

# Rheology of Cellulosic *N*-Methylmorpholine Oxide Monohydrate Solutions

S. PETROVAN,<sup>1</sup> J. R. COLLIER,<sup>1</sup> G. H. MORTON<sup>2</sup>

<sup>1</sup> Department of Chemical Engineering, The University of Tennessee, 419 Dougherty Engineering Building, Knoxville, Tennessee 37996-2200

<sup>2</sup> Buckeye Technologies, Inc., 1001 Tillman, P.O. Box 80407, Memphis, Tennessee 38108-0407

Received 7 September 1999; accepted 28 December 1999

**ABSTRACT:** Shear dynamic and elongational rheology of concentrated solutions of cellulose in *N*-methylmorpholine oxide monohydrate (lyocell) were investigated at different temperatures and for two Hencky strains. Shear thinning and strain thinning behavior is characteristic for dynamic viscosity and effective elongational viscosity of lyocell solutions. Body forces, enthalpy, and entropy of orientation are high at low temperature and high deformation rates, showing a strong orientation effect. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1369–1377, 2000

**Key words:** lyocell solution; effective elongational viscosity; shear viscosity; dynamic moduli; entropy of orientation;

## INTRODUCTION

Rheological characteristics of the polymer melts and solutions are of paramount importance for all processing procedures. For example, the fiber spinning and bubble blowing processes are sensitive to the variation of the rheological properties, particularly in the formation and drawing stages. Due to the elongational character of flow in these stages, the elongational viscosity plays a fundamental role for the quality of the resultant fibers and films.

This paper presents the elongational and dynamic rheological measurement results on a 14% lyocell solution prepared from dissolving pulp. Also, fundamentals for a new technique of elongational viscosity measurement are given.

## THEORETICAL CONSIDERATIONS

### Fundamentals of Elongational Viscosity Measurement

Elongational flow is the dominant mode of fluid flow when a rapid change of shape such as stretching is involved in the operation. A unique process for characterization of the elongational rheology of polymer melts and solutions at processing strain rates has been developed.<sup>1</sup> It was initially demonstrated that an essentially pure elongational flow could be obtained in the core of core/skin coextrusion; this was accomplished experimentally using a core/skin viscosity ratio of 100 to 30, and a core/skin flow rate ratio of about 10 was maintained.<sup>2,3</sup> Experimental measurements on a pilot scale coextrusion system in a planar slit die using tracer particles and an image analysis system confirmed the predicted behavior and demonstrated the ability to achieve a constant elongational strain rate in the core layer.<sup>4</sup>

Electrodischarge machined semihyperbolic convergent conical dies were designed to generate

---

Correspondence to: J. R. Collier.

*Journal of Applied Polymer Science*, Vol. 77, 1369–1377 (2000)  
© 2000 John Wiley & Sons, Inc.

a constant elongational strain rate throughout the core; to accomplish this, the flow channel decreases as  $R^2z = C_1$ , where  $z$  is the flow direction and  $R$  is the radius of the flow channel. Two conical dies are being used having Hencky strains  $\epsilon_h$  of 6 and 7;  $\epsilon_h = \ln(\text{area reduction})$ . This concept was implemented on an Advanced Capillary Extrusion Rheometer (ACER), Rheometric Scientific, by replacing the capillary die with one of these hyperbolic converging axisymmetric dies to determine the uniaxial elongational viscosity of several polymer melts and solutions. Elongational strain rates up to  $740 \text{ s}^{-1}$  can be achieved in this rheometer with the two dies (the range includes processing rates). In attempting to develop a correction factor for skinless measurements, it was discovered that the orienting effect of the melt dominates the flow so strongly that shearing gradients near the wall were insignificant and both skinless and lubricated polypropylene samples data fell on the same curves.<sup>1</sup>

Analysis of this flow was accomplished using the measured pressure and volumetric flow rate data, and mass, momentum, and energy balances.

A stream function,

$$\Psi = -\frac{\dot{\epsilon}}{2} r^2 z \quad (1)$$

and a potential function,

$$\Phi = \dot{\epsilon} \left( \frac{r^2}{4} - \frac{z^2}{2} \right) \quad (2)$$

describe the system with the pressure as a linear function of  $\rho \dot{\epsilon} \Phi$ , and

$$v_z = -\frac{1}{r} \frac{\partial \Psi}{\partial r} = -\frac{\partial \Phi}{\partial z} \quad (3)$$

$$v_r = \frac{1}{r} \frac{\partial \Psi}{\partial z} = -\frac{\partial \Phi}{\partial r} \quad (4)$$

define the velocity components.

The basic equations describing the flow are the scalar equations of continuity (mass balance), motion (momentum balance), and energy (energy balance)<sup>5</sup>:

$$\frac{D\rho}{Dt} = -\rho[\nabla \cdot \mathbf{v}] \quad (5)$$

$$\rho \frac{Dv}{Dt} = -\nabla P + [\nabla \cdot \boldsymbol{\tau}] + \rho \mathbf{b} \quad (6)$$

$$\rho \frac{D\hat{H}}{Dt} = -[\nabla \cdot \mathbf{q}] + (\boldsymbol{\tau}:\nabla\mathbf{v}) - \frac{DP}{Dt} \quad (7)$$

where  $\boldsymbol{\tau}$ , a second-order tensor, denotes the stress, and the first-order tensor (i.e., vector) quantities  $\mathbf{v}$  and  $\mathbf{q}$  denote velocity and energy flux, respectively. The body force term  $\mathbf{b}$  is discussed in greater detail below; it is a first-order tensor, which was found to represent primarily the force necessary to orient the material; this term would also include a gravitational component if the latter were significant. The first-order tensor operator  $\nabla$  denotes the gradient. The scalar terms  $P$ ,  $\rho$ , and  $\hat{H}$  are the pressure, density, and enthalpy per unit mass, respectively.

Since the convergence of the flow channel was designed to force a constant elongational strain rate, the flow is homogeneous and the elongational stress components were also constant.<sup>1</sup> This result coupled with insignificant shearing gradients caused the stress gradient terms in the momentum balance equation to be zero, and the inertial terms were also negligible (pressure gradients calculated from them were two to three orders of magnitude lower than observed and were independent of fluid character). Therefore, as a result of the imposed pressures (1.15–42.6 MPa at elongational strain rates of  $0.02$ – $136 \text{ s}^{-1}$ , for a polypropylene of 300,000 molecular weight<sup>1</sup>), the momentum balance equation suggested that significant body forces must be necessary to orient the fluid. Furthermore, the energy balance, expressed in terms of enthalpy for this controlled isothermal system, revealed a significant enthalpy change consistent with transformation to an ordered liquid crystalline form (which may be metastable and induced due to flow). The calculated body forces and the enthalpy change both suggest a transformation to an oriented liquid crystalline form, consistent with the earlier work in which flow through a linearly converging die was followed by a sharp temperature gradient, thereby crystallizing the polypropylene inside the die.<sup>6,7</sup>

As a result of this analysis, the elongation viscosity  $\eta_e$  and the effective elongational viscosity  $\eta_{\text{eff}}$  in both Cartesian and cylindrical coordinates are<sup>1</sup>

$$\eta_e = + \frac{\Delta P}{\dot{\epsilon} \epsilon_h} + \frac{\rho \Delta \hat{H}}{\dot{\epsilon} \epsilon_h} \quad (8)$$

and

$$\eta_{eff} \equiv + \frac{\Delta P}{\dot{\epsilon} \epsilon_h} \quad (9)$$

where  $\Delta P$  is the pressure gradient,  $\rho$  the density, and  $\dot{\epsilon}$  the elongational strain rate. The definition of  $\eta_{eff}$ , as given by eq. (9), in effect assumes that the enthalpy change is included in the viscosity term.

The elongational strain rate can be calculated by using

$$\dot{\epsilon} = \frac{v_0}{L} (\exp \epsilon_h - 1) \quad (10)$$

where  $\epsilon_h$  is the Hencky strain, defined as

$$\epsilon_h = \ln \frac{A_{en}}{A_{ex}} \quad (11)$$

$A_{en}$  is the entrance area,  $A_{ex}$  the exit area,  $L$  the centerline length, and  $v_0$  the initial velocity at the entrance cross-section area.

The enthalpy change associated with the flow-induced transformation to what can be considered a metastable liquid crystalline form can be estimated as follows. The effective Trouton ratio is  $\eta_{eff}/\eta_s$  (where  $\eta_s$  is the shear viscosity measured at the same temperature and at an equivalent magnitude shear rate). If the assumption is made that the non-Newtonian character of the fluid in excess of that reflected in  $\eta_s$  is due to the resistance to orientation, then the actual Trouton ratio would be  $\eta_e/\eta_s = 3$ . By measuring  $\eta_s$  then  $\eta_e = 3\eta_s$ , and substituting  $3\eta_s$  into the above equations, enthalpy per unit volume,  $\Delta H = \rho \Delta \hat{H}$ , can be calculated from the resultant equation:

$$\Delta H = -\dot{\epsilon} \epsilon_h (\eta_{eff} - 3\eta_s) \quad (12)$$

This implies that the term  $(\eta_{eff} - 3\eta_s)$  is a viscosity-related measure of the orientation development due to this flow geometry and that the fluid does not remain in an isotropic state during flow. The entropy change  $\Delta S$ , indicating the degree of orientation that develops can be determined from  $\Delta G = \Delta H - T\Delta S$ , where  $G$  is the Gibbs free energy

and  $T$  is the absolute temperature. The assumption is made that the Gibbs free energy change approaches zero for this steady state, quasi-equilibrium flow resulting in

$$\Delta S = \frac{\Delta H}{T} \quad (13)$$

## EXPERIMENTAL

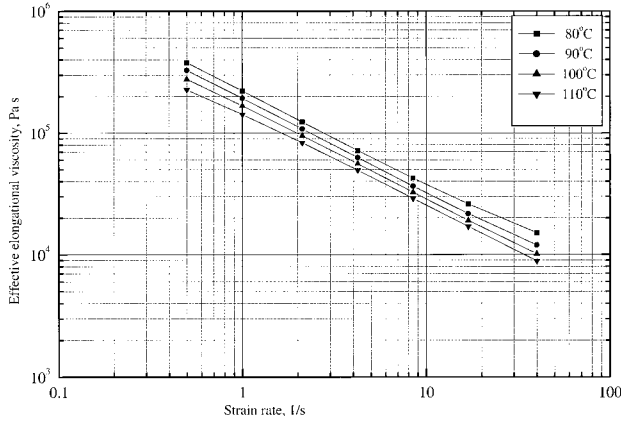
### Materials

The lyocell solution was supplied by Buckeye Technologies, Inc., Memphis, Tennessee. This solution consisted of 14% cellulose from a dissolving pulp having cupriethylenediamine (CED) viscosity (0.5%) 5.2 cP,  $DP_w$  855,  $\alpha$ -cellulose 94.7%,  $\beta$ -cellulose 3.3%,  $\gamma$ -cellulose 2.0%, pentosans 2.0%, and 7.3% extractable in 10% NaOH, dissolved in N-methylmorpholine oxide monohydrate.

### Equipment and Experimental Technique

Elongational viscosity measurements were done on an ACER-2000 instrument. Two semihyperbolic dies of Hencky strain 6 and 7 were used to measure the elongational flow properties. The pellets of the solid lyocell sample were charged into the barrel and allowed to melt and attain the prescribed steady state temperature. Then the experiments were performed by sweeping the chosen elongational strain rates until a steady state of pressure was accomplished, for each strain rate in turn. Data on steady state pressure differences were used to calculate the effective elongational viscosity by using eq. (9). From a single charge of the barrel, one or more viscosity curves were obtained. All the viscosity data presented in this report have been obtained by using only fresh lyocell solutions.

Dynamic rheological measurements were performed on Bohlin VOR 405 and TA rheometers, using the parallel plate geometry. Strain sweep measurements were performed at different frequencies in order to determine the limits of the linear region, recorded between 0 and 100% strain. The dynamic experiments were done between 0.02 and 0.18 strain. In order to avoid the water uptake by the sample in the time of preparing and running the experiment, the edges of the specimen and the plates were covered with a thin



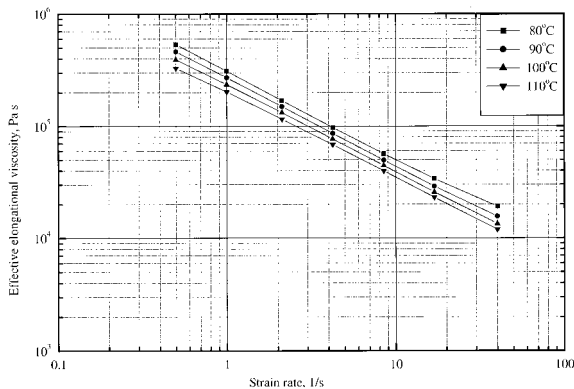
**Figure 1** Effective elongational viscosity of lyocell solution at Hencky strain 6.

layer of viscosity standard silicon oil of 29.1 Pa s viscosity. Data on time, temperature, frequency, phase angle, dynamic viscosity, moduli, torque range of the torsion bar, amplitude, and the strain were recorded, saved, and converted to a text file. For better reproducibility, all the experiments were done by using only one torsion bar, previously calibrated and recalibrated from time to time with the same standard viscosity.

**RESULTS AND DISCUSSION**

**Elongational Viscosity**

In Figures 1 and 2 is plotted the effective elongational viscosity, at Hencky strains 6 and 7, in the range of elongational strain rates 0.5–40 1/s. A general trend of “strain thinning” behavior is no-



**Figure 2** Effective elongational viscosity of lyocell solution at Hencky strain 7.

ticed at both Hencky strain 6 and 7, but higher viscosities are recorded at higher Hencky strain. It seems that both in case of temperature and Hencky strain influence the effective elongational viscosity curves are parallel lines, a fact that suggests that it is worth trying to find a master curve.

If we suppose that the effective elongational viscosity–temperature relationship obeys the Arrhenius law and take temperature  $T_0 = 353.16$  K as reference temperature, then the viscosity at any temperature is given by

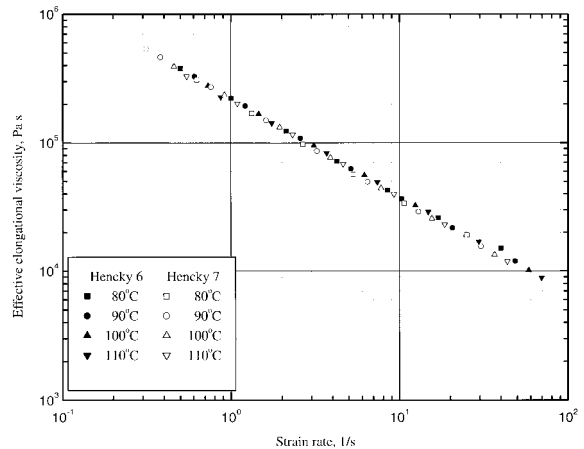
$$\eta_{eff} = \eta_0 \exp \left[ \frac{E_a}{R} \left( \frac{T_0 - T}{T_0 T} \right) \right] \quad (14)$$

where  $\eta_0$  is the viscosity at reference temperature. Taking also into account the effect of the Hencky strain, with the reference Hencky strain  $\epsilon_{h0} = 6$ , the following general equation may be written:

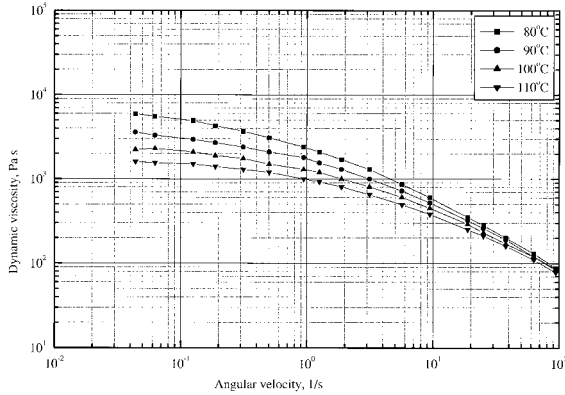
$$\eta_{eff} = \eta_{00} \left( \frac{\epsilon_h}{\epsilon_{h0}} \right)^{2.303(\epsilon_h - \epsilon_{h0})} \exp \left[ \frac{E_a}{R} \left( \frac{T_0 - T}{T_0 T} \right) \right] \dot{\epsilon}^{(n-1)} \quad (15)$$

In eq. (15)  $\eta_{00}$  and  $n$  are consistency index and flow index at reference conditions, respectively, in the power law equation for effective elongational viscosity, that is,

$$\eta_{eff} = \eta_{00} \dot{\epsilon}^{(n-1)} \quad (16)$$



**Figure 3** Master curve for effective elongational viscosity of lyocell solution.



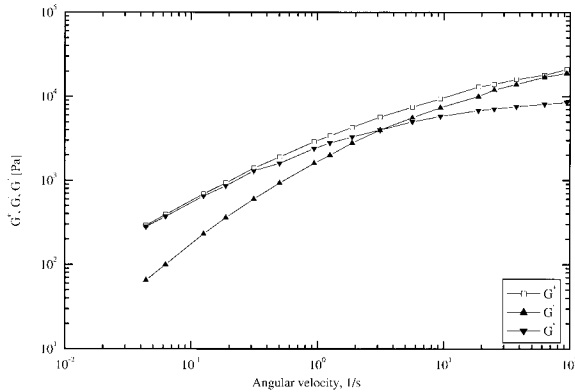
**Figure 4** Dynamic viscosity of lyocell solution.

The shift factors for the influence of temperature and Hencky strain are calculated with eqs. (17) and (18):

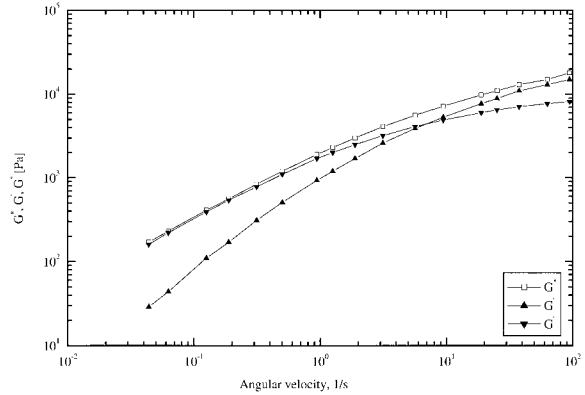
$$a_T = \exp\left[\frac{E_a}{R(1-n)}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \quad (17)$$

$$a_h = \left(\frac{\epsilon_h}{\epsilon_{h0}}\right)^{2.303/1-n} \quad (18)$$

Due to the curvature of the log viscosity –  $1/T$  plots, an average of the activation energy  $E_a$  was calculated from the values obtained at all the strain rate tested and for both Hencky strains. Also, an average of the flow index was calculated. These values are  $E_a = 3.77$  kcal/mol and  $n = 0.24$ . By using the shift factors calculated with eqs. (17) and (18), the master curve from Figure 3 results, showing a good accuracy of the shifting procedure.



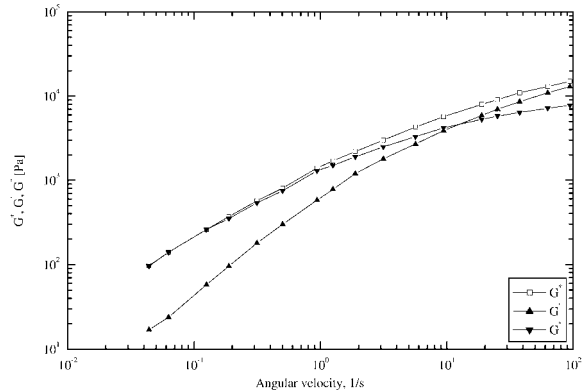
**Figure 5** Dynamic moduli of lyocell solution at 80°C.



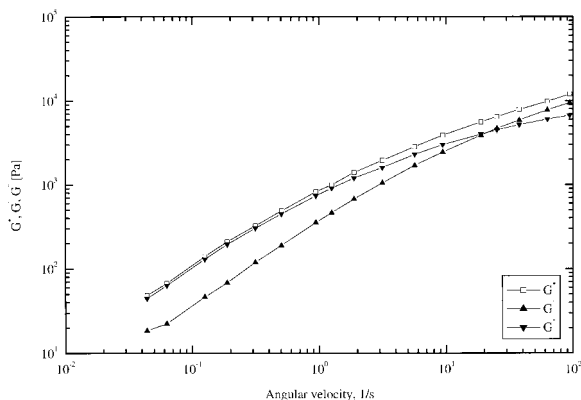
**Figure 6** Dynamic moduli of lyocell solution at 90°C.

### Dynamic Viscosity and Moduli

Dynamic viscosity for the lyocell solution at 80, 90, 100, and 100°C is presented in Figure 4. As in case of effective elongational viscosity, the dynamic viscosity shows a trend of shear thinning behavior. At low angular velocities, a Newtonian range is noticed. Also, it is interesting to note that the influence of temperature on dynamic viscosity is lower as the shear rate is higher, this behavior being different as compared with effective elongational viscosity, where the same temperature effect is recorded for all the elongational strain rates. Zero shear viscosities were determined by fitting the experimental data on dynamic viscosity with the Cross model.<sup>8</sup> From these data the corresponding flow activation energy of 12.9 kcal/mol was calculated, assuming that the influence of temperature on dynamic viscosity of lyocell solution obeys the Arrhenius model. This value of activation energy is comparable with the flow ac-



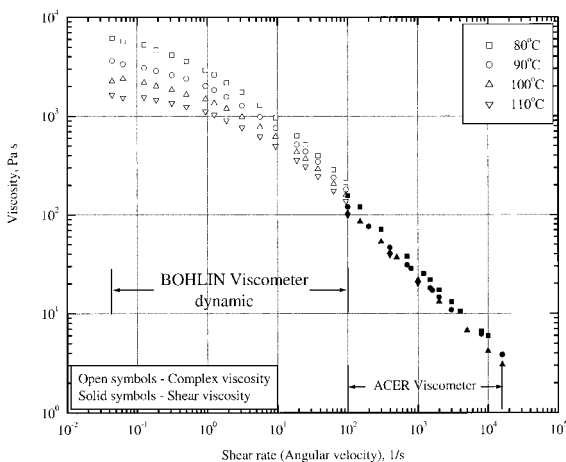
**Figure 7** Dynamic moduli of lyocell solution at 100°C.



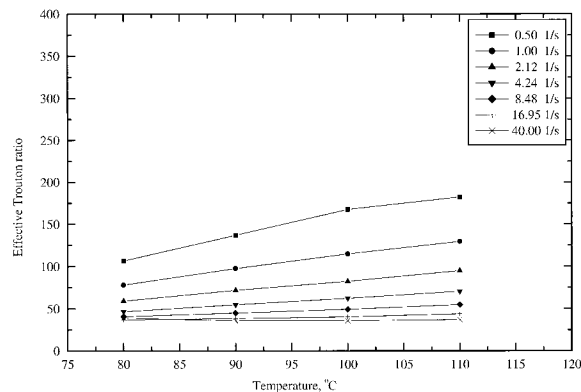
**Figure 8** Dynamic moduli of lyocell solution at 110°C.

tivation energy of some polymer melts, like polyethylene (25 kJ/mol), polystyrene (60 kJ/mol), and polycarbonate (85 kJ/mol).<sup>8</sup>

Dynamic moduli, presented in Figures 5–8, show almost the same pattern for all temperatures. At low deformation rates the lyocell solution behaves most likely as a viscous liquid (loss modulus  $G''$  being larger than storage modulus  $G'$ ) but at high angular velocities elastic properties develop. The two domains of viscoelastic behavior are separated by the so-called crossover point, which is shifted to higher angular velocities as the testing temperature is increased. This means that at higher temperatures the lyocell solution behaves as a viscous liquid over the almost whole range of the tested angular velocity.



**Figure 9** Complex and shear viscosity of 14% lyocell solution.



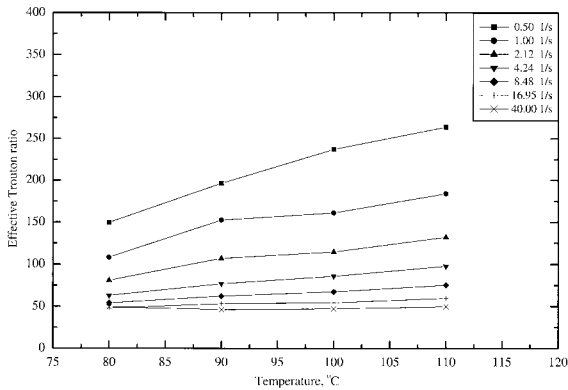
**Figure 10** Trouton ratio for lyocell solution at Hencky 6.

Even though the angular velocity of the crossover point is temperature dependent, the moduli values at the crossover are essentially constant since the samples are identical and therefore have the same average molecular weight.

### Trouton Ratio

The effective Trouton ratio is the ratio between effective elongational viscosity and shear viscosity at the strain rate equal to shear rate and is a good measure of the deviation from Newtonian behavior for a particular solution or melt. Running the ACER in the same range of shear rates as the elongational strain rates is rather difficult so that, considering that the Cox–Merz rule applies for lyocell solution—as seen from Figure 9—the complex viscosity was used for calculating the Trouton ratio. This characteristic is presented in Figures 10 and 11, at Hencky strains 6 and 7. It is seen that the effective Trouton ratio increases with the increase of the solution temperature at low deformation rates but a slightly reversed trend is recorded at the higher deformation rates. This is due to the fact that the shear viscosity is more temperature dependent at low shear rates and seems to be less affected by the thermal energy at high frequency. Higher values of the Trouton ratio are recorded at Hencky strain 7, and this is, of course, due to the higher effective elongational viscosity at that level of cross section area reduction.

As a rough approximation, the Trouton ratio is about 50–100 at high deformation rates. This ratio increases to about 182 at 110°C, 0.5 1/s angular velocity, and at Hencky strain 6, showing

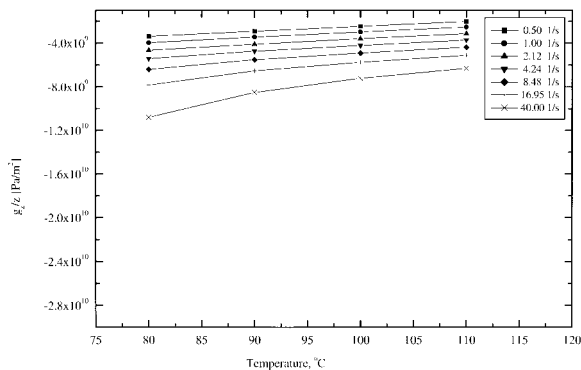


**Figure 11** Trouton ratio for lyocell solution at Hencky 7.

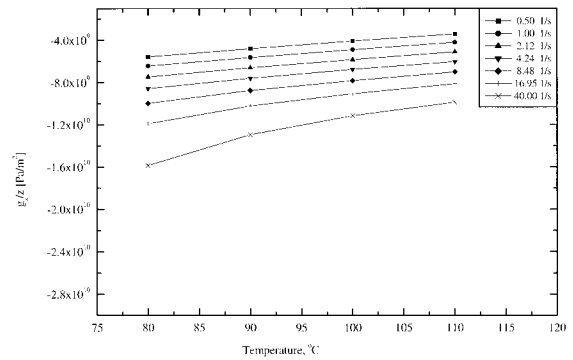
again a larger temperature dependency of shear viscosity as compared with the elongational viscosity, except at very high deformation rates. This is seen from the trend of the two types of viscosity curves. In case of dynamic shear viscosity, the curves converge as the angular velocity increases, but they are parallel for the effective elongational viscosity. At Hencky strain 7, 110°C, and 0.5 1/s deformation rate, Trouton ratio increases to about 264.

**Body Forces**

Calculated body forces that the applied pressure must overcome in order for the flow and orientation to develop are plotted in Figures 12 and 13. At low shear or strain rates, the body forces (negative in sign) are lower in magnitude and this corresponds to the lower entropy changes (as discussed below), thereby indicating less orientation development. Also, at high temperatures the body



**Figure 12** Body forces for lyocell solution at Hencky strain 6.

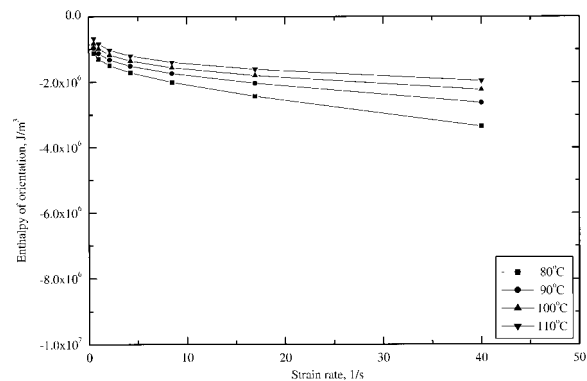


**Figure 13** Body forces for lyocell solution at Hencky strain 7.

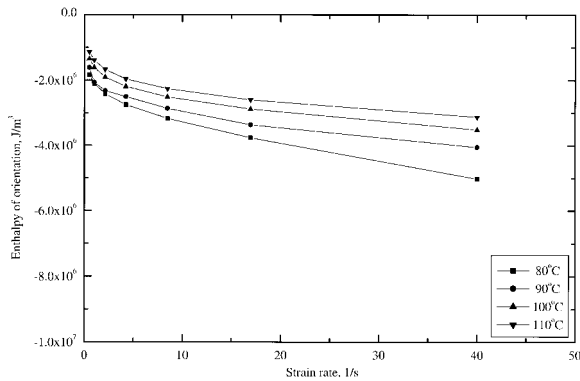
forces are lower due to the lower viscosity. Increasing the Hencky strain—that is, making the geometry more constrained for the flow—determines an increase of the body forces. It should be expected that as body forces are higher the higher is the orientation of the structural components of the flowing system.

**Orientation Effects**

Enthalpy of orientation, calculated according to eq. (12), is plotted as a function of strain rate for different temperatures in Figures 14 and 15. The influence of the deformation rate is much higher at low deformation rates (the initial slope of all curves is higher and asymptotically approaches zero as the strain rate increases). Additionally, solution temperature has a greater influence at high deformation rates, probably due to “a better use” of the drag or draw effect at low temperature, when due to the higher viscosity of the solution, the deformation process is better sustained, re-



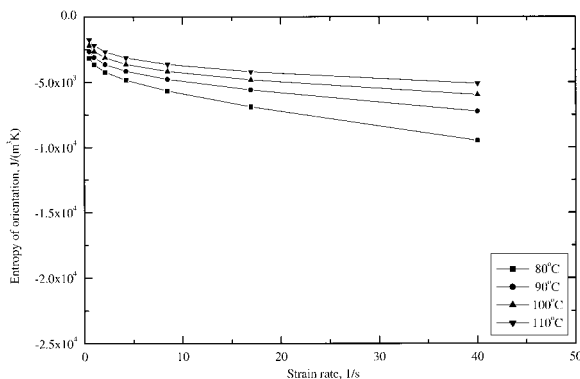
**Figure 14** Enthalpy of orientation for lyocell solution at Hencky 6.



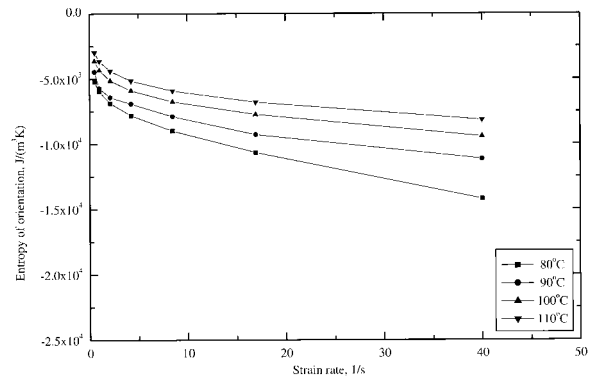
**Figure 15** Enthalpy of orientation for lyocell solution at Hencky 7.

sulting in an enhanced orientation. This hypothesis seems to be true if we also take into account the fact that the lower temperatures have a higher influence on enthalpy change at Hencky strain 7—that is at a higher rate of cross-section area reduction. Therefore, both strain rate and Hencky strain have an enhanced influence on orientation as the temperature is lower or the viscosity of the solution is higher.

Changes in the entropy of orientation, as calculated with eq. (13), are presented in Figures 16 and 17. The general trend is as for the change in the enthalpy. Poor orientation is recorded at high temperatures, due to lower viscosity of the solution. The increase in Hencky strain has a beneficial effect on orientation due to the enhanced draw effect at Hencky 7 as compared with Hencky 6. This interpretation of the orientation effects takes into account only the flowing throughout the die channel. After the exit of the “solution dope” from the die, relaxation phenomena start to



**Figure 16** Entropy of orientation for lyocell solution at Hencky 6.



**Figure 17** Entropy of orientation for lyocell solution at Hencky 7.

manifest and certainly they are determined by the flow history. Pressure relaxation experiments done on the same solution showed initial times of relaxation comparable with those for polymer melts and strongly dependent on the deformation history.

## CONCLUSIONS

Elongational viscosity of concentrated solutions of cellulose in *N*-methylmorpholine oxide monohydrate shows a strain thinning behavior and the same temperature influence, irrespective of the strain rate. Increasing the Hencky strain brings about an increase of the elongational viscosity. By introducing appropriate shift factors for the influence of temperature and Hencky strain, it is possible to plot a master curve for the elongational viscosity–strain rate relationship. Shear thinning behavior is characteristic for dynamic viscosity of lyocell solutions. Temperature sensitivity of the dynamic viscosity is higher at reduced shear rates and vanishes as the deformation rate increases. Trouton ratio generally increases with the increase of temperature, being almost constant at moderate to high deformation rates. Body forces, enthalpy of orientation, and entropy of orientation are high at low temperature and high deformation rates, all these showing a strong orientation effect. As expected, the orientation is higher at higher Hencky strain. At low angular velocities, the lyocell solution behaves as a viscous liquid, the elastic component in viscoelastic behavior decreasing as the temperature of the solution is increased. Temperature, Hencky strain, and deformation rates can be used as parameters to



control the rheological and orientation behavior of lyocell solutions, and finally the characteristics of the resultant products.

## REFERENCES

1. Collier, J. R.; Romanoschi, O.; Petrovan, S. *J Appl Polym Sci* 1998, 69, 2357–2367.
2. Collier, J. R. U.S. Patent 5,357,784, 1994.
3. Pendse, A. V.; Collier, J. R. *J Appl Polym Sci* 1996, 59, 1305.
4. Kim, H. W.; Pendse, A.; Collier, J. R. *J Rheol* 1994, 38, 831.
5. Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. *Transport Phenomena*; Wiley: New York, 1960.
6. Collier, J. R. *Midland Macromolecular Monograph No. 6, Flow Induced Crystallization*; Midland, MI, 1979.
7. Collier, J. R.; Lakshmanan, K.; Ankrom, L.; Upadhyayula, V. in *Structure-Property Relationship for Polymeric Solids*; Plenum Press, New York, NY, 1983.
8. Macosko, C. W. *Rheology, Principles, Measurements, and Applications*; VCH Publishers, New York, NY, 1994.