

Drawing and orientation-relaxation behaviour of monodisperse linear and 3-arm star polystyrenes

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The drawing and orientation-relaxation behaviour of monodisperse linear and 3-arm star polystyrenes was studied as functions of temperature, strain-rate and relaxation-time. Differences in birefringence were found for linear and star polymer, with the same span molecular weight (M_s), drawn to large strains above the glass transition temperature (T_g) for time-scales close to, or longer than, the chain retraction-time (τ_B). There were also significant differences in birefringence between stars with different molecular weights. At T_g , for time-scales shorter than τ_B , birefringence was found to depend upon the polymer M_s and not topology. Below T_g , birefringence was also found to be independent of M_s . A comparison has been made between experiment and theory. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The deformation behaviour of bulk glassy polymers in tension and hydrostatic extrusion has previously been studied^{1,2}. Shrinkage force and birefringence measurements were combined to investigate the stress-optical rule and rubber elasticity theory. Orientation-relaxation information for star and linear polymers has been acquired using Monnerie's i.r. dichroism method³⁻⁶ which concurs with the Doi-Edwards 'tube' model⁷. It has been established that the branch point does not affect the linear viscoelasticity in the long-chain branched polymers, such as star-, H- and tree-shaped. However, non-linear viscoelasticity, particularly in extension, has not been extensively addressed. In this study, we have extended the temperature range of drawing experiments from well above the glass transition temperature (T_g), where previous data has been acquired³⁻⁶, down to temperatures below T_g . The drawing experiments have been designed to investigate the orientation-relaxation behaviour of monodisperse linear and 3-arm star molecules, with equivalent span molecular weight, at time-scales appropriate to the chain retraction (the B-process).

Birefringence and orientation-relaxation studies of 3-arm stars and linear polystyrenes have been compared with the Doi-Edwards tube model. The model has recently been successfully extended to polymer systems with various molecular topologies such as star, tree⁸,

H-shaped⁹ and comb structures. The tube dilation effect for star polymers^{10,11} has also been tested. Well-defined polymers with tailored molecular topology and chain-length are required to compare experimental data with theory. In the current work anionic polymerization techniques have been used to produce monodisperse linear and 3-arm star polystyrenes with molecular weights ranging from 10^5 (100 K) for the linear to 3×10^5 (300 K) for the star. The low dispersity of molecular weight of our model compounds ensures that there is neither a plasticizing effect due to the presence of short chains nor any observable molecular weight distribution effect. Experiments with 3-arm stars have not previously been accomplished in the low entanglement molecular weight range and the deviation from the conventional Doi-Edwards model was expected to be significant.

THEORY

In the Doi-Edwards tube model⁷, after a step change in strain the relaxation in orientation of a deformed polymer chain in its surroundings (modelled as a tube with a diameter of one entanglement) can be divided into three stages. The first stage is a local motion between entanglement points known as entanglement Rouse relaxation (process A). This process is fast because the relaxation length in the chain is no longer than one entanglement, i.e. it does not feel the constraint from the tube. The characteristic relaxation-time of the entanglement motion is controlled by the friction coefficient of

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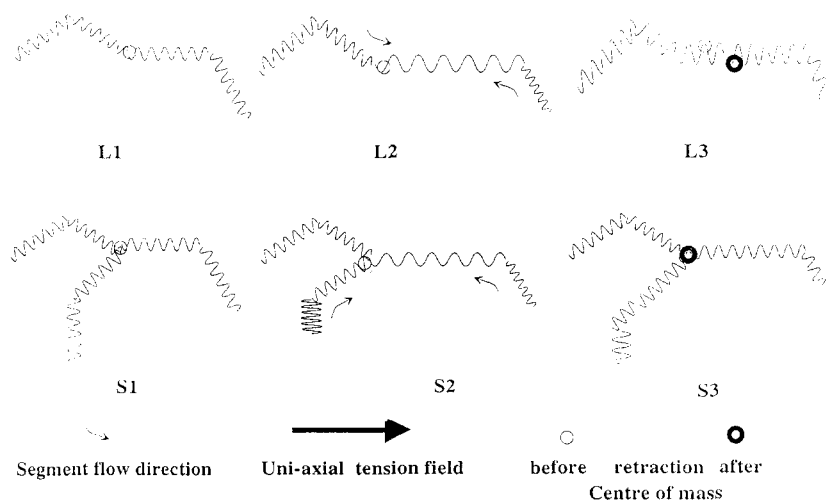


Figure 1 Branch point effect on mass transport through centre of mass in the B-process

the polymer which is independent of molecular weight. The second relaxation is by chain-retraction (process B), which is a curvilinear chain-length equilibration. This occurs on a time-scale which is proportional to the square of the molecular weight. The third stage (process C) is diffusive relaxation. For linear chains, this is a snake-like motion which was called 'reptation' by de Gennes⁸. Reptation involves disentanglement by curvilinear diffusion from the initially deformed tube towards an equilibrium isotropic conformation. For branched chains, reptation is replaced by a chain-end diffusion process.

The characteristic retraction and reptation times (τ_B and τ_C) can be estimated from the entanglement Rouse time (τ_A): $\tau_B = N^2\tau_A$ and $\tau_C = 3N\tau_B$, where N is the number of entanglements per chain. The entanglement molecular weight (M_e) for polystyrene³ is 18 000. At 115°C, the entanglement Rouse time for polystyrene is 28 s⁶.

Branch point effect

A simple model is presented here to account for the linear and star chain retraction (process B) relaxation. If we apply a uniaxial tension field to randomly orientated segments of a molecular chain (Figure 1, L1 and S1), the segments in the same direction as the strain-field will be stretched and the segments that are perpendicular to the strain direction will be compressed (Figure 1, L2, S2). In the B-relaxation process, the repeat units in the compressed parts of the chain flow towards the stretched parts of the chain (Figure 1, L3, S3). In a linear chain this flow can happen between the two halves of the chain so that the position of the centre of mass is moved. In a star molecule this slip of material from one half of the chain to the other is prohibited because of the pinning effect of the extra arm at the branch point. The B-relaxation of the star is slower than the retraction of the equivalent linear structure because the B-relaxation process of the star lacks the assistance from the flow of material through the branch point.

When the arm of the star is relatively short the percentage of repeat units which would, in the absence of the pinning effect, be transported from one half of the chain to the other during retraction process is on average relatively high. However, when the molecular chain is

relatively long, the random nature either side of the branch point is sufficient to achieve a relaxed state equilibrium so that the need for the repeat units to equilibrate over the two halves of the chain is reduced. Therefore, a significant difference between the B-process relaxation for the linear and star molecules only occurs when the chain is up to a few entanglement molecular weights in length.

In the Doi-Edwards (DE) model, the 'strain-thinning' or 'damping' of the stress arises from the loss of entanglements during the B-process. This leads to a dominant pre-factor of $\langle \mathbf{E} \cdot \mathbf{u} \rangle^{-1}$ where \mathbf{E} is the strain tensor and \mathbf{u} a unit vector. The average $\langle \mathbf{E} \cdot \mathbf{u} \rangle$ is taken over all orientations. When the number of segments along a chain is small, the pre-averaging approximation is not accurate, and the fluctuations about the average segment stretch are important. Averaging this pre-factor over Gaussian fluctuations in $\langle \mathbf{E} \cdot \mathbf{u} \rangle$ of variance $(\sqrt{M/M_e})$ leads to an increased stress for shorter arms of magnitude (M_e/M) . This constitutes a correction to the pre-averaged DE result. Any relaxation of stress is accompanied by a loss of birefringence because of the existence of a constant stress-optical coefficient. The ratio of residual birefringence between the star and the equivalent linear molecules with M_a/M_e entanglements per arm has not been reported before and is therefore the ratio of the corrected values

$$\beta = \frac{\Delta n(\text{star})}{\Delta n(\text{linear})} = \frac{1 + (M_e/M_a)}{1 + (M_e/2M_a)} \quad (1)$$

We may carry this modification through to the fully time- and strain-dependent Doi-Edwards result for stress decay. To do this we employ the modified pre-factor of equation (1) in the expression from the pre-averaged theory*

$$\Delta n(t, \lambda) = C \left[\beta^{1/2} + \left(\alpha(\lambda) - \beta^{1/2} \right) \sum_{p=1}^{\infty} h(p) e^{-2p^2 t / \tau_B} \right]^2 \times f(\lambda) G(t) \quad (2)$$

Here, C is the stress-optical coefficient, β is the coefficient describing the molecular topological effect on retraction,

*Doi, M. and Edwards, S. F. 'Theory of Polymer Dynamics' p. 253, equation (7.137)

and M_a and M_e are the arm and entanglement molecular weights respectively, and

$$h(p) = \begin{cases} 1 & \text{linear} \\ \begin{cases} 2 & p = \text{odd} \\ 0 & p = \text{even} \end{cases} & \text{star} \end{cases} \quad (2a)$$

$$G(t) = G_0 \left[\frac{8}{\pi^2} \sum_{p,\text{odd}} \frac{e^{-p^2 t / \tau_C}}{p^2} \right] \cong G_0$$

the plateau modulus for $t \ll \tau_C$ (2b)

$$\alpha(\lambda) = \frac{1}{2} \lambda [1 + A(\lambda)] \quad (2c)$$

$$f(\lambda) = \frac{15}{4} \frac{\lambda^3 + 0.5}{\lambda^3 - 1} \frac{1}{1 + A(\lambda)} \times \left[1 - \frac{4\lambda^3 - 1}{2\lambda^3 + 1} A(\lambda) \right] \quad (2d)$$

where

$$A(\lambda) = \frac{\sinh^{-1}(\sqrt{\lambda^3 - 1})}{\sqrt{\lambda^3(\lambda^3 - 1)}} \quad (2e)$$

and $G_0 = 2.1 \times 10^5$ Pa, calculated³ from M_e . The stress-optical coefficient in the rubbery state¹³ is -5×10^9 Pa⁻¹.

Rouse relaxation spectra

The longest characteristic Rouse (chain retraction) time (τ_B) for the linear and star are the same because their span molecular weights are the same. However, their Rouse relaxation-time spectra are different because for the linear polymer the retraction can occur from both ends whereas in the star polymer the arm is fixed at one end (branch point) and retraction therefore only occurs from the other end. The Rouse modes can be characterized as

Linear: $\tau_R/1^2, \tau_R/2^2, \tau_R/3^2, \tau_R/4^2, \tau_R/5^2, \dots, \tau_R/n^2$
 Star: $\tau_R/1^2, \tau_R/3^2, \tau_R/5^2, \tau_R/7^2, \tau_R/9^2, \dots, \tau_R/(2n-1)^2, \dots$

The longest (characteristic) relaxation-time occurs when n equals 1, which is the retraction time for the whole chain (τ_B). The second longest Rouse relaxation-time is $\tau_R/4$ for linear chains, and $\tau_R/9$ for the star molecules. The relative contribution to residual orientation from the longest relaxation is higher in the star than in the equivalent linear because there are less Rouse modes in the retraction process for the star (Figure 2). The relative contribution from the n th Rouse mode to the residual retraction stress is equal to

$$\frac{e^{-2n^2 t / \tau_R}}{\sum_i e^{-2i^2 t / \tau_R}}$$

At the onset of the B-relaxation process, e.g. when t equals $0.01 \tau_B$, 31.3% of the total retraction stress in the star and 17.7% of the total retraction stress in the linear is contributed by the longest Rouse mode ($n = 1$). When t is $0.1 \tau_B$, the values become 82.6% for the star and 55.3% for the linear (Table 1). The relaxation is slower in the star than in its equivalent linear because of the larger

percentage contribution from the longest Rouse time for the star molecules. At τ_B , the contribution from the longest Rouse mode is still higher in the star (100%) than the linear (99.7%).

EXPERIMENTAL

Synthesis

Monodisperse linear and 3-arm star polystyrenes were synthesized in a 5-litre stainless steel reactor under anaerobic conditions. The anionic polymerization of styrene (Aldrich) was initiated with *sec*-butyllithium (1.3 M in cyclohexane, Aldrich) with the reaction carried out as a dilute solution in cyclohexane (May and Baker, h.p.l.c. grade) maintained at 40°C. At the completion of the polymerization, 1,3-butadiene (Union Carbide) was added to the resulting polystyryllithium chains in quantities sufficient to introduce an average of two diene units per chain-end. This copolymerization reaction sterically aids the subsequent coupling reaction. A sample of linear polystyrene was removed from the reactor, precipitated, dried and characterized by gel permeation chromatography (g.p.c.). A calculated amount of trichloromethylsilane (Aldrich) was then injected into the remaining polyanion solution, serving to couple 'living' polymer chains into 3-arm star polystyrene. The coupling reaction does not produce star material quantitatively from the linear precursor, and so uncoupled linear polymer was later removed from the linear-star mixture by a fractional precipitation

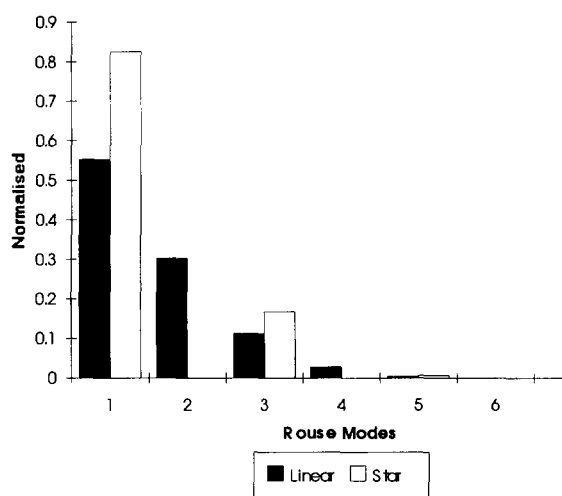


Figure 2 Contribution to retraction stress from Rouse mode spectra for star and equivalent linear polymers

Table 1 Contribution (%) to retraction stress from the first few Rouse modes in both linear and star polymers

n^a	t/τ_B							
	0.1		0.2		0.5		1	
	Linear	Star	Linear	Star	Linear	Star	Linear	Star
1	55.3	82.6	74.4	96.1	95.2	100	99.7	100
2	32.3	0	22.4	0	4.7	0	0.25	0
3	11.2	16.7	3.0	3.9	0.03	0.03	0	0
4	2.78	0	0.18	0	0	0	0	0
5	0.45	0.68	0	0	0	0	0	0
6	0.05	0	0	0	0	0	0	0

^a n stands for the n th Rouse mode

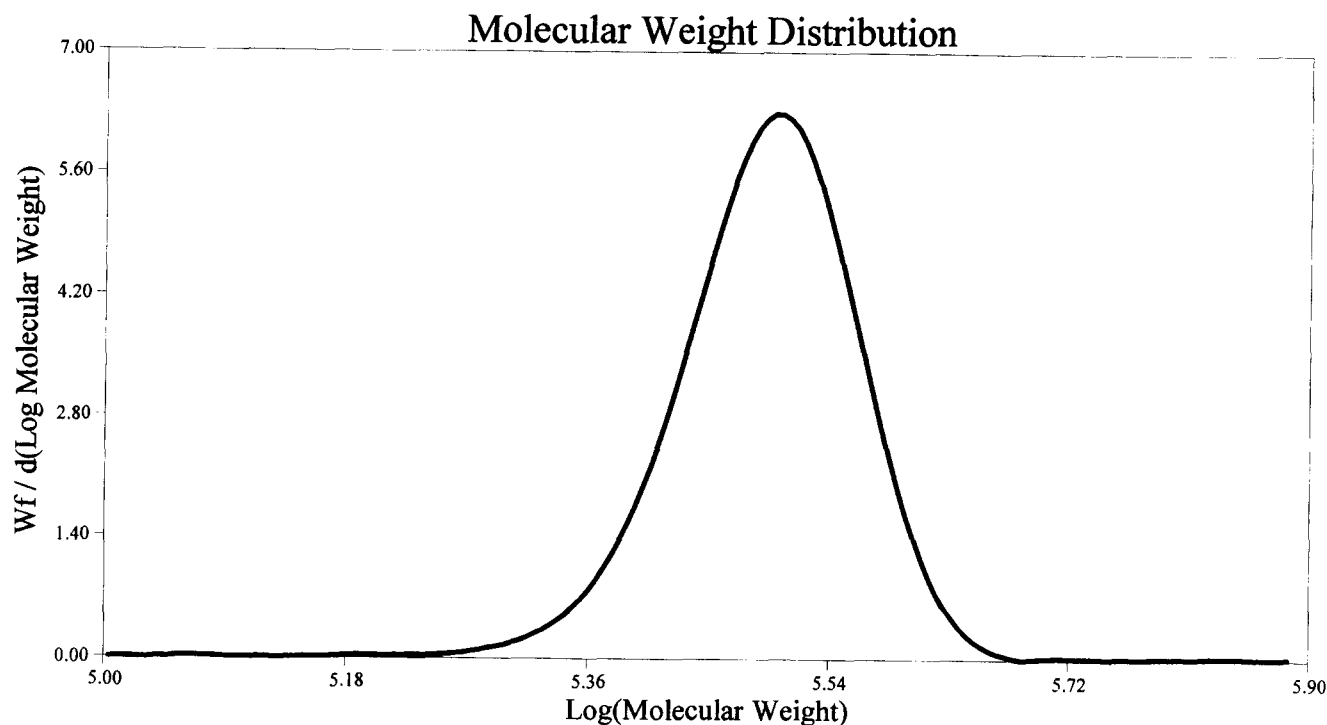


Figure 3 Molecular weight distribution of S200 and its linear precursor

Table 2 Molecular weights for polystyrenes employed in the drawing and relaxation experiments

Polymer	M_n	M_w	M_w/M_n	Assigned M_s
L110	106 800	111 900	1.05	107 000
S85	127 600	133 500	1.05	85 000
S110	164 900	172 900	1.05	110 000
S200	299 800	309 100	1.03	200 000

Band broadening corrections were not applied to these data

procedure. The 'purified' star polystyrene was recovered and analysed by g.p.c.

Characterization

The molecular weights and molecular weight distributions (MWD) of the linear and 3-arm star polystyrenes were determined by a triple detector g.p.c. system (Waters refractive index detector R401, Viscotek differential viscometer DV110 and Viscotek RALLS LD600) with a set of $5 \times$ PLgel $10 \mu\text{m}$ mixed-bed columns. Tetrahydrofuran was used as the eluent at a flow-rate of 1 ml min^{-1} . From previous research¹², the span molecular weight (M_s) is the pertinent molecular characteristic in the study of rheological properties. Therefore, M_s is the molecular characteristic employed to designate the materials used in this study (Table 2).

G.p.c. was used for quality control to ensure that linear material had been removed completely, within the limits of detection, from the star polymer to be analysed in the subsequent drawing experiments. The MWD for a 3-arm star polystyrene, S200, is presented in Figure 3. The structures of L110, S85, S110 and S200 are illustrated in Figure 4.

The glass transition temperature (T_g) of the polystyrenes synthesized for the current work were all determined to be 105°C , using a Perkin-Elmer DSC7 at a scan rate of $10^\circ\text{C min}^{-1}$.

Sample preparation

The polystyrene samples were compression moulded from powder in the temperature range $160\text{--}200^\circ\text{C}$ at a pressure of 10 MPa; a process designed to remove air bubbles. The compression moulded thin films were used directly for drawing-birefringence measurements and also for micro-spinning. Direct micro-spinning from powder is difficult because mono-filaments break during the drawing process if air bubbles are present. Mono-filaments were spun, using cut-up compression moulded films as feed stock, to the chosen diameter by controlling the ram and winding speeds.

The micro-spinning technique offers advantages over samples produced on a lathe. Firstly, only small quantities of sample are necessary. Secondly, the mono-filament surface is smooth which is a vital property when studying drawing properties. Therefore, further sample preparation, such as cutting or polishing,

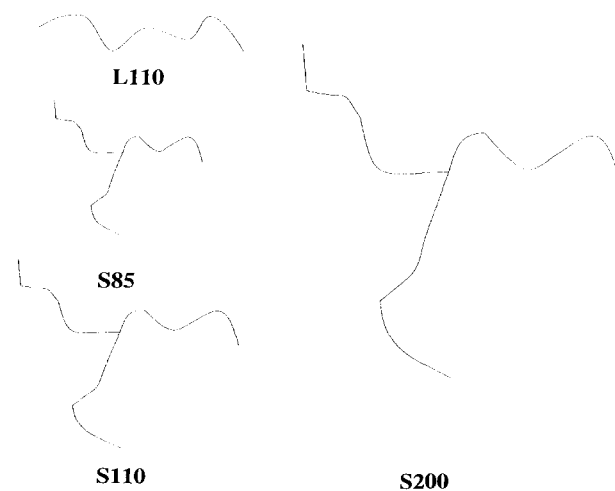


Figure 4 Molecules used in this study

is not needed. Furthermore, the mono-filament diameter can be relatively easily controlled. The films and mono-filaments were produced to 200 μm in thickness and diameter respectively.

Drawing and birefringence

Thin films and mono-filaments of linear and 3-arm star polystyrenes were relaxed at 120°C for 30 min. The relaxation process eliminates orientation caused by compression moulding or the micro-spinning processes and erases previous thermal history. Samples were marked at 2 mm intervals to enable localized measurement of the draw-ratio, as a function of position along the samples, to correlate with local measurements of birefringence. The samples were then heated to 120°C for 10 min before being cooled slowly to the drawing temperature.

Samples were drawn at three different strain rates at 100, 105, 110, and 115°C in an Instron Environmental Chamber (A351-14), which has a temperature control of $\pm 0.5^\circ\text{C}$ (see Table 3). After drawing, samples were allowed to relax at constant length for various times, from 0 to 60 min, at the drawing temperature. The drawn samples were then quenched to below their glass transition temperature using an aerosol coolant.

The drawing inhomogeneity (necking) is a common phenomenon in all of our drawing experiments. Therefore, we were able to obtain a set of birefringence vs draw-ratio data for each sample under investigation during a single drawing experiment. This inhomogeneity may be induced by such factors as a local temperature variation along the sample, uneven sample geometry or even a density fluctuation within the sample. The local draw-ratio was measured from the separation of the marks drawn on the sample. The existence of inhomogeneous draw means that various regions of the sample may not have seen a true uniaxial stress state and constant strain rate throughout the draw. However, this error is compensated to some extent by measuring many average strains at 2 mm intervals throughout the sample length.

For the monodisperse linear 110 k material in this study, designated L110 ($M_n = 106.8\text{ k}$), the number of entanglements in the chain (N) equals 6. The chain retraction time τ_B is therefore about 17.5 min and the characteristic reptation time τ_C is about 5.3 h. The retraction time for monodisperse star molecules can be estimated using the formula for the linear with the same span molecular weight. The approximate chain retraction time for the star S200 ($M_n = 300\text{ k}$) used in this study is thus estimated to be 56 min.

The C-relaxation time for the star polymer is much longer than for the equivalent linear chains according to the Doi-Edwards model⁷. The characteristic relaxation-times for the polystyrenes at the different temperatures used in this study are summarized in Table 3. Values referring to linear PS100 and star Star500 from the literature³⁻⁶ are also provided.

The high draw-ratio experimental time-scale at 115°C, in the current work, is close to the end of the B-process retraction time for L110 and S110 but only midway through for S200. The low draw-ratio experiments cover the beginning of the B-process for all our materials. In addition, the relaxation experimental time-scale covered the complete range of the B-processes for all of the samples.

Table 3 Drawing conditions for experiments around τ_B

Temp ($^\circ\text{C}$)	Samples	Gauge length (cm)	Figure
100	S110, S200	4, 5	5a
105	S85, L110, S110, S200	4 ^a	5b
110	S85, S110, L110	3.5	5c
115	S110, L110	5	5d

Cross-head speed 1 cm min^{-1} , draw ratio 2 for all experiments

^a Draw ratios of S200 at 105°C was 2.4. At 110°C, draw ratio was 3

To provide a simple measure of chain orientation after uniaxial deformation, the birefringence of the polymers was measured using an Ehringhaus compensator in a Carl Zeiss Jena Polmi-A optical microscope at ambient temperature. In previous studies of drawn polystyrene, a change in sign of the birefringence has been observed under certain conditions¹³. In this study, all of the results are in the negative birefringence region.

Three drawing experiments were designed to study the orientation-relaxation behaviour with time-scales:

- (i) Shorter than the B-process relaxation time. A fixed draw-ratio of 1.5 (low draw-ratio) at several nominal strain-rates and various temperatures for experimental times of no longer than 2 min to study linear viscoelasticity.
- (ii) Close to the B-process relaxation time. A maximum draw-ratio of greater than 3.5 (high draw-ratio) with a constant initial strain-rate at a given temperature for at least 5 min to study non-linear viscoelasticity.
- (iii) Longer than the B-process relaxation-time. A relaxation experiment with a draw-ratio of 2 at given nominal strain-rates at 115°C. The samples were kept at a fixed length in an oven to relax for different times, from 1 to 60 min, before being quenched to room temperature to study orientation-relaxation. The experimental time is called either decay time or referred to as time-scale.

Mono-filaments of the samples were used in all the above experiments except for experiment (ii) where thin sample films were employed. The inhomogeneity of deformation (necking) in the samples allowed the measurement for a range of draw-ratios and corresponding birefringences on a single specimen. A curve of birefringence vs draw-ratio was thus obtained for each single sample.

RESULTS AND DISCUSSION

High draw-ratio behaviour

The experimental results for films of L110, S85, S110 and S200, drawn at 100, 105, 110 and 115°C to a high nominal draw-ratio, are shown in Figures 5a-d. The drawing conditions are summarized in Table 3. In all of the experiments employing method (ii) above, the cross-head speed was 1 cm min^{-1} and the nominal (average) draw-ratio was designed to be 2.

In plots of birefringence vs draw-ratio for star polymers (Figure 5a) the birefringence of S110 and S200 at 100°C (below T_g) are found to be independent of molecular weight. The curves are also observed to reach a plateau value of approximately -0.045 when the draw-ratio is higher than 3.5, which is the draw-ratio observed in the neck. This maximum birefringence value for star polystyrene drawn at a temperature below T_g is in

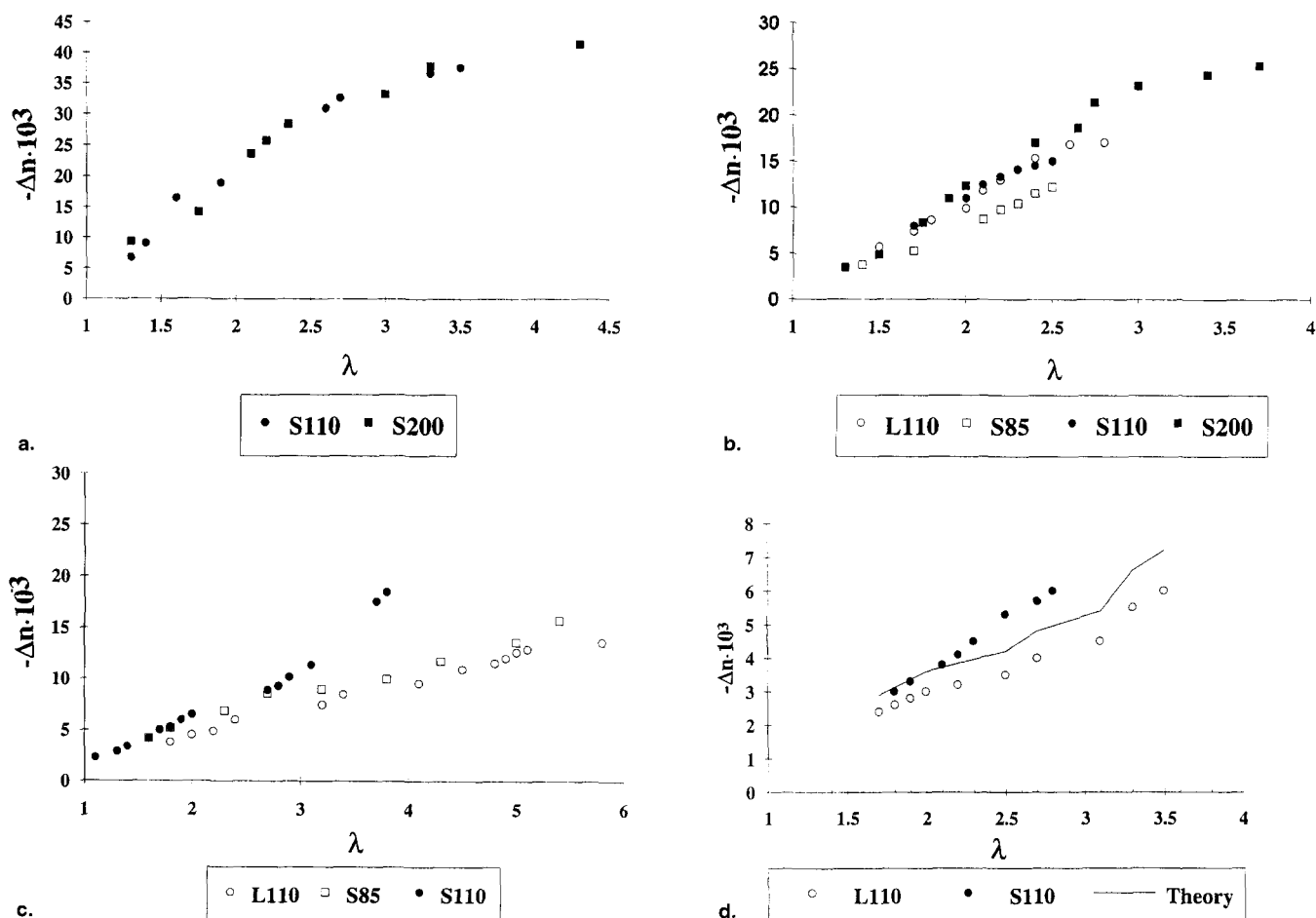


Figure 5 High draw-ratio behaviour: Birefringence vs draw-ratio for samples L110, S85, S110 and S200 at temperatures (a) 100, (b) 105, (c) 110 and (d) 115°C

agreement with the reported birefringence value for linear polystyrene (-0.048)¹⁴ when drawn at high strain rates. Therefore, the maximum birefringence for polystyrene is found to be independent of the molecular topology of the samples.

At T_g (Figure 5b) 105°C the birefringence for the polystyrene samples decreases in the order $S200 > S110 \sim L110 > S85$. It is evident that the higher the span molecular weight (the larger the radius of gyration), the higher the birefringence at any draw-ratio. The molecular topology has only a small effect. However, in the glass transition region the properties of polymers are very temperature sensitive. Small differences in T_g between these materials would then lead to significant differences in behaviour at the same drawing temperature and so these tentative conclusions must not be overstated.

Above T_g (Figures 5c, d) the birefringence of the linear polymer (L110) is lower than that of the equivalent star (S110). In fact at 110°C (Figure 5c) the birefringence of L110 is even lower than that of S85 at the same draw-ratio, even though its span molecular weight is larger. This provides evidence that the star polymers have a higher birefringence and a slower relaxation than the linear polymers. Therefore, molecular topology has a more profound effect at temperatures above T_g .

Comparing high draw-ratio behaviour with theory

The stress vs draw-ratio curves were calculated using the Doi–Edwards (DE) model for the linear and the

modified Doi–Edwards (MDE) model for the equivalent star. Using the experimental stress-optical coefficient¹³ calculated birefringence values, without any disposable parameters from the original nor the modified Doi–Edwards model for the linear and equivalent star respectively, were compared with the experimental data in this research. In Figure 5d, the birefringence of linear polymer L110 was shifted up by the factor 1.2 [calculated from equation (1)], to compare with the equivalent star polymer S110, and a good agreement was observed between the birefringence for the star and the linear polymer, as predicted by theory when the experimental time-scale is not significantly longer than τ_B .

The quantitative results from our modified Doi–Edwards model, taking into account the branch point effect on the retraction process, are shown in Figures 6a and b. The theoretical values for birefringence are calculated from the Doi–Edwards model assuming (i) a step-strain input to different strain values, followed by stress-relaxation for a time of (a) 11.6 min and (b) 7 min and (ii) a constant stress-optical coefficient taken from the literature¹³. DE_0 is calculated from Doi–Edwards model at time 0 and $DE(t)$ at time t . In Figure 6a, the data provided are for L110 which was drawn at 115°C for 11.6 min at a constant rate to a nominal draw-ratio of 2. Orientation relaxation was occurring throughout this drawing process and in principle the results should therefore lie between the DE_0 and $DE(t)$ curves, as is

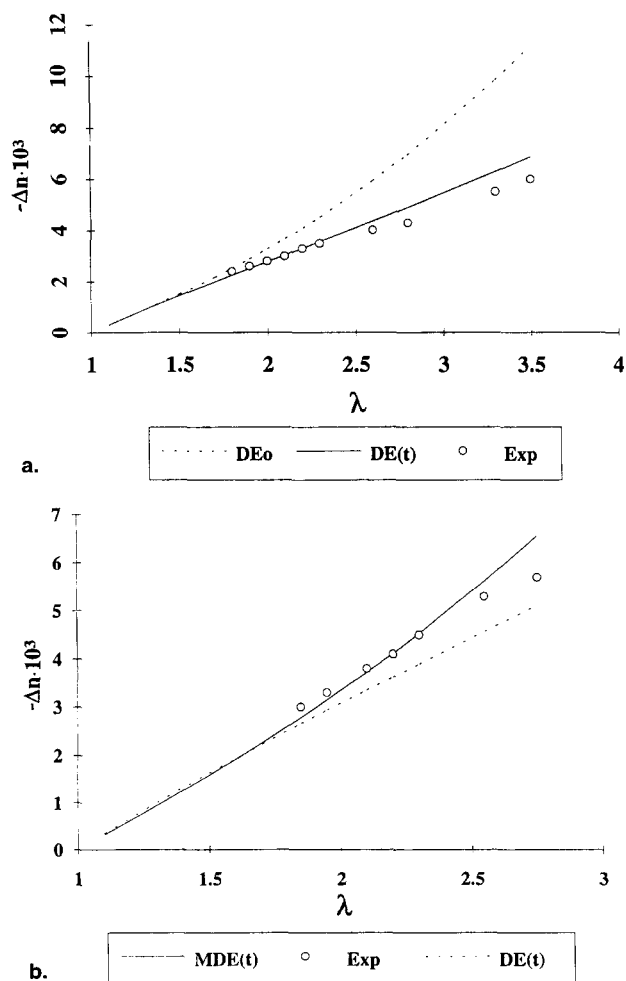


Figure 6 Experimental, Doi-Edwards and modified Doi-Edwards comparison for samples (a) L110 and (b) S110

observed at small strains. This shows a good agreement between experiment and theory at relatively small strains. The deviation from the calculated curves at high strains may be explained either by the non-linear viscoelasticity of the polymer or by the onset of the C-relaxation process.

In Figure 6b, $DE(t)$ is calculated from the original Doi-Edwards model and compared with data from drawing for 7 min at constant rate. This model produced a lower value of birefringence at all measured strains. $MDE(t)$ is calculated from the modified Doi-Edwards model [equation (2)] with the branch point pinning effect of the centre of mass motion. The modified Doi-Edwards model clearly improved the description of the orientation-relaxation for the star molecules. The experimental birefringences for S110 are slightly higher than the values calculated from the modified Doi-Edwards model at small strains, however this trend is reversed at large strains. This finding was also observed for L110. The differences between calculated and experimental values at small strains are small and can probably be explained by the variation between our experimental procedure which involved drawing at a constant nominal strain-rate and a true step-strain experiment: although this effect is difficult to quantify it is clear that the birefringence from the step-strain experiment should be lower than from constant strain-rate, as observed, because of the longer time for decay.

The deviation at high strains can be explained by the argument proposed above for the linear polymer in terms of non-linearity.

Low draw-ratio behaviour

In the uniaxial tensile experiments, the orientation of the polymer sample is sensitive to the strain-rate and drawing temperature. The final orientation increases with increasing strain-rate and decreases with increasing drawing temperature. The quantitative relationship between drawing time (reciprocal of strain-rate) and temperature in the linear region is summarized by the WLF equation, which describes the time-temperature superposition principle over a wide temperature range. Extensive results on polystyrene can be found in the literature³⁻⁶.

(a) *Temperature effect.* The orientation-deformation properties of the star and linear polystyrenes in the linear small strain regime was studied. The birefringence vs draw-ratio plots for L110, S85, S110 and S200 after drawing at 105, 110 and 115°C, are presented in Figures 7a-d. The materials all behaved similarly, due to the experimental time-scale being much shorter than the characteristic relaxation-time of the B-process even at 115°C. Therefore, birefringence differences caused by the B-process relaxation cannot be detected at such short time-scales and non-linear viscoelasticity cannot be detected at such small strains. When drawing to a low draw-ratio in the temperature range around and above the glass transition, a higher orientation was achieved at a lower temperature whilst keeping other experimental drawing conditions constant.

(b) *Strain-rate effect.* Samples of L110, S85, S110 and S200 were drawn to a nominal draw-ratio of 1.5 at several strain-rates at 115°C. The birefringence vs draw-ratio curves are shown in Figures 8a-d. The effect of strain history upon birefringence is similar for all the samples of differing topology and molecular weight. The higher strain rate at this temperature produces a higher orientation at a given draw-ratio. There is not a difference in the linear viscoelasticity between linear polystyrene and the equivalent star polymer. This finding is in agreement with other reports³⁻⁶. The following relaxation experiment was designed to detect the relaxation effect more directly, specifically that of the branch point.

Relaxation behaviour

To determine if orientation-relaxation occurs in the time-scale as the experiments, L110, S110 and S200 were drawn at 5 cm min⁻¹ from 4 cm to 8 cm (i.e. to a nominal draw-ratio of 2) at 115°C. The samples were then left in an oven for decay-times of between 1 and 60 min. For the longest decay-time, the results were not expected to be significantly different from a step-strain experiment. The birefringence was measured for each sample at room temperature.

The birefringence decreases both with the decay-time and the whole experimental time. For example, S200 in Figure 9, the birefringence at a draw-ratio of 2 decreased from approximately -4×10^{-3} after 0.8 min drawing and 1 min relaxation in the oven, to about -2×10^{-3} after 0.8 min drawing and 60 min relaxation in the oven.

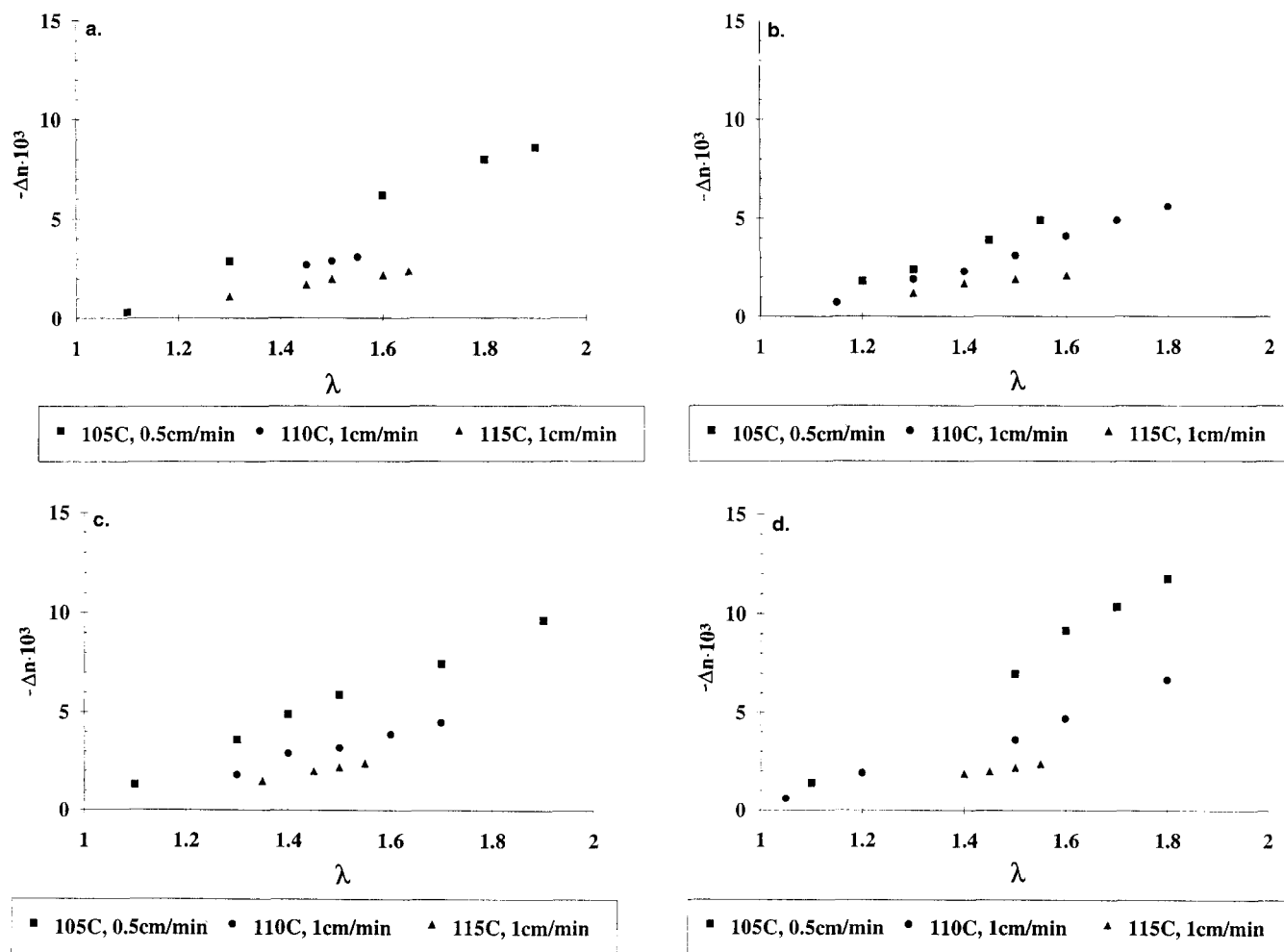


Figure 7 Temperature effect at low draw-ratios at a constant nominal draw rate for samples (a) L110, (b) S85, (c) S110, (d) S200

The birefringence values for L110, S110 and S200 at different draw-ratios, after 5 and 60 min relaxation, are presented in Figures 10a and b respectively. In Figure 10a, the birefringence of S200 is higher than both that of S110 and L110, i.e. a molecular weight effect on birefringence is presented. Samples of S110 and L110 have the same span molecular weight, but the birefringence of S110 is higher than that for L110, which means that the extra arm of S110 affects the birefringence under the experimental conditions. In the short time-scale, molecular topology affects the orientation of the polymer chain but not to a great extent in the range of molecular weights investigated here. The radius of gyration determines the orientation in the short time-scale ($t < \tau_B$).

Comparing Figure 10a to 10b, the difference in birefringence between S200 and S110 is relatively greater at a long decay time (60 min) than at a shorter decay time (5 min). In Figure 10b, the birefringence of S110 is higher than for L110, although they have the same span molecular weight. This implies that the star polymer relaxes more slowly than its equivalent linear polymer on the longer time-scale ($t > \tau_B$), particularly at high strains as shown further in Figures 5c, d.

The birefringence of S200 is evidently higher than both that of L110 and S110 after 60 min relaxation. The longest (characteristic) relaxation-time for the B-process (τ_B) for the equivalent linear to S200 is about 56 min at 115°C. After 60 min relaxation, the orientation that has

yet to relax by the chain retraction process for the equivalent linear is about one-third. For the star the percentage of molecules yet to relax is higher, thus the relatively high birefringence at 60 min for the S200.

The difference in birefringence between L110 and its equivalent star (S110) is relatively small when the time-scale is much shorter than τ_B . When it is close to τ_B , the difference is larger.

Inhomogeneity of the drawing behaviour (necking) was observed in the relaxation process. Examining Figure 10b, it is evident that the birefringence vs λ curves for samples relaxed for 60 min are not lines with gradient 45° passing through the origin (1, 0). The lines are far more levelled, i.e. the low draw-ratio birefringence is higher than ideal and the birefringences at high draw-ratios are lower than expected.

In Figure 11, the orientation-relaxation results at a draw-ratio of 2 for L110, S110 and S200 are presented. The x-axis is time relative to the appropriate characteristic B-relaxation time, τ_B , on a logarithmic scale and the y-axis is residual birefringence on a logarithmic scale. This takes into account the molecular weight effect on the B relaxation and it would be quite tempting to suggest that a universal curve for the retraction process is produced in Figure 11. Theoretically, for the Rouse chain-retraction process the slope of the curve⁷ would be expected to be -0.5, which is quite close to our experimental results.

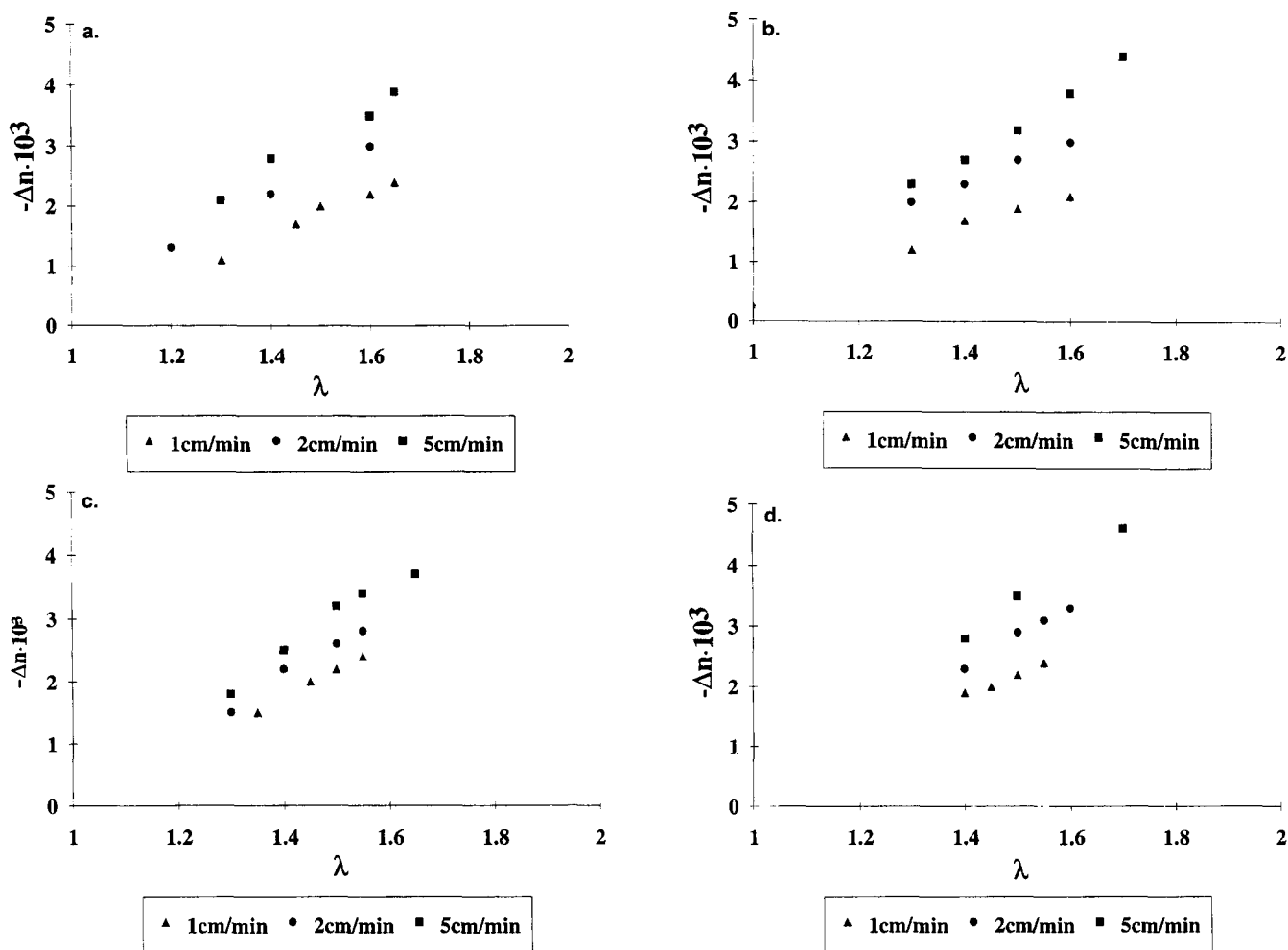


Figure 8 Strain rate effect at low draw-ratios at 115°C for samples (a) L110, (b) S85, (c) S110, (d) S200

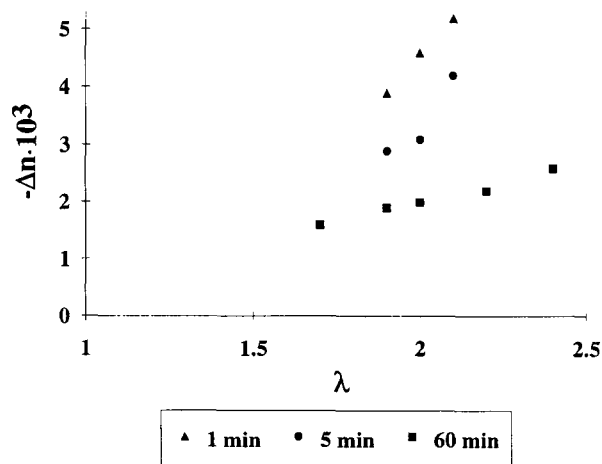


Figure 9 Relaxation of S200 after drawn at 5 cm min⁻¹: for 1–60 min at 115°C

According to the Doi–Edwards tube model, the residual stress at time t after a step-strain for a characteristic relaxation-time τ is about $e^{-t/\tau}$. In Table 4, the τ_B for L110 at 115°C is about 17.5 min and τ_C is about 5.3 h.

For L110 and S110, after 1 min drawing and 5 min relaxation, the residual retraction stress is $\exp(-6/17.5)$ for the linear polymer, which is approximately 70% of

Table 4 Characteristic relaxation-times for B- and C-processes from the DE tube model

Sample	$M_s/10^3$	τ_B/min (115°C)	τ_C/h (115°C)	τ_B/h (110°C)	$\log \tau_B/\tau_A$	$\log \tau_C/\tau_A$
S85	86	10.5		1.3	1.35	
L110	107	17.5	5.3	2.2	1.56	2.82
S110	110	17.5		2.2	1.57	
S200	198	56.5		7.0	2.08	
PS100	119	20	6.5	2.5	1.64	2.94
Star500	500	360		44	2.9	

the original retraction stress. The difference in birefringence in the early stage (6 min) of the B-relaxation process suggests that there is a difference in the B-relaxation spectra for the linear and star polymers. The higher contribution from the longest retraction time in the star molecule leads to a slower B-relaxation and a higher birefringence for the star than its linear counterpart.

After 60 min relaxation, the residual retraction stress is $\exp(-61/17.5)$ which is nearly equal to zero. In terms of the C-process the residual reptation stress is $\exp(-1/5.3)$ which is about 85% of the total reptation stress. So after 60 min relaxation at 115°C, the chain retraction process for the L110 has finished and about 15% of the residual reptation stress has been relaxed by reptation. S110 has almost the same span molecular weight as L110. So after 60 min relaxation, the chain retraction relaxation is almost

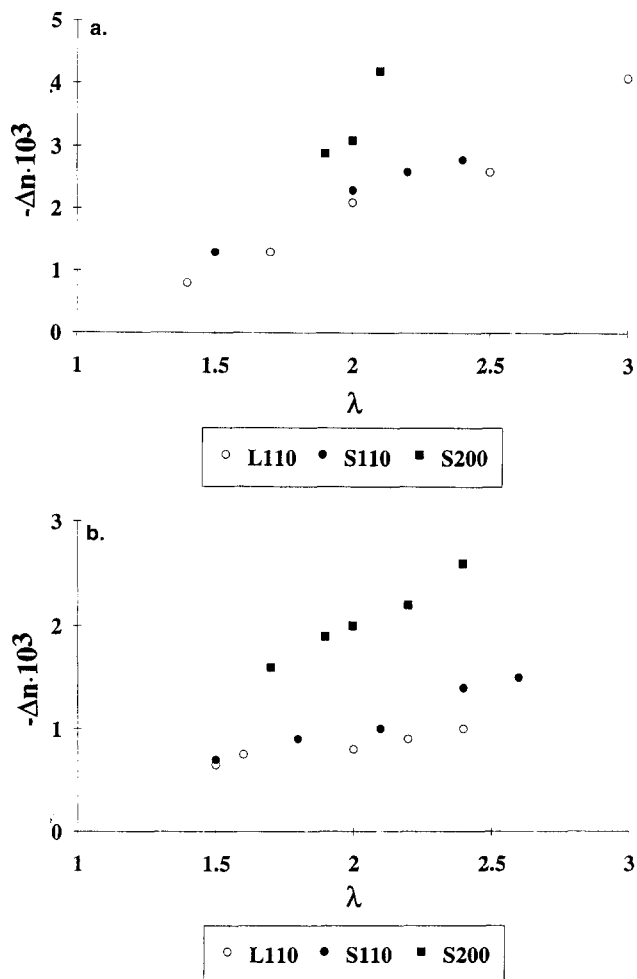


Figure 10 (a) L110, S110, S200 at a draw-ratio of 2 relaxed for 5 min at 115°C. (b) L110, S110, S200 at a draw-ratio of 2 relaxed for 60 min at 115°C

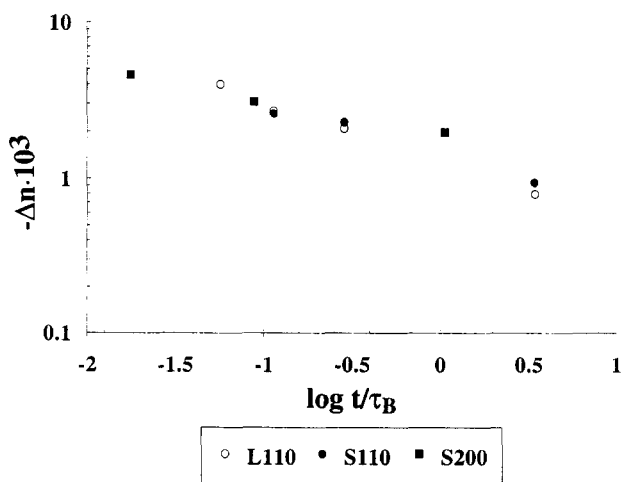


Figure 11 Relaxation of L110, S110, S200 at 115°C a draw-ratio of 2 for different time-scale

complete. The logical explanation for the observed difference is that the C-process for the linear is faster than that of the star. However, one should not expect a large difference between L110 and S110 in the C-process in the light of the recently developed tube dilation effect⁸⁻¹⁰ which claims that the C-process characteristic relaxation-time for the star is not as long as calculated from the

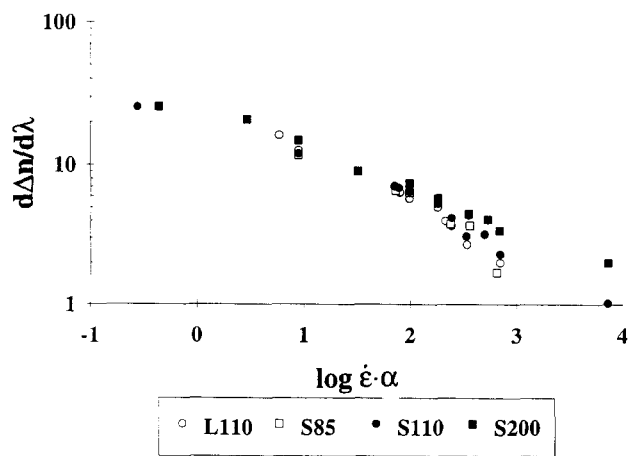


Figure 12 Strain rate effect on the rate of increase in birefringence: linear and star polymers

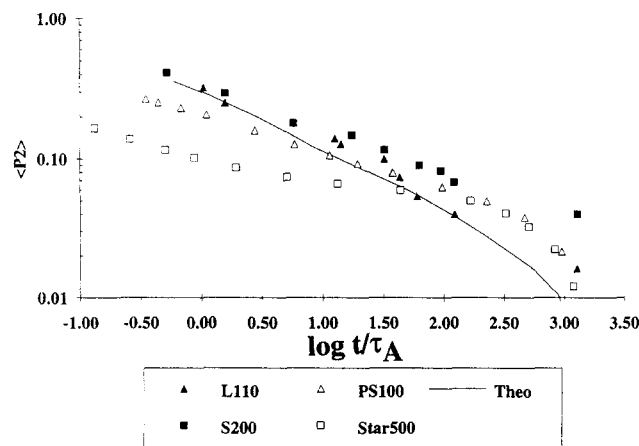


Figure 13 Relaxation curves for PS linear and star polymers at 115°C

original Doi–Edwards model due to the chain-ends acting as diluents for a long time-scale relaxation. This effect is expected to be more significant for star polymers with relatively short arms.

Relaxation-curves

From the drawing and relaxation experimental results, relaxation curves for the essentially monodisperse star and linear polystyrenes at a reference temperature of 115°C have been obtained (Figure 12). Each point on the relaxation curve, for a particular sample, was obtained from one of the curves in Figures 5, 7 and 8 by calculating the slope (of small draw-ratio when necessary) of the birefringence vs draw-ratio lines at a certain temperature and strain rate. These points were then superimposed by using Plazek's shifting factors¹⁵ and the WLF equation. The τ_B and τ_C values for all the polymers can be found in the last two columns of Table 4.

It is clear that for a short experimental time-scale, the relaxation behaviour of all the materials are independent of molecular weight and topology. Differences in relaxation behaviour occur at experimental times close to the beginning of τ_B which depends on both molecular weight and topology. After τ_B S200 always has the highest residual orientation because it is the star polymer with the longest chain under investigation. By the end of the B-process and thereafter S110 has a higher residual birefringence than L110 due to its star topology.

L110, $M_n = 107$ k, is comparable to Jasse, Tassin and Monnerie's PS100³ which had a molecular weight of 118 k and dispersity index of 1.12. The number of entanglements per chain is approximately 6.5 for PS100 and 6 for L110. This leads to retraction-times of 20 min for PS100 and 17.5 min for L110. One would expect their relaxation curves to be similar. The comparison of Monnerie's PS100 and L110 from the present work is presented in Figure 13. The curve for PS100³ at 120°C was shifted to 115°C by adding 0.7 to the log time-scale (Plazek's shifting factor). Using a $\Delta n_{\text{inf}} = -0.048$ (for $\log t/\tau_A > 1$), as reported by Vancso¹⁴, and assuming a linear relation in our logarithm strain-rate regime, the results for our birefringence vs draw ratio slope were converted into $\langle P_2(\cos\theta) \rangle$. Our results were re-scaled using the same factor as reported in the literature³, $\log t/\tau_A = 0.25$ and $-\log \dot{\epsilon} \cdot \alpha_T = 1.0$.

It is evident that the behaviour of L110 is similar to Monnerie's PS100 at long experimental time-scale. On a shorter time-scale the orientation of L110 appears higher than PS100 but very close to the theoretical value for a standard step-strain stress relaxation. The difference between the relaxation behaviour of L110 and PS100 may be explained by our results for the short time-scale being obtained from experiments with a relatively small strain, whereas Tassin and Monnerie's experiments were carried on to a high strain. PS100 was drawn to a draw-ratio of 4, which may trigger a non-linearity for the stress-optical law at this temperature, and thus lead to a lower value of orientation, particularly in the short relaxation time-scale. The relaxation behaviour of L110 and PS100 on the longer time-scale are very similar. It is quite clear that the Doi-Edwards theory predicts a faster relaxation process than was observed in either of the experiments.

Also presented are the relaxation curves for a 6-armed star with a span molecular weight 500 k (Star500) and our 3-arm star with a span molecular weight of 200 k (S200). Our results are generally higher than Monnerie's. A closer fit between Monnerie's and our results was observed in the medium to long time-scales, whereas at short time-scales our results are closer to the theoretical value and higher than Monnerie's results.

The polymer chains that we studied were not long enough to observe the transition from the A- to the B-process because the characteristic relaxation-times for these processes are not so significantly different that the completion of the A-process will be discerned in the curve. This point has been validated by the Doi-Edwards tube theory for low molecular weight linear polymer and also by previous experiments³ for linear polymers of molecular weight from 100 k to 500 k. The transition in this study was not observed to be as sharp as predicted theoretically.

CONCLUDING REMARKS

The drawing behaviour of linear and star polystyrenes is independent of molecular weight and molecular topology at temperatures below T_g . In the linear viscoelastic region, at temperatures above T_g , at short time-scale and

low strains the drawing behaviour of 3-arm stars is similar to that of the linear polymers of equivalent span molecular weight. The topology is not observed to influence the orientation-relaxation. However, significant differences between 3-arm stars and their equivalent linear polymers can be seen at long time-scale ($t \geq \tau_B$) and high strains (non-linear viscoelasticity region) at temperatures above T_g . The topological effect is negligible at short time-scale. In the early stages of the retraction, the molecular weight effect is dominant and the molecular topological effect is relatively small, whereas in the latter stage of the B process the reverse becomes true.

The topological effect on orientation-relaxation can be explained by the flow of repeat-units through the branch-point being strongly hindered by the extra arm in the star molecules. In the linear molecules, the segments in the less aligned half of the chain are free to slip towards the more aligned half of the chain and thus the centre of mass moves. This effect is particularly strong when the number of entanglements in the arm is small and will reduce as the arm molecular weight increases.

By taking into account the branch point pinning effect on the centre of mass motion, the modified Doi-Edwards tube model gave a better description than the original tube model for orientation-relaxation of branched polymers with arms not much longer than a few entanglements.

Finally, our experimental results generally concur with those predicted by the Doi-Edwards theory. In the long time-scale our results are close to those of Monnerie's experiments, whereas the Doi-Edwards model had predicted lower values.

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REFERENCES

- 1 Rietsch, F., Duckett, R. A. and Ward, I. M. *Polymer* 1979, **20**, 1133
- 2 Kahar, N., Duckett, R. A. and Ward, I. M. *Polymer* 1978, **19**, 136
- 3 Tassin, J. F. and Monnerie, L. *Macromolecules* 1988, **21**, 1846
- 4 Jasse, B., Tassin, J. F. and Monnerie, L. *Prog. Colloid. Polym. Sci.* 1993, **92**, 8
- 5 Lantman, C. W., Tassin, J. F., Sergot, P. and Monnerie, L. *Macromolecules* 1989, **22**, 483
- 6 Lantman, C. W., Tassin, J. F., Monnerie, L., Fetters, L. J., Helfand, E. and Pearson, D. S. *Macromolecules* 1989, **22**, 1184
- 7 Doi, M. and Edwards, S. F. *J. Chem. Soc. Faraday Trans. 2* 1978, **74**, 1789, 1802, 1818; 1979, **75**, 32
- 8 McLeish, T. C. B. *Europhys. Lett.* 1988, **6**, 511
- 9 McLeish, T. C. B. *Macromolecules* 1988, **21**, 1062
- 10 Ball, R. C. and McLeish, T. C. B. *Macromolecules* 1989, **22**, 1911
- 11 McLeish, T. C. B. and O'Connor, K. P. *Makromol. Chem., Macromol. Symp.* 1992, **56**, 127
- 12 Bauer, B. J., Fetters, L. J., Graessley, W. W., Hadjichritidis, N. and Quack, G. F. *Macromolecules* 1989, **22**, 2337
- 13 Inoue, T., Okamoto, H. and Osaki, K. *Macromolecules* 1991, **24**, 5670
- 14 Vancso, G., Snetivy, D. and Tomka, I. *J. Appl. Polym. Sci.* 1991, **42**, 1351
- 15 Plazek, D. J. *J. Phys. Chem.* 1965, **69**, 3480