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Characterization of molecular orientation in hot stretched polystyrene

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Differential scanning calorimetry (DSC) and birefringence was used to study molecular orientation of polystyrene. Models were developed relating the orientation and stress levels to the temperature, strain rate and amount of stretch. The number of relaxations observed on the DSC was influenced most by the temperature of stretch. At a temperature of 1.03 T_g K, maximum relaxation peaks and maximum tensile properties were developed over a range of molecular weights and molecular weight distributions. At given process conditions, birefringence was found to be influenced by $\bar{M}_w$, while DSC enthalpy was influenced by $\bar{M}_n$.

1. Introduction

The end-use properties of an article made of discrete polymer molecules depends on intermolecular attractions; it is thus obvious that any process that increases the mutual alignment of molecules will result in increased intermolecular contact and a change in end-use properties. Physical properties, such as yield strength and impact strength, can be improved by the introduction of molecular orientation [1]. It is well known that the processing of thermoplastic parts can lead to specimens which contain molecular orientation and thus contain frozen-in stresses. This article attempts to describe these phenomena in a fundamental way in terms of a readily controllable process and material parameters. This publication is part of a recent effort to study the nature of molecular orientation of polystyrene molecules in order to take advantage of it in the production of polystyrene parts via injection moulding and injection blow moulding processes [2, 3].

Molecular orientation should be distinguished from crystallinity because this article deals only with non-crystalline polystyrene. Both phenomena are based on alignment of segments of polymers but the crystalline state requires periodic and regular placement of the atoms of the chain relative to each other, whereas oriented molecules need only be aligned. The measurement of the amount of orientation imparted to a part under different conditions of strain has aided the understanding of orientation and its relationship to physical properties.

The commonly used physical methods of polymer characterization [4] cannot be used to investigate orientation and one normally has to resort to birefringence, small-angle neutron scattering, infrared dichroic measurements [5] and differential scanning calorimetry (DSC) [2]. Orientation is characterized here on polystyrene via birefringence and DSC. A simple technique with which to measure the average birefringence of a clear sample has been described [6]. Rogers [2] has used the exotherm on a DSC scan of an oriented part to examine injection blow moulded polystyrene. Here the two techniques are compared and related for a particular resin oriented under a set of conditions.

2. Experimental procedure

2.1. Materials

A commercially available polystyrene (685D, Dow Chemical Company) was chosen to study the effects of processing conditions and was used in previous studies [2]. For the study of molecular parameters and tensile properties, a series of anionic polymers was selected. Details of the polymers can be found in Table I.

2.2. Sample preparation

Relatively thin tensile bars (0.78 mm) were prepared from injection-moulded colour chips by compression moulding the chip into a flat sheet and then cutting the bars out with a router. The chip was pressed at 175 °C and 35 MPa for 5 min and then 175 °C and 210 MPa for 5 min. This resulted in a uniform sheet, approximately 0.78 mm thick. No orientation could be observed with crossed polarizers. The sheets were then routed to produce the standard dog-bone-shaped test bars.

2.3. Sample orientation

Test bars were strained as part of a two-level, three-factor designed experiment to look at the effect of strain rates, temperature, elongation and their interactions on the orientation of polystyrene. The test specimens were strained in an Instron Universal Testing Instrument and fitted with an oven to allow for straining at elevated temperatures. The oven was modified with water jets to quench the samples from the temperatures at which they were strained to well

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TABLE I Molecular parameters for monodispersed and polydispersed polystyrene

Sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$
685D	105 700	300 300	314 000	2.84
120	93 060	111 200	152 200	1.19
170	131 500	172 900	218 500	1.31
330	187 400	282 100	302 600	1.51
498	202 700	451 300	528 800	2.22

below T_g, to prevent the sample from relaxing. Samples were pulled in triplicate and in a random order. The general location of the experiments in space was chosen to simulate injection moulding and injection blow moulding processes as closely as possible. Oven temperatures ranged from 120 to 160 °C. Strain rates varied from 5 to 25 cm min^{-1} and elongation varied from 100% to 400%. It was decided that these variables were the most likely important factors in the amount of orientation that was developed in a thermoplastic part. The effects of other variables, such as molecular weight, were studied separately. Factors such as molecular weight degradation during processing and antioxidant were considered to be insignificant.

2.4. Measurement of orientation

2.4.1. Birefringence

Average birefringence ($\Delta\eta$) of a sample was determined with a Beckman Du-7 spectrophotometer, a single-beamed instrument with a wavelength range of 190 to 800 nm. The visible region from 600 to 800 nm was scanned in the percentage transmission mode which displayed a wave pattern with up to five minima. A sample was scanned at 600 nm min^{-1} when placed between crossed polarizers with the axis of polarization at 45° to the axis of orientation. The optical retardation, Γ_t, was calculated from Equation 1 by plotting the inverse of each minima versus an index, m, for that minima.

$$\frac{1}{\lambda_m} = \frac{1}{\Gamma_t}m + \frac{1}{\Gamma_t}(m_o + 1/2) \qquad (1)$$

where λ_m is the wavelength at the mth fringe, $m = 0, 1, 2, \ldots$, Γ_t the total relative retardation, and m_o is the actual fringe number for $m = 0$ fringe factor of 1/2 due to parallel polarizers.

Retardations were converted to birefringence, $\Delta\eta$, from Equation 2.

$$\Delta\eta = \eta_1 - \eta_2 = \Gamma_t/T \qquad (2)$$

where T (cm) is the thickness of the sample measured using a digital micrometer.

2.5. Differential scanning calorimetry

All samples were studied by means of a DuPont 910 DSC cell/base with a DuPont 9900 data control station. The temperature and cell calibration was maintained under statistical control using indium and mercury standards. The scanning temperature was from −10 to 210 °C at 20 °C min^{-1}. The cell was constantly flushed with nitrogen gas at a flow rate of 50 ml min^{-1}.

Samples of approximately 5 mm diameter were stamped from the oriented test bars at the location where the birefringence measurement had been made. The samples were placed in an aluminium test pan containing a drop of silicone oil to ensure good thermal contact with the surface of the pan. The pans were crimped to ensure further that thermal contact was maintained during the scan. Two consecutive heating scans were made in the DSC on each sample, with free cooling of the sample being undertaken between scans. Both first and second scans were important, the first being more representative of the structure of the oriented part, while the second revealed structural details of the annealed part.

2.6. Strain recovery

The percentage strain that could be recovered from stretched bars was determined by placing the bars in a heated oven at 120 °C and slowly raising the temperature to 140 °C at 1 °C min^{-1}. The percentage strain recovered was calculated from the dimensions of the bar relative to its original dimensions.

3. Results

3.1. Thermal analysis

A typical DSC scan is shown in Fig. 1 for a uniaxially stressed bar. Also shown is the scan obtained on a second heating cycle above T_g and the disappearance of the exothermic peaks. This is typical of the scans found previously for biaxially stressed containers [7].

The energy represented by the area under these exothermic peaks of Fig. 1 has been assigned to the energy released when the chains in the oriented polymer are allowed to relax and are thus related to an energy of orientation. Table II contains a summary of the conditions of the stretches, peak positions obtained in the designed experiment using sample 685D.

One difficulty with the procedure was the determination of the start and end point of the exotherm and a second difficulty encountered was the distinction of a peak from base-line drift and noise. It was

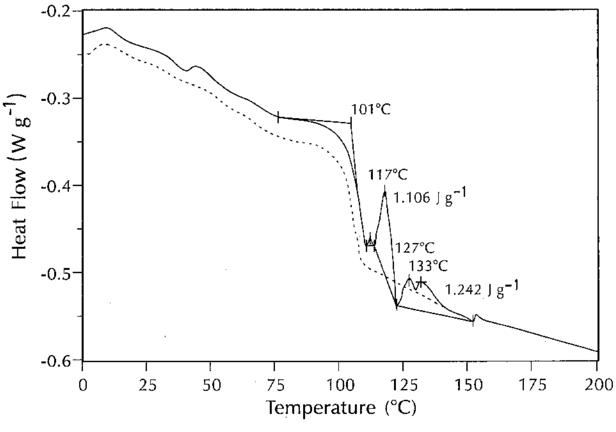

Figure 1 DSC scan for uniaxially stressed bar.

TABLE II Designed experiment, orientation of 685D

Conditions Rate (cm min^{-1})	T (°C)	E (%)	Birefringence ($\times 10^3$)	DSC exotherm (10^2 J g^{-1})	DSC peak position (°C)
2	120	100	3.598	10.22	115, 121
2	120	100	3.593	23.69	119, 125
2	120	100	2.857	14.73	118, 122
10	120	100	5.190	8.499	120, 128
10	120	100	4.663	11.98	114, 118, 135
10	120	100	5.983	19.82	115
2	160	100	0.162	16.00	120
2	160	100	0.282	13.22	120
2	160	100	0.258	8.23	119
10	160	100	0.541	8.90	121, 145
10	160	100	0.451	9.26	117, 139
10	160	100	0.286	9.79	119, 134
2	120	400	8.705	237.11	112, 117, 127, 133
2	120	400	9.959	339.04	113, 115, 123
2	120	400	6.304	222.40	116, 121, 136
10	120	400	13.41	324.9	120, 123
10	120	400	12.82	125.3	115, 121
10	120	400	13.51	229.2	115, 120
2	160	400	0.328	0.367	118
2	160	400	0.154	0.702	117
2	160	400	0.070	0.678	118
10	160	400	0.414	2.874	117
10	160	400	0.513	4.189	119
10	160	400	0.216	7.801	118

helpful to superimpose the second scan over the first scan to determine what were the real relaxations.

The number of relaxations observed per sample was dependent on the temperature of stretch with low-temperature stretches leading to a larger number of peaks. Fig. 2 shows a series of histograms plotting the number of peaks on the DSC trace for a given set of conditions. Peak positions in samples that contain multiple relaxations followed the general equation

$$T_j = 1.03\,T_i \qquad (3)$$

for $T_j > T_i > T_g$ and $(j - i) = 1$ where T is the temperature (K) of the peak minimum.

Rogers [7] has reported a similar equation for biaxially oriented polystyrene. The literature [3] has also reported relaxations around and above the glass transition for poly(methyl methacrylate) and polycarbonate. The observations of multiple peaks occurring on the DSC scan in the temperature range greater than T_g has been assumed to be due to the molecular chain changing conformation in more than one plane. Here, however, the molecules are supposedly oriented in one plane. The samples that were stretched did, however, change dimensions in more than one direction.

3.2. Stress, strain and the DSC

When a polymer chain is oriented, energy is stored as a change in conformational entropy of the individual chains. The theory of rubber elasticity can describe how work can be stored in a system [1].

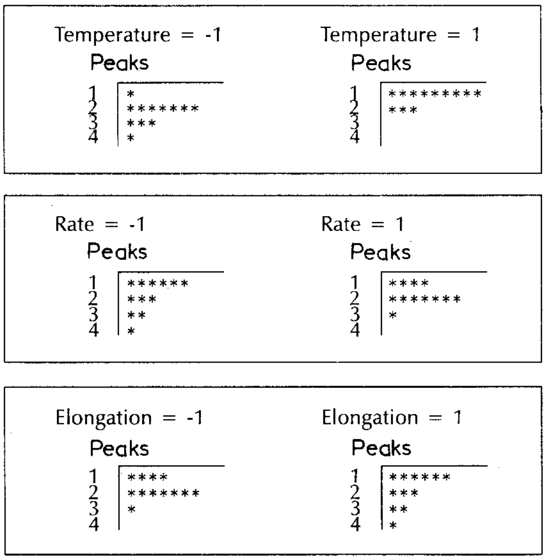

Figure 2 Histogram plot of DSC peaks occurring under various process conditions.

Essentially the work, W, at approximately constant volume, can be written

$$W = \sum_{i=1}^{3} \sigma_i \, \mathrm{d}\varepsilon_i \qquad (4)$$

where σ and ε are the shear stress and rate of strain, respectively.

The stress can be taken as the product of the strain and the modulus, G, which is a function of strain rate, $\dot{\varepsilon}$, strain and temperature, T.

$$\sigma_i = G_i(\dot{\varepsilon}, T)\varepsilon_i \qquad (5)$$

The first law of thermodynamics defines the internal energy as the sum of the energy added to the system by heat processes, dH, and the work performed, dw. When an oriented sample is heated to a temperature at which it can flow, then the stored energy can be released. An entire cycle of heating, stretching, cooling and re-heating involved no chemical change, thus

$$dH = -dw \qquad (6)$$

Substituting Equation 5 into Equation 4 and remembering the equality Equation 6, gives

$$\Delta H = 1/2G_1\varepsilon_1^2 + 1/2G_2\varepsilon_2^2 + 1/2G_3\varepsilon_3^2 \qquad (7)$$

For an incompressible fluid

$$\varepsilon_1 + \varepsilon_2 + \varepsilon_3 = 0 \qquad (8)$$

Substituting Equation 8 into Equation 7, again using the relationship Equation 5,

$$\Delta H = 1/2(\sigma_1 - \sigma_3)\varepsilon_1 + 1/2(\sigma_2 - \sigma_3)\varepsilon_2 \qquad (9)$$

Thus a plot of stress times the recoverable strain versus the enthalpy released should give a straight line with a zero intercept and a slope of one-half. This is shown in Fig. 3 for some typical data, where the slope is essentially one-half.

This relationship enables us to overcome some of the problems with using birefringence for measuring orientation, as it is impossible to measure birefringence on opaque samples and difficult to measure orientation on biaxially oriented samples.

3.3. Birefringence

Birefringence, $\Delta\eta$ is related to the stress through the stress optical coefficient, C, by

$$\Delta\eta = C\sigma \qquad (10)$$

and Equation 9 may be rewritten as

$$\Delta H = \frac{\Delta\eta_{13}}{2C}\varepsilon_1 + \frac{\Delta\eta_{23}}{2C}\varepsilon_2 \qquad (11)$$

The birefringence stress imparted to the test bars was correlated with the stress recorded by the Instron testing machine load cell during the stretching experiments. The correlation coefficient between the two parameters was only 0.72. The correlation between Instron load and energy released on heating in the DSC was worse at 0.28. These results suggest that the stress–strain curves developed during the stretching process do not provide a good indicator to orientation in a cooled sample. This was not too surprising because at the instant when the sample had reached its designed maximum stretch, the sample was quenched below T_g, and the external forces removed. The material maintained its overall dimensional state, but retained sufficient internal heat to allow the chains to relax to a degree.

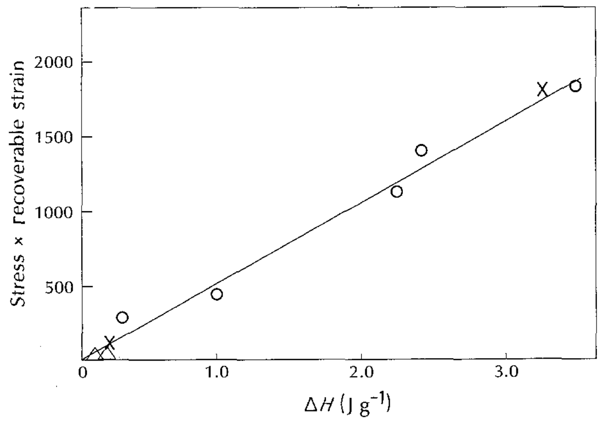

Figure 3 Recoverable strain × stress versus enthalpy. (○) 120 °C stretch, (×) 140 °C stretch, (Δ) 160 °C stretch.

3.4. Tensile properties versus molecular weight

The effect of molecular weight on mechanical properties has been known for a number of years [8]. Tensile strength and per cent elongation increase to limiting values as molecular weight is increased. Our data for the unstretched sample are shown in Figs 4 and 5, respectively, and in Table III. Because of the limited number of anionic samples available for this study, literature values are also included [8]. Both sets of data fitted remarkably well.

Polystyrene is basically a brittle polymer having low elongation to break values. Practical considerations have shown that, when polystyrene is orientated between 100 and 140 °C, the properties may be improved and it is known in general terms that the higher the temperature the more stretch is required for optimum properties. As shown in Table III, maximum tensile properties are obtained at a stretch temperature of 120 °C, independent of molecular weight or molecular weight distribution. At this temperature well-defined tensile yield points are developed. Tensile break values are more than double those for the unorientated samples. As we approach the liquid–liquid relaxation temperature of 160 °C [2, 7], sufficient slippage or disentanglement of the polymer chains can occur and it becomes less obvious whether the samples have a yield point.

3.5. Process models

The process model developed using a relatively broad molecular weight sample, 685D, revealed complex molecular motions.

In the first stages of the test procedure, deformation was achieved by applying a force to the sample above its T_g. At an instant of stretching when deformation had reached some given value, the polymer was quenched below T_g and the external force removed. Thus the introduced stresses are of two types: orientational stresses introduced by deformation of the molten polymer and thermal stresses resulting from quenching the sample below T_g.

Orientational stresses are the result of relatively large-scale deformation of the polymer and originate from a change in conformational entropy of the polymer chain. Regression analysis of the data gave a linear relationship between birefringence and process

TABLE III Orientation and tensile properties

Sample	Stress temp. (°C)	Stress birefringence	DSC			Tensile[a]		
			T_1 (°C)	T_2 (°C)	ΔH	T_y (p.s.i.)	T_b (p.s.i.)	E_b (%)
685D	Blank						3552	1.55
	120	105.9	124.6	138.4	0.18	6766	8437	2.75
	140	37.8	160.0		4.2	7806	7959	3.34
	160	14.2	125.2	138.0	0.4		6233	1.89
NAPS 120	Blank							
	120	81.5	120.8	129.0	0.15			
	160							
NAPS 170	Blank						4305	1.13
	120	89.3	123.0	132.0	1.1	8088	9670	2.24
	160	0.87					6154	1.66
NAPS 330	Blank						4745	1.17
	120	102.2	125.7		3.1	10000	10214	2.37
	160	11.8					4929	1.54
NAPS 498	Blank						4817	1.08
	120	122.1	120.7	130.0	3.6	7594	9126	1.85
	160	18.2	119.4		0.18	7162	7027	2.58

[a] T_y = tensile strength at yield. (10^3 p.s.i. = 6.89 N mm^{-2}).
T_b = tensile strength at break.
E_b = elongation at break.

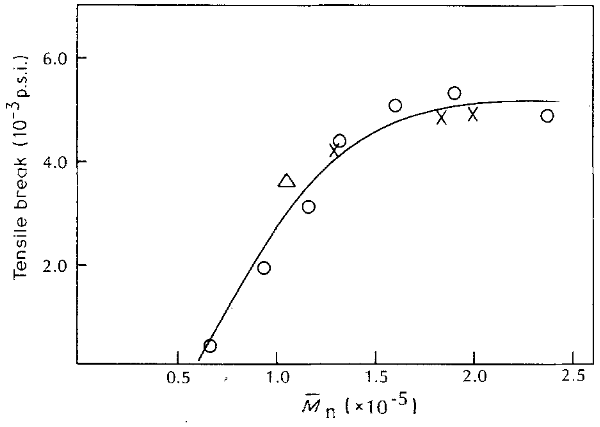

Figure 4 Tensile break versus number-average molecular weight. (○) Literature values [8], (×) anionic polymers, (Δ) 685D sample. 10^3 p.s.i. = 6.89 N mm^{-2}.

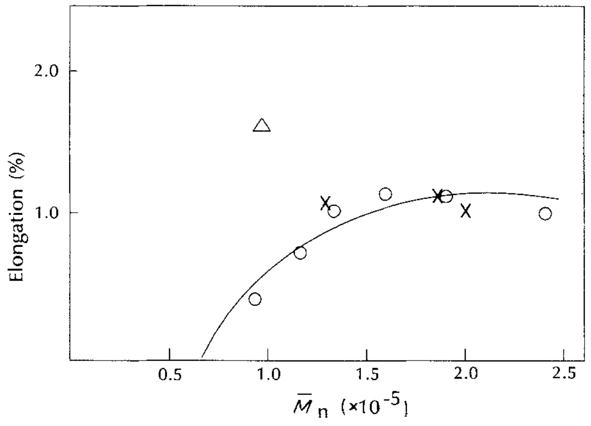

Figure 5 Elongation at break versus number-average molecular weight. (○) Literature values [8], (×) Anionic polymers, (Δ) 685D sample.

conditions.

$$\ln(\Delta\eta) = -6.61 + 0.28R - 1.62T - 0.28TE \quad (12)$$

with a correlation coefficient of $r^2 = 0.96$. R was the rate of stretching (cm m^{-1}), at a temperature of T°C. E was the per cent elongation.

In the second stage of an experiment, the orientational and thermal stresses were measured as enthalpy change by differential scanning calorimetry. The relationship between enthalpy (ΔH) and process conditions were more complex

$$\ln(\Delta H) = -1.88 + 0.18R - 1.32T + 0.23E + 0.28RT + 0.29RE - 1.18TE + 0.29RTE \quad (13)$$

with a correlation coefficient of $r^2 = 0.95$ correlation.

The largest contribution to orientation can be achieved with a decrease in the temperature of stretch. This was seen for both $\Delta\eta$ and ΔH measurements and was reflected in the tensile measurements. This has a very important consequence from a practical point because the fabrication dimensions of a part are frequently fixed.

The number of enthalpic peaks increased with decreasing temperature of stretch and with increasing rate of stretch.

When measured by either $\Delta\eta$ or ΔH, orientation was found to increase linearly with stretch ratio at all temperatures and strain rates studied. In the same way, a decrease of orientation, at a given stretch ratio, was observed when either the temperature was increased or the strain rate was decreased. Similar findings have been found elsewhere [9].

A least-square analysis between $\Delta\eta$ and ΔH gave a linear relationship with a correlation coefficient of $r^2 = 0.97$.

$$\Delta\eta = 0.00288 + 0.000216\Delta H \quad (14)$$

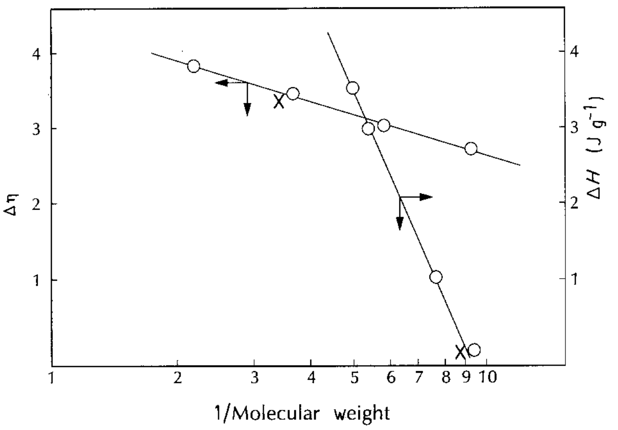

Figure 6 Orientation measured by birefringence and DSC, versus molecular weight. (○) Anionic polymers, (×) 685D sample.

3.6. Molecular models

Birefringence provides a convenient method of measuring internal stress, without destroying a sample. The anionic polymers were pulled under one set of conditions, 100% extension at 5 cm min^{-1} at 120 and 160 °C. The birefringence stress versus average molecular weight, $\bar{M}_w$ is plotted in Fig. 6 for the temperature 120 °C. As might be anticipated, the relationship was linear. A similar graph but with greater slope was obtained at 160 °C, except for the 120 sample. The molecular weight of this sample was too low and viscous and elastic flow occurred on stretching and the sample collapsed. The broad distribution sample, 685D, also fell on the same curve. The results are given in Table III.

Whereas birefringence orientation was dependent upon weight-average molecular weight, orientation measured as enthalpy by DSC was dependent on number-average molecular weight, Fig. 6, and appears to be independent of $\bar{M}_w/\bar{M}_n$ ratio.

Examination of the DSC scans showed the presence of multiple peaks in the case of the broad molecular weight distribution samples but single peaks occurred with the narrower distribution samples. Shoulders on some peaks, however, were evident and one can speculate that under the correct processing conditions, multiple peaks would have developed. The maximum number of peaks occurred at the lowest processing temperature (1.03 T_g) and the temperature of maximum tensile development.

4. Discussion

The model developed here separates adequately the process parameters that influence the orientation of polystyrene. Selection of the correct parameters allows one to develop maximum properties for a given molecular weight sample.

The model was based on uniaxial stretching and some compromise may be necessary to obtain balanced properties for the case of biaxial orientation. However, in general, stretching should be carried out within the rubbery plateau region and preferably at a temperature equal to 1.03 T_g K.

As might be predicted, the higher the average-weight molecular weight ($\bar{M}_w$), higher will be the tensile properties. However, at the same $\bar{M}_w$, a product having a broader molecular weight distribution ($\bar{M}_w/\bar{M}_n$), will have lower mechanical properties.

During the stretching process not only do the macromolecular chains orientate, but conformational changes may also occur. These conformational changes would involve such changes as atomic bond distances, angles and twists.

Birefringence is a well-established technique for measuring stress related to segmental orientation of the chain backbone and is sensitive to local displacements only revealed by local zones of optical anisotropy [10]. Thermal analysis is sensitive not only to local deformation but also to deformation of the entire network. This is revealed as multiple relaxation peaks in a DSC scan.

5. Conclusions

Differential scanning calorimetry and birefringence are useful techniques for measuring molecular orientation in polystyrene. It was apparent that DSC yields more information than birefringence. These techniques were used to determine the ideal operating conditions for the production of plastic parts with acceptable levels of orientation. It was found that temperature is the process variable that has the greatest influence on the residual stress frozen into the part. The two techniques were useful in the testing of resins that will lead to acceptable parts.

Acknowledgements

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