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Oxidative stabilization of oriented acrylic fibres–morphological rearrangements

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Changes in orientational and lateral order when an acrylic fibre is treated thermally at temperatures just below where stabilization reactions occur rapidly are characterized experimentally. Significant morphological rearrangements are shown to precede the onset of these reactions and also during these reactions. These changes are found to depend on the dimensional constraints imposed during thermal annealing. If shrinkage is allowed, the orientation of the ordered phase in the fibres increases but only at the expense of significant orientational relaxation in the less ordered fraction. Imposing dimensional constraints during annealing leads to a rapid increase in the overall order of the precursor. Possible ways of taking advantage of this tendency in a high-temperature drawing are discussed.

1. Introduction

Manufacture of carbon fibres from polyacrylonitrile-based precursor fibres involves:

(a) a thermo-oxidative stabilization stage which converts the precursor to an infusible structure;

(b) a carbonizing heat-treatment to drive off the non-carbon elements; and

(c) an optional high-temperature treatment to improve the mechanical properties of carbon fibres.

The properties of the final carbon fibre are affected by the chemical composition and morphology of the acrylic fibre and the chemical and morphological changes occurring during stabilization and carbonization. Many studies on isolated aspects of these different stages in carbon fibre manufacture have been reported [1–40]*. A comprehensive experimental study has been initiated in our laboratories to establish the material and process interactions with the properties of the ultimate carbon fibre. This study includes both chemical (e.g., comonomer and end group compositions) and morphological aspects of the precursor and the subsequent changes in them during stabilization and carbonization. The initial activity has concentrated primarily on the role of polymer composition in the kinetics of stabilization [41] and on identifying a set of parameters for characterizing morphological order and their interpretation. We report here the results of our initial efforts on the latter aspect, especially in relation to the stabilization stage.

1.1. Morphology

Information from wide-angle X-ray diffraction (WAXD) and electron microscopy studies on acrylic fibres shows clearly the existence of a basic morphological unit with a lateral dimension of the order of 5 to 10 nm in which the molecules are arranged in a laterally ordered hexagonal array [42]. Orientation of these laterally ordered units has also been determined from WAXD studies. The chemical changes that occur during stabilization can alter this lateral order and WAXD measurements with fibres at different stages of stabilization would reflect the nature of only the "surviving" ordered fraction. Studies have been conducted by Hinrichsen [9] with WAXD and by Thorne and Marjoram [10], with a combination of WAXD and birefringence measurements, to

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*[1–3] Reviews; [4–13] heat-treatment and morphology of acrylic fibres; [14–30] reactions and kinetics of stabilization; [31–40] carbon fibre formation, structure and properties.

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identify the changes that occur in orientational and lateral order in the precursor as it goes through stabilization. The latter found that birefringence increased monotonically with the extent of disappearance of nitrile groups while the orientation from WAXD showed a slight increase initially followed by a steady decrease. The birefringence data of Thorne and Marjoram can be replotted to reflect the birefringence of the new species appearing in stabilization by using the following equation:

$$\Delta n = f_s \Delta n_s + (1 - f_s)\,\Delta n_p + \Delta n_f,$$

where Δn, Δn_s and Δn_p are, respectively, the birefringences of the fibre at any stage of stabilization, the new species and the unconverted fraction of the original material. Δn_f is the contribution from form birefringence and f_s is the fraction of new species in the fibre. The negligibly small birefringence of oriented acrylic fibres indicates that $(1 - f_s)\Delta n_p + \Delta n_f$ can be neglected. Thus, one gets

$$\Delta n \simeq f_s \Delta n_s$$

or

$$\Delta n_s \simeq \frac{\Delta n}{f_s}.$$

The data of Thorne and Marjoram [10], when replotted to give the birefringence of the species appearing in stabilization, indicate that the orientation of the new species appearing throughout the conversion is significant and that this orientation lies within a narrow range.

Rose [7] and Warner *et al.* [13] have observed an initial sharpening, followed by a gradual broadening of the equatorial peak in WAXD when an acrylic fibre is annealed at 230° C. This indicates an association of laterally ordered domains prior to the depletion of order in them through chemical conversion. Based on X-ray diffraction and electron microscopical studies, the latter have also presented a morphological model of acrylic fibres consisting of fibrils in which connected regions of disordered and partially ordered regions alternate.

Small-angle X-ray scattering (SAXS) studies with wet-spun acrylic fibres show scattering from microvoids that is typical of wet-spun fibres [43]. The characteristic "long period" reflecting density fluctuations which one observes normally in oriented synthetic fibres, however, is absent in these fibres. If the difference between the densities of the laterally ordered domains and the regions where such order is absent is very small, SAXS would fail to differentiate between the presence and absence of such order. Scattering from fibres that have been thermally annealed shows a pronounced long period [5, 13], indicating the possible existence of periodic order in the precursor.

The work reported in the literature shows clearly the existence of significant repetitive and orientational order in the acrylic precursors and at least a partial persistence of the orientational order through the stabilization process. It would be safe to say that the morphology of the precursor, including possible distribution of defects, would influence greatly the morphology of the carbon fibre produced from it. It is our aim to identify the relevant, measurable morphological parameters and to keep an account of the changes in them as a precursor is taken through the different stages of the carbon fibre process. We report here the results of our initial efforts to characterize the changes in an acrylic precursor fibre when it is treated thermally at temperatures just below where the stabilization reactions occur rapidly. Significant morphological rearrangements are shown to precede the onset of these reactions and also during these reactions. These changes are found to depend on the constraints imposed on the fibre during thermal annealing. These annealing experiments show a tendency towards rapid "self ordering" of the precursor. Possible ways of taking advantage of this tendency are discussed.

2. Experimentation

2.1. Wet-spinning of precursor fibres

All the experiments were done on fibres spun in our laboratory by redissolving commercial acrylic fibres (type 43 Orlon; Merge No. 630 N43) supplied by Du Pont. The spinning conditions are given in Table I.

2.2. Thermal analysis

A Du Pont 990 thermal analyser was used to determine the range of temperatures where the

TABLE I Spinning conditions

Dope concentration	20% wt/wt in DMF
Spinneret	100 holes, 3 mil* diameter
Coagulation bath composition	60:40::DMF:H_2O
Coagulation bath temperature	25° C
Jet stretch	0.7
Draw ratio	3 or 6 in boiling H_2O
Drying temperature	110° C

*1 mil ≡ 1/1000 in.

stabilization reactions occur rapidly in the precursor used in this study. At a heating rate of 5° C min^{-1} the exotherm associated with these reactions was observed at temperatures above 285° C.

2.3. Thermal annealing

The annealing experiments were carried out in an air-circulated oven, preheated to the required temperature before the sample is introduced. To determine if constraints imposed on the fibres influence the changes during this process, experiments were conducted with free allowance for fibre shrinkage and under conditions where such shrinkage is prevented by holding the fibre at constant length. For free length annealing (FLA) the fibres were suspended from clips in the oven and for constant length annealing (CLA) the filaments were wound on rigid frames with just enough tension to remove any natural crimp in them. The temperature chosen for these experiments were below that of the onset of rapid reactions determined from thermal analysis.

2.4. X-ray experiments

Phillips X-ray units 4100 and 12215 (Norelco) at 40 kV and 25 mA were used to obtain flat plate diffraction photographs and equatorial intensity scans, used for estimates of the average lateral dimension of laterally ordered morphological units. A G.E. goniometer with a 2 mm square beam was used to measure azimuthal intensity profiles. The fibres were wound carefully by hand at a minimum tension as a parallel array on the sample holder (a frame with a central circular opening). In the case of constant length annealing, the precursor fibre was wound on the X-ray diffraction sample holder and the annealing was carried out with these pre-mounted samples. Sample preparation from free annealed fibres was difficult because of the entanglements and crimp caused by annealing in the air-circulated oven.

Size of the laterally ordered domains were estimated with the width at half the maximum intensity of the 100 peak at $2\theta = 17°$ obtained from the equatorial scan using the Scherer equation [44]. Corrections to account for crystal imperfections and instrument broadening were neglected. The estimated average lateral size is also referred to as the "crystal size" in this report.

Assuming a hexagonal lateral packing, Hermans' orientation function for the orientation with respect to the fibre axis of the chain segments in the laterally ordered regions was calculated from azimuthal intensity scans of the 100 reflection.

Hermans' orientation function of chains in the crystal, f_c, is given by [44],

$$f_c = -2\left[\frac{3\langle\cos^2\phi\rangle_{100}^{-1}}{2}\right],$$

where

$$\langle\cos^2\phi\rangle = \frac{\int_0^{\pi/2} I_{100}(\phi)\sin\phi\cos^2\phi\,d\phi}{\int_0^{\pi/2} I_{100}(\phi)\sin\phi\,d\phi}.$$

2.5. Sonic modulus

A dynamic modulus tester PPM-5, made by H. M. Morgan Company, was used for measurement of sonic velocity. The sonic modulus, E, was calculated in g denier^{-1}* by using the equation [45]

$$E = 11.3C^2$$

where C is the sonic velocity in km sec^{-1}.

The following semi-empirical equation can be used for estimating the Hermans' orientation function, f_s, of the sample with respect to the fibre direction [46]

$$f_s = 1 - \frac{E_{us}}{E_s},\dagger$$

where E_s = sonic modulus of the sample and E_{us} = the sonic modulus of an isotropic sample of the same material. Since we could not make isotropic samples differing from the annealed precursor fibres only in orientation distribution, the orientation functions of the constant length annealed samples were estimated using the sonic moduli of the corresponding free annealed fibres in the place of the isotropic reference. The free annealed samples do show a preferred orientation and so their sonic moduli would be higher than those of the fully isotropic ones. Thus the orientation functions computed here would be lower bounds for the actual values, i.e.,

$$f_{CLA}(t, T) = 1 - \frac{E_{us}(t, T)}{E_{CLA}(t, T)} > 1 - \frac{E_{FLA}(t, T)}{E_{CLA}(t, T)}$$

where $f_{CLA}(t, T)$ is the orientation function of constant length samples annealed for time t at

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*Denier = weight (g) of 9000 m.

†This semi-empirical equation assumes a single-phase material. It is used here only for the purpose of comparison.

TABLE II Short-time annealing experiments. Total annealing time 2 min; temperature of annealing 230° C; no evidence of chemical reactions

Precursor D.R.	Treatment condition	Shrinkage (%)	Initial modulus (g denier^{-1})	Breaking elongation (%)	Sonic modulus (g denier^{-1})	f_c	Crystal size (nm)
3	Orig.	–	61	13	95	0.54	5.4
3	CLA	–	70	16	120	0.69	8.9
3	FLA	16	43	23	57	0.59	8.9
3	CFLA	Negligible	67	17	120	0.69	9.9
6	Orig.	–	73	9	130	0.63	4.7
6	CLA		85	13	145	0.75	8.1
6	FLA	16	57	14	78	0.63	8.5
6	CFLA	Negligible	78	12	142	0.75	9.4

temperature T, E_{us} is the sonic modulus of unoriented sample; E_{CLA} is the sonic modulus of constant length annealed sample; and E_{FLA} is the sonic modulus of free annealed sample.

2.6. Mechanical properties

A mini Instron model 1130 was used with a 5000 g load cell. The gauge length and the elongation rates were 10 and 5 in. min^{-1} (25.4 and 12.7 cm min^{-1}) respectively. Since the fibres annealed for more than an hour were extremely brittle, they were tested at an elongation rate of 2 in. min^{-1} (5.08 cm min^{-1}).

3. Results and discussion

3.1. Short-time annealing

The annealing experiments in the present study were carried out at temperatures below 285° C so that the morphological rearrangements occurring in a short time before the onset of the chemical reactions can be separated from those occurring at longer times as a consequence of them.

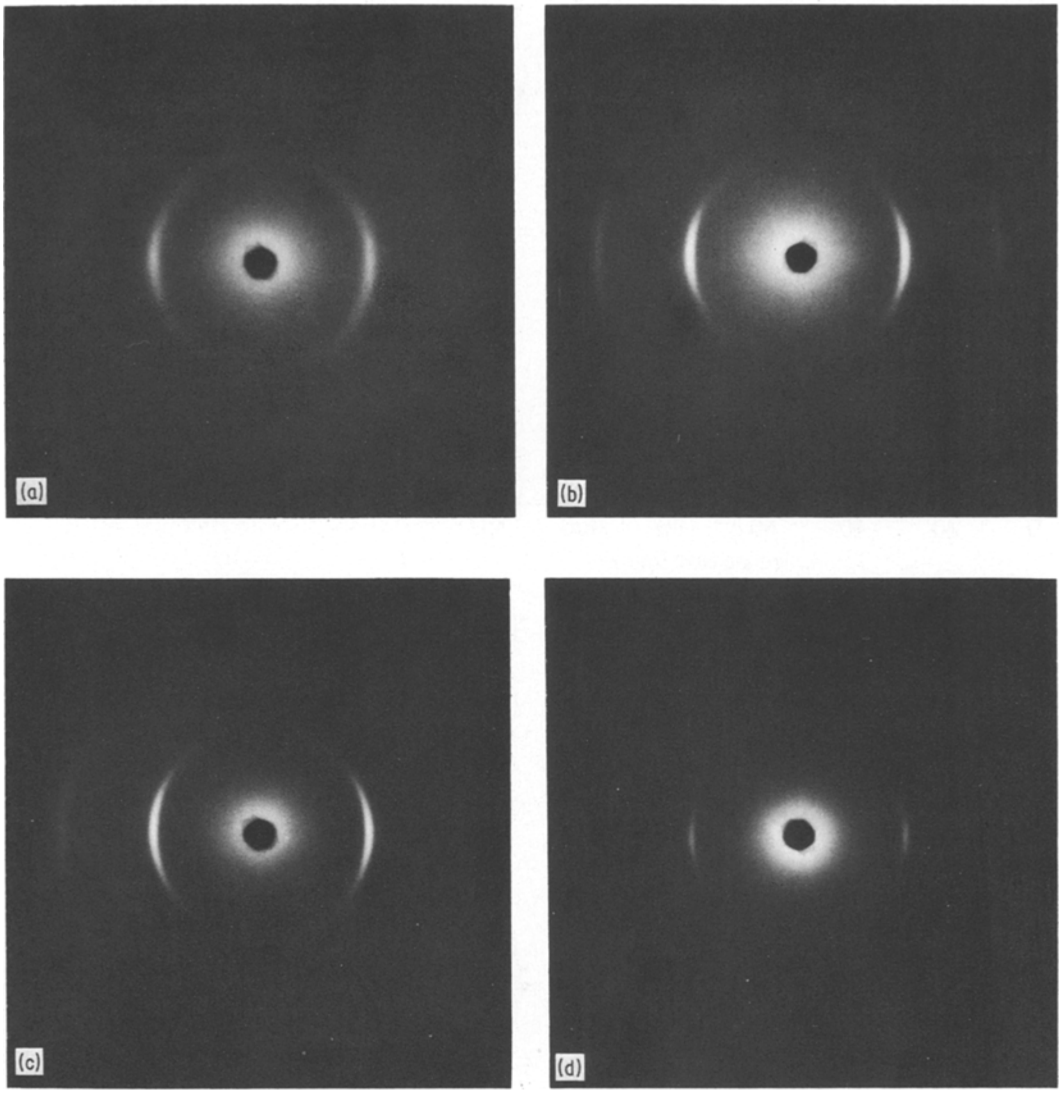
Exploratory short-time (2 min) annealing experiments were conducted at 230° C. These were carried out under free (FLA) and constant length (CLA) conditions as well as a combination of constant length followed by free annealing (CFLA). The last experiment was included to determine if any changes introduced initially in the presence of the constraint are erased to a significant extent by subsequent treatment without constraint. The results are given in Table II and show clearly that the orientation of the ordered fraction in the material as well as the overall orientation (inferred from sonic modulus) show a significant increase when a constraint against shrinkage is imposed on the fibres. Annealing the precursor under free conditions, however, results in considerable decrease in the overall orientation but shows simultaneously an increase in the orientation of the ordered phase. This indicates clearly the presence of a significant fraction in the material other than the ordered phase. The connections provided by the ordered phase do transfer macroscopic constraints to the rest of the material, thus preventing significant relaxation of orientation. The results from the CFLA experiments (1 min CLA + 1 min FLA) show that the order induced in constrained annealing is likely to be retained in the subsequent treatment under free conditions.

Significant shrinkage in fibres annealed under free conditions without decrease in the orientation of the ordered phase implies that the less ordered morphological units link successive oriented crystals along the fibre direction. The average lateral dimension of the oriented laterally ordered crystals is estimated to be around 5 nm in the unannealed fibres, in agreement with the estimate provided by Warner *et al.* [13]. Since the calculations neglect line broadening from possible imperfections in lateral order, it tends to underestimate the average size.

Increase in the orientation of the ordered phase can be attributed to lateral and longitudinal association in ordered bundles during annealing. The estimated average lateral size of these bundles increases significantly as a consequence of this association.

3.2. Time-scale annealing

In order to follow the progressive changes in morphology brought about by high-temperature treatment, the precursor fibres were treated for varying lengths of time at 270° C. This temperature was chosen to provide a reasonable period before



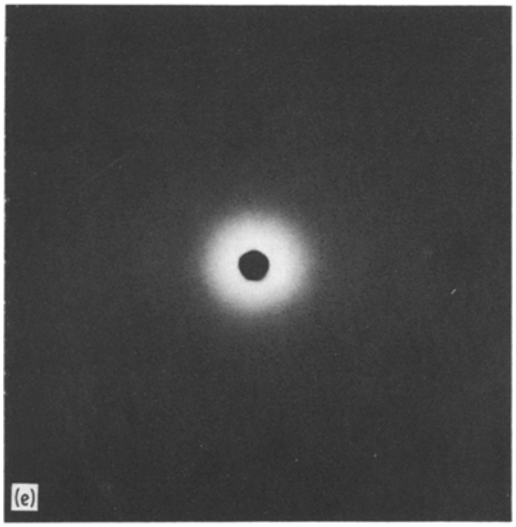


Figure 1 Flat-plate WAXD photographs of fibres (precursor draw ratio = 6) annealed at 270° C in air. (a) Precursor, (b) CLA for 4 min, (c) FLA for 4 min, (d) CLA for 48 min, (e) CLA for 128 min. Exposure time: (a) to (d) 2 h; (e) 4 h.

the onset of significant stabilization reactions in the material. Figs 1a to e show flat-plate WAXD photographs of samples exposed to 270° C in air for various durations. The initial significant increase in the orientation and the size of the ordered phase can be seen here. Quantitative measures of these at different stages of heat-treatments are shown in Fig. 2 (CLA) and Fig. 3 (FLA). The data show clearly that the orientational changes of the ordered phase measured here are a direct consequence of the initial association of segments into these domains followed by

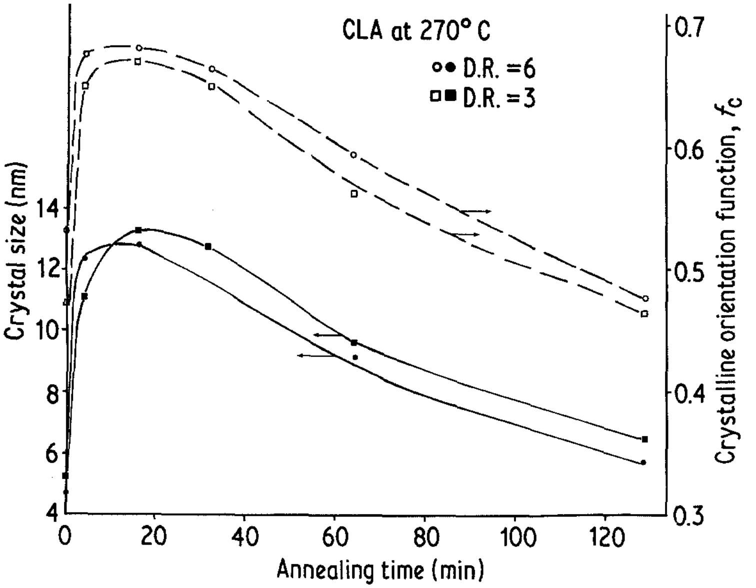


Figure 2 Average lateral size and Hermans' chain orientation function of the ordered phase in CLA fibres. Annealing temperature 270° C; precusor draw ratio: ○, ● 6 and □, ■ 3.

the "lateral order → lateral disorder" transformation caused by the stabilization reactions. The latter proceeds, by necessity, inwards from the boundaries of ordered domains, leading to a decrease in the average size of these domains.

The sonic modulus data of these fibres are shown in Fig. 4. One is tempted, at first glance, to interpret the data as indicating a decrease in the overall orientation at long annealing times. The change in the chemical nature resulting from the stabilization reactions would be expected to change the intrinsic physical properties of the material. The estimation of Hermans' orientation functions from the sonic moduli of the thermally treated fibres should take into account the changes in the sonic moduli of the reference isotropic sample. As discussed earlier, lower bounds for the orientation functions of CLA samples can be obtained using the equation

$$f_{\mathrm{CLA}} = 1 - \frac{E_{\mathrm{FLA}}}{E_{\mathrm{CLA}}}.$$

Typical values of these are given in Table III, which shows that the overall orientation of the material does not change significantly with the occurrence of stabilization reactions.

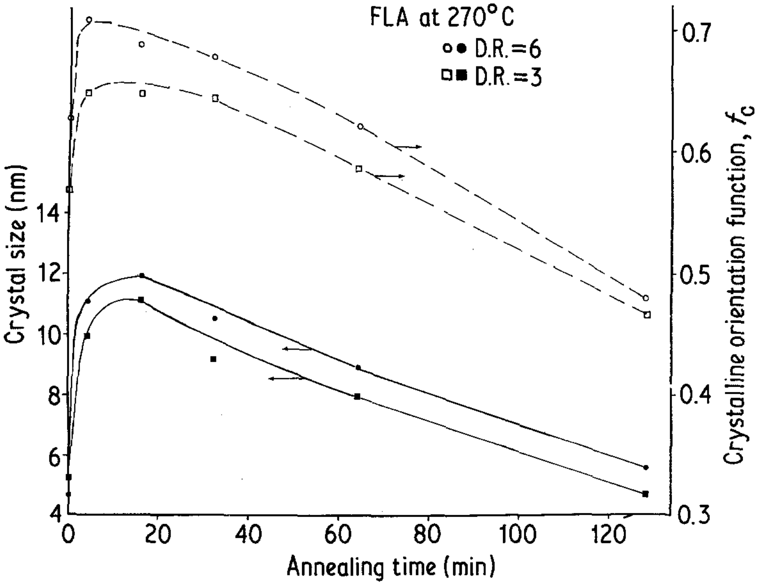


Figure 3 As in Fig. 2 but for FLA fibres.

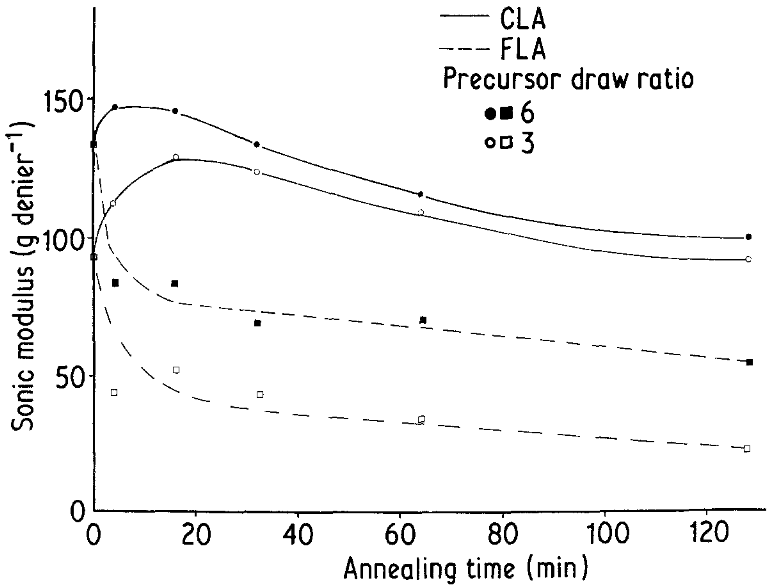


Figure 4 Sonic modulus of fibres annealed at 270° C.

The data from the FLA experiments (Figs 3 and 4) provide clear evidence for the existence of a phase of lower order than the ordered phase. In the absence of macroscopic constraints which prevent shrinkage, this phase can undergo significant orientational relaxation at high temperatures on a time scale that is much shorter than that in which detectable extent of reactions can take place in the material.

3.3. Pre-stabilization high-temperature drawing

The results from constant length annealing revealed a tendency in the precursor fibres towards self ordering with a significant increase in orientation. We have conducted exploratory experiments to determine if this tendency can be utilized to significantly improve the orientational and lateral order in the precursor. The results from a drawing experiment, where the fibre is drawn through a one-foot oven, are given in Table IV and typical flat-plate WAXD photographs are shown in Fig. 5. In the case where the fibre is passed through the oven without any drawing (draw ratio = 1.0), the morphological rearrangements are seen to occur on a very short time scale (the residence time in the oven here is 4 sec). The overall orientation can be increased significantly by drawing under these conditions where considerable mobility exists for allowing rearrangements along with a natural tendency toward ordering.

4. Conclusions

Significant morphological rearrangements take place in acrylic precursor fibres at temperatures comparable to those in a stabilization process. These changes, which occur both prior to and after the onset of detectable chemical reactions, depend to a large extent on the dimensional constraints imposed during annealing. Annealing in the absence of dimensional constraints causes a significant shrinkage and a decrease in overall orientation, but the orientation of the ordered phase increases. If fibre shrinkage is not allowed,

TABLE III Sonic modulus-based overall orientation of constant length annealed fibres. Temperature = 270° C

D.R.	Annealing time (min)	Sonic modulus (g dernier^{-1})		Lower bound for sonic modulus-based orientation function, f_{CLA}
		CLA	FLA	
6	4	147	79	0.46
6	16	145	79	0.45
6	32	133	68	0.49
6	64	115	69	0.40
6	128	99	54	0.45

TABLE IV High-temperature drawing experiments. Precursor D.R. = 6, drawing speed = 15 ft min^{-1} (457 cm min^{-1}), oven temperature = 240° C, length of oven = 1 ft

Sample	Elongation (%)	Initial modulus (g denier^{-1})	Sonic modulus (g denier^{-1})	f_c	Crystal size (nm)
Original	9	73	133	0.63	4.7
D.R. = 1.0	12	76	145	0.75	10.7
D.R. = 1.2	10	111	176	0.79	11.1
D.R. = 1.4	8	124	190	0.81	11.5

the overall orientation increases and this orientation is retained in subsequent annealing under free conditions.

It is well known that such morphological changes occur during thermal annealing of oriented synthetic fibres. Significant orientational relaxation of uncrystallized segments can occur without decrease in the crystalline orientation when drawn fibres are annealed under free conditions [47, 48]. The connectivity which exists along the axial direction in the oriented fibres necessitates the allowance for macroscopic shrinkage if orientational relaxation is to occur in the uncrystallized segments. Thus, annealing with dimensional constraints leads to a significant increase in overall orientational order brought about by increase in the orientation of the ordered phase without orientational relaxation in the less ordered phase.

The responses to thermal treatments of the acrylic fibres in the present study confirm the presence of at least two phases, one laterally ordered and the other a less ordered phase which contains segments that tend to be mobile at high temperatures. The latter segments are anchored in the ordered phase and macroscopic constraints are transmitted via the ordered phase to these segments, preventing significant orientational relaxation in them. The well established fibrillar morphology of drawn acrylic fibres, coupled with the mechanical response and changes in morphological parameters during annealing support the morphological model proposed by Warner *et al.* [13], namely connected alternating regions of lateral order and disorder along the fibrils. Relaxation of orientation in the disordered regions of such a morphology should lead to a significant decrease in the sonic modulus but without decrease in the orientation of the ordered regions. The results from free length annealing experiments (Figs 3 and 4) support clearly this contention.

The combination of sonic modulus and average orientation and lateral size of the ordered phase is useful in characterization of orientational changes during thermal treatment of acrylic fibres in which both morphological and chemical transformations take place. Trends in both crystalline and overall orientation, which are not always the same can be

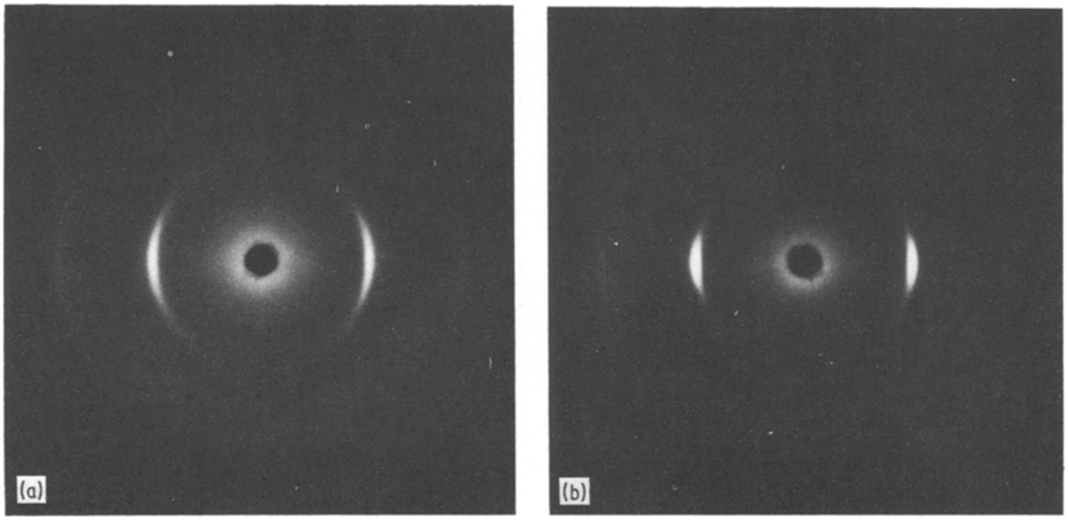


Figure 5 Flat-plate WAXD photographs (exposure time = 2 h) of fibres drawn at 240° C. Draw ratio: (a) 1.0 and (b) 1.4.

inferred from this combination. The favourable role of dimensional constraints during thermal treatment is especially made clear by this combination of techniques.

There is a tendency towards self ordering at high temperature in the presence of dimensional constraints. This has been shown to be advantageous in a high-temperature drawing that produces fibres with improved orientational and lateral order. This improvement occurs without loss of breaking elongation which suggests that the overall perfection also increases simultaneously. The importance of preventing shrinkage and the significant improvement in carbon fibre properties that result from stretching in the early stages of oxidizing acrylic fibres were shown by Watt and Johnson [33]. These effects were attributed by them to increased polymer chain orientation that is reflected ultimately in the carbon fibre. These favourable changes in morphological order may be obtained in a short-time high-temperature drawing process. The significance of these and possible reduction in microvoids induced by such high-temperature drawing in the manufacture of carbon fibres is being investigated.

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