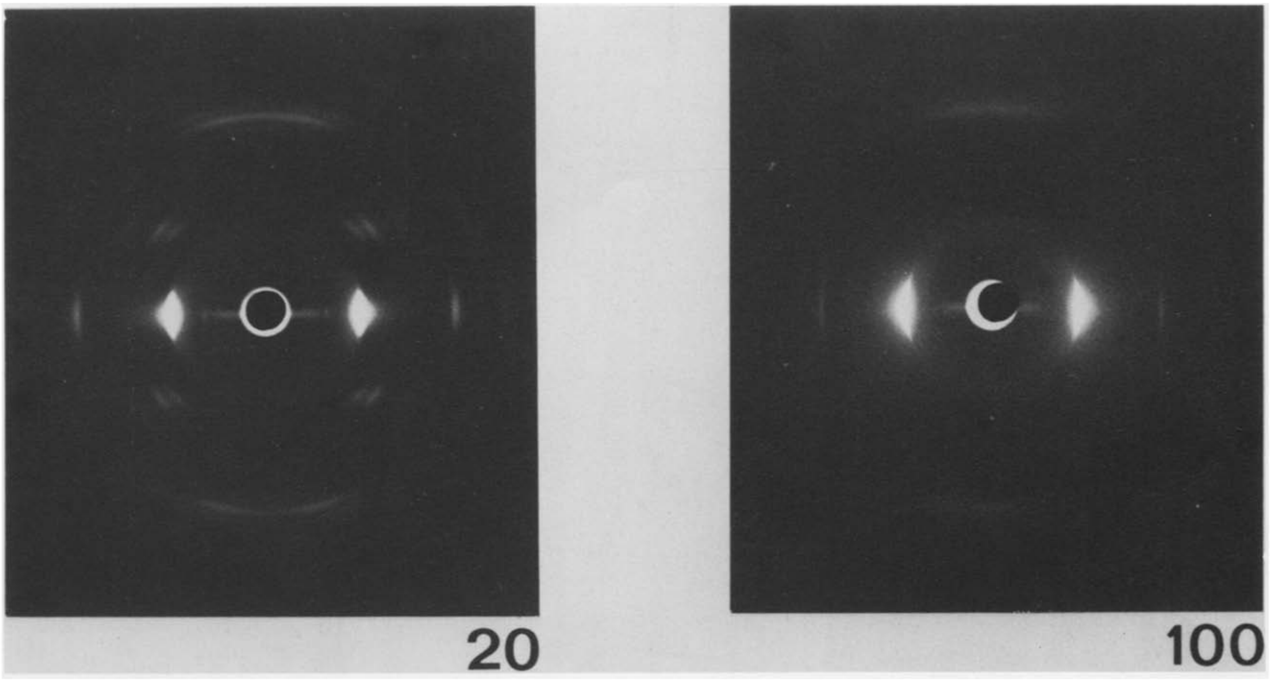

Figure 7 WAXS patterns of coextruded *trans*-1,4-PB (*EDR* = 15) recorded at *T* = 20°C and 100°C

DISCUSSION

Trans-1,4-polybutadiene is a flexible, linear polymer with a dynamic conformational disordered (condis) pseudo-hexagonal crystal structure in the temperature region from ~70 to ~140°C[14,15]. A condis crystal is considered to be a mesophase of linear, flexible macromolecules and has a macroscopic appearance in between a solid and a liquid[14].

Under special conditions linear polyethylene also exhibits a conformational disordered hexagonal phase[14,15], which is very similar to the condis phase of *trans*-1,4-PB. In previous studies it was already shown that ultra-drawn polyethylene fibres cannot sustain any applied stress in the hexagonal condis phase due to an increased molecular mobility[16–19].

Melt-crystallized *trans*-1,4-PB cannot be deformed to high draw ratios via tensile drawing in the temperature range from 70 to 140°C (*Figures 1* and *8*). However, *trans*-1,4-PB can be coextruded in the hexagonal condis phase to high (extrusion) draw ratios (*Figure 3*). Premature sample failure is prevented during coextrusion by forcing the material through a conical die. Elastic recovery measurements indicate that the macroscopic and molecular draw ratios are virtually identical, which indicates that coextrusion in the pseudo-hexagonal crystal phase is highly effective in generating chain orientation/extension (*Figure 6*). Moreover, these measurements show that relaxation of orientation during or after coextrusion of *trans*-1,4-PB in the condis phase does not occur despite the high mobility in this phase.

The Young's modulus and tensile strength of *trans*-1,4-PB increase significantly with increasing extrusion draw ratio (*Figures 4* and *5*). However, the maximum attainable Young's modulus and tensile strength is rather low (respectively ~20 GPa and ~0.4 GPa) compared with, for instance, gel-spun ultra-drawn ultra-high-molecular-weight PE fibres[1–3].

CONCLUSIONS

High-temperature uniaxial deformation of *trans*-1,4-polybutadiene is only possible via deformation processes involving extrusion and not via tensile drawing. This rather unusual behaviour is attributed to a solid–solid phase transition to a highly mobile pseudo-hexagonal conformational disordered crystal structure. Significant relaxation of molecular orientation during coextrusion in the condis phase does not occur. Consequently, highly oriented *trans*-1,4-PB tapes, with an enhanced modulus and tensile strength, can be produced. Moreover, the maximum attainable Young's modulus and tensile strength can probably be further increased by increasing the molecular weight of *trans*-1,4-PB.

REFERENCES

1 Smith, P., Lemstra, P. J. and Booy, H. C. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 877

2 Smith, P., Lemstra, P. J., Kalb, B. and Pennings, A. J. *Polym. Bull.* 1979, **1**, 733

3 Smith, P. and Lemstra, P. J. *Polymer* 1980, **21**, 1341

4 Capaccio, G. and Ward, I. M. *Nature (Phys. Sci.)* 1973, **243**, 143

5 Capaccio, G. and Ward, I. M. *Polymer* 1974, **15**, 233

6 Capaccio, G. and Ward, I. M. *Polymer* 1975, **16**, 239

7 Gibson, A. G., Davies, G. R. and Ward, I. M. *Polymer* 1978, **19**, 683

8 Gibson, A. G. and Ward, I. M. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 2015

9 Griswold, P. D., Zachariades, A. E. and Porter, R. S. *Polym. Eng. Sci.* 1978, **18**, 861

10 Dijkstra, D. J. Ph.D. Thesis, Rijksuniversiteit Groningen, The Netherlands, 1988

11 Hikmet, R. Ph.D. Thesis, University of Bristol, 1985

12 Natta, G., Porri, L., Corradini, P. and Morero, D. *Chim. Ind.* 1958, **40**, 362

13 Möller, M. *Makromol. Chem., Rapid Commun.* 1988, **9**, 107

14 Wunderlich, B. and Grebowicz, J. *Adv. Polym. Sci.* 1984, **60/61**, 1

15 Wunderlich, B., Möller, M, Grebowicz, J. and Bauer, H. *Adv. Polym. Sci.* 1988, **87**, 45

16 Lemstra, P. J., Bastiaansen, C. W. N. and Meijer, H. E. H. *Angew. Makromol. Chem.* 1986, **145/146**, 343

17 Lemstra, P. J., van Aerle, N. A. J. M. and Bastiaansen, C. W. M. *Polym. J.* 1987, **19**, 85

18 van Aerle, N. A. J. M. and Lemstra, P. J. *Makromol. Chem.* 1987, **189**, 1253

19 Bastiaansen, C. W. M. and Lemstra, P. J. *Makromol. Chem., Makromol. Symp.* 1989, **28**, 73