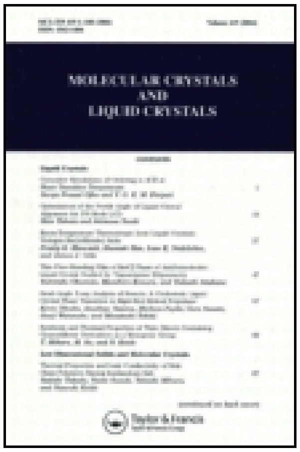

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Viscosity and WLF-Type Behavior of Mesophase Pitches

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Version of record first published: 20 Apr 2011.

To cite this article: F. F. Nazem & I. C. Lewis (1986): Viscosity and WLF-Type Behavior of Mesophase Pitches, Molecular Crystals and Liquid Crystals, 139:3-4, 195-207

To link to this article: http://dx.doi.org/10.1080/00268948608080127

Mol. Cryst. Liq. Cryst., 1986, Vol. 139, pp. 195–207
0026-8941/86/1394–0195/$20.00/0

Viscosity and WLF-Type Behavior of Mesophase Pitches

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(*Received March 10, 1986*)

Viscosity measurements for petroleum-derived mesophase pitch have been made as a function of isotropic content and temperature. The viscosity-temperature data have been used to determine activation energies as a function of isotropic content. It has been found that a William-Landel-Ferry (WLF) type plot can be used to fit the viscosity and temperature data through use of an appropriate shift factor. Mathematical expressions were developed to correlate viscosity with temperature and isotropic content.

Keywords: pitch, mesophase, viscosity, activation energy, shift factor, WLF

I. INTRODUCTION

The mesophase which develops in carbonaceous systems is a rather unique liquid crystalline material. Mesophase pitch consists of a eutectic mixture of polynuclear aromatic compounds with the nature and extent of mesophase development being related to both molecular size and concentration.[1,2] The carbonaceous mesophase, like pitches in general, exhibit a glass transition and gradual melting to a fluid state. The rheology of mesophase pitch has been discussed in a number of publications.[3-8] A variety of rheological phenomena were reported for mesophase pitches including: Newtonian, Pseudo-Newtonian and Non-Newtonian flow, stress-overshoot and undershoot, die swell, elasticity, Weissenberg Effect, etc., with the flow characteristics being attributed to the liquid crystalline and complex polymeric composition of the pitch.[7]

In order to clarify the flow behavior of the carbonaceous mesophase, a series of mesophase pitches made from a given precursor at rigidly controlled reaction conditions has now been utilized to investigate the dependence of viscosity on mesophase content and on temperature. This study has also been used to demonstrate the applicability of a classical polymer theory to the viscosity of liquid crystalline pitch.

II. EXPERIMENTAL

A. Materials

The mesophase pitches used in this study were similar to those described by Chwastiak and Lewis.[9] They were all produced in the laboratory by heat treating a precursor nonmesophase petroleum pitch in an inert atmosphere, at a constant temperature of 390°C. The precursor pitches were transformed to mesophase pitch through polymerization and volatiles removal[2] with the final mesophase contents ranging from 66% to 96%. The different mesophase contents were achieved by simply varying the total reaction time. The properties of the pitches are given in Table I. "Softening Points," (Ts), were determined by the Mettler ASTM procedure.[10] The glass transition temperatures, (Tg), were computed by thermomechanical analysis (TMA) techniques using a Perkin-Elmer TMA apparatus.[11] The isotropic contents of the mesophase pitches were determined from polarized light photomicrographs of annealed samples of the mesophase pitches.[12]

B. Apparatus

Viscosity of the pitches was measured on a concentric-cylinder Haake viscometer. The apparatus was substantially modified to improve both the accuracy and reproducibility of measurements.[7,8] In order to at-

TABLE I

Properties of the mesophase pitches

Mesophase pitch	Glass transition temperature, Tg, °C	Mettler softening point, Ts, °C	Percent isotropic content
A	235	339	4
B	225	334	11
C	221	329	17
D	210	324	20
E	195	312	34

tain the high temperatures needed for the mesophase pitches, the original heating chamber of the commercial viscometer was replaced with an electrical furnace capable of being controlled within ± 1°C up to 400°C. To minimize the thermal expansion effect, the original steel sample cell was replaced by a polished ceramic cell. Provisions were made for the cup to be inserted into the heating chamber without the possibility of lateral movement during the test.

Modifications were also made in the bob and rotor assembly to minimize instrumental vibrations and shear rate variations in the flow field. In order to maintain rigidity and reduce the gap size, the universal joint and motor stand of the instrument were replaced by a vertical lathe which held the motor, torque transducer and the rotating shaft.

Nitrogen was introduced above the sample cell from an inlet at the bottom of the heating chamber to prevent oxidation of the pitches during measurement. The sample temperature was continually monitored with a chromel-alumel thermocouple permanently seated in the housing surrounding the sample cup, and located about one centimeter from the actual sample.

C. Viscosity Measurement Procedure

Subsequent to assembling the cup and the bob, adjustments were made to ensure bob-cup concentricity. The bob was then slowly lowered into the cup to touch the bottom and immediately raised by 3/10,000 inch to establish "zero position" on the vertical position dial gauge. The bob was then removed from the cup, but still firmly attached to the vertical lathe.

A fixed amount of pulverized mesophase pitch was compression molded into a pellet and placed in the viscometer cup. The bob was partially lowered into the cup and the sample cell totally assembled. Upon heating the cell, the solid pellet converted to molten pitch in an inert atmosphere. The bob was, then, slowly lowered to the "zero position" and squeezed the pitch to occupy the entire gap between the cup and the bob.

When the test specimen reached the desired steady state temperature, it was sheared at a fixed shear rate sufficiently long to attain a constant torque. The shear rate was varied from run to run in the experiment by changing the rate of bob rotation. The following equations were used to calculate the shear rate, $\dot{\gamma}$, and the viscosity, η:

$$\dot{\gamma} = \frac{\Omega}{1 - K} \tag{1}$$

and

$$\eta = \frac{\tau(1 - K)}{2\pi R^2\Omega[K^2L + K^3R/3]} \tag{2}$$

where τ is the steady state torque, K is the ratio of bob-to-cup radii, R is the bob radius, Ω is angular velocity, and L is the height of the bob in the concentric-cylinder region.

Viscosities were measured over a range of achievable shear rates, with the minimum varying from 0.22 $\sec^{-1}$ to 1.35 $\sec^{-1}$, and the maximum varying from 7.42 $\sec^{-1}$ to 14.70 $\sec^{-1}$. The tests were run for each pitch at three equivalent temperatures of 13°C, 18°C, and 23°C above their Mettler softening points. A common temperature could not be used because of the different fluidity of the pitches.

III. RESULTS AND DISCUSSION

A. Viscosity versus shear rate

Viscosity-shear rate plots for the pitches at the three equivalent relative temperatures are shown in Figures 1 to 3. As shown in these plots, the pitches initially demonstrated a yield type behavior followed by "Pseudo-Newtonian" regions where the viscosities appear to be independent of shear rate. The slight rise in viscosity as a function

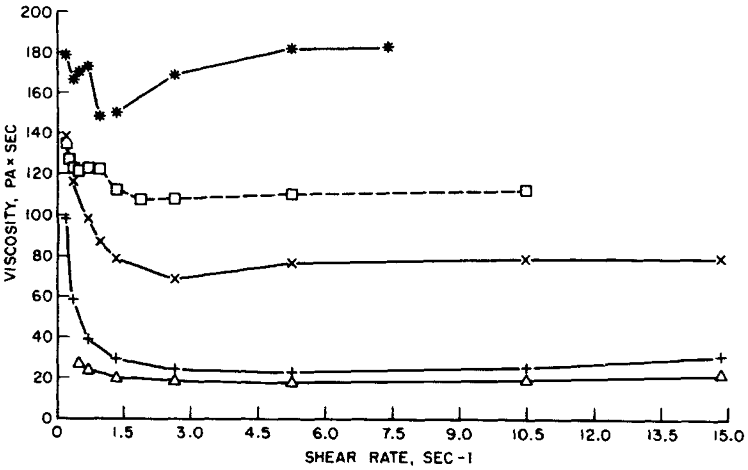

FIGURE 1 Viscosity measurements at 13°C above softening point. Pitch A = *, pitch B = □, pitch C = ×, pitch D = +, pitch E = △.

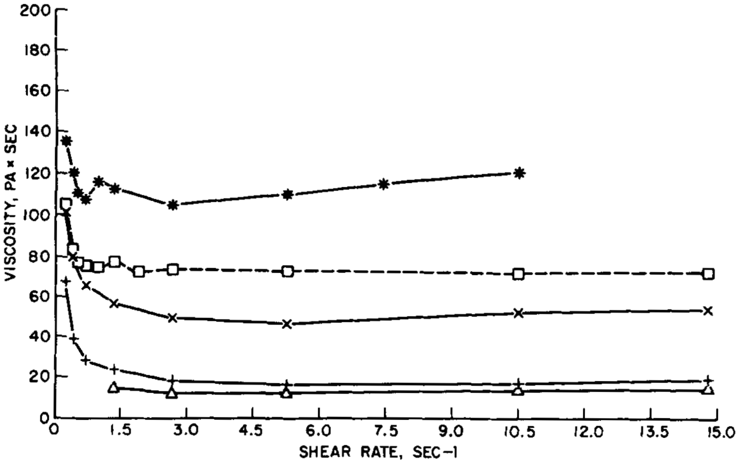

FIGURE 2 Viscosity measurements at 18°C above softening point. Pitch A = *, pitch B = □, pitch C = ×, pitch D = +, pitch E = △.

of shear rate above about 3.0 $\sec^{-1}$ for some measurements is within the accuracy of the measurements and should not be considered a shear-thickening behavior. The viscosity-shear rate dependence of these pitches is very similar to that found for other conventional liquid crystals.[13–15] The yield phenomenon which occurs at low shear rates can be attributed to structural changes with shearing.[13,14]

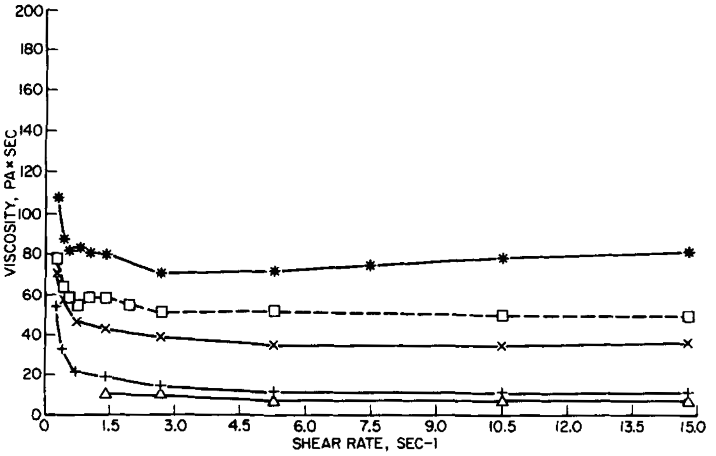

FIGURE 3 Viscosity measurements at 23°C above softening point. Pitch A = *, pitch B = □, pitch C = ×, pitch D = +, pitch E = △.

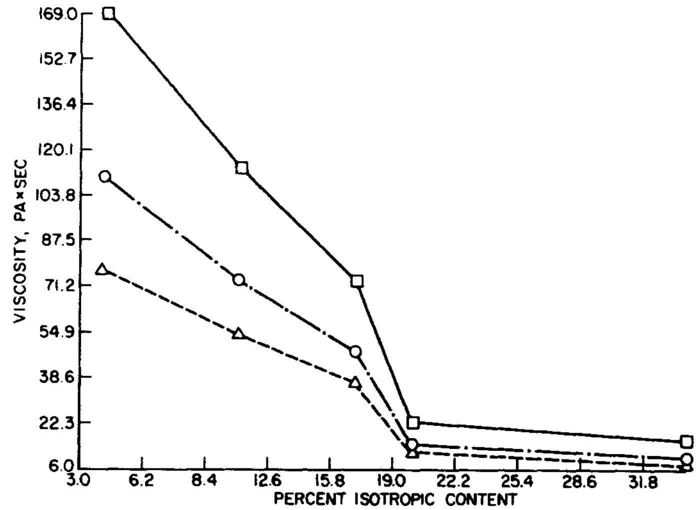

FIGURE 4 Viscosity versus isotropic content as a function of relative equivalent temperature (RET). □ = at 13°C RET, ○ = at 18°C RET, and △ = at 23°C RET.

It is readily apparent in Figures 1–3 that the shapes of the individual viscosity-shear rate curves are essentially identical at each of the temperatures.

B. Viscosity versus isotropic content

The "Pseudo-Newtonian" viscosities for the five mesophase pitches at each equivalent relative temperature are plotted against isotropic content in Figure 4. From the plots, it is apparent that the viscosity at the same relative temperature increases with decreasing isotropic content. This result is consistent with the observation that the anisotropic phase is the continuous phase in the mesophase range studied and thus controls the viscosity. This result is also in agreement with the evidence that the average molecular weight of mesophase pitches increase with increasing conversion to mesophase.[16]

C. Temperature dependence of viscosity

From the viscosity data at the three different temperatures, the dependence of viscosity on temperature can be described by an Arrhenius-type equation:

$$\eta = \eta_0 \operatorname{Exp}(\Delta E/RT) \qquad (3)$$

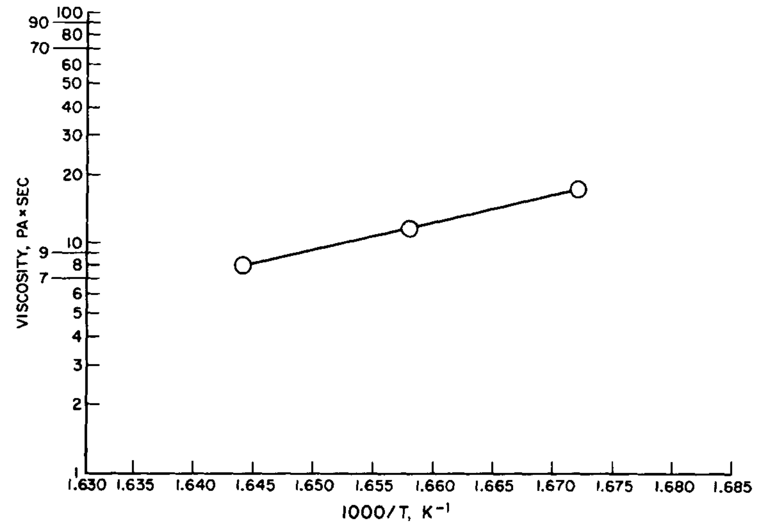

FIGURE 5 Activation energy plot for viscosity of sample E within the "Pseudo-Newtonian" range.

Figure 5 shows a plot of the logarithm of viscosity versus inverse temperature for sample E. As shown in Figure 5, an adequate straight line can be drawn, irrespective of shear rate in the "Pseudo-Newtonian" region. The activation energy can be determined from the slope of the lines while the temperature coefficient can be obtained from the intercept. The calculated values of activation energy and temperature coefficient of viscosity are listed in Table II for the five mesophase pitches. The general trend observed is that of increasing activation energy with increasing mesophase concentration in the pitch. From the activation energies, viscosities of the mesophase pitches can be calculated for any temperature. For example, Table III

TABLE II

Activation energies and temperature coefficients from the shear rate independent regions

Pitch	Percent isotropic	ΔE, activation energy (Kcal/mole)	η_0, temperature coefficient, (Pa sec)
A	4	71.2	2.2×10^{-23}
B	11	58.8	2.1×10^{-19}
C	17	56.4	6.8×10^{-19}
D	20	45.7	8.9×10^{-16}
E	34	49.2	1.8×10^{-17}

TABLE III

Calculated viscosities at glass transition temperatures

Pitch	Percent isotropic	Tg (°C)	Viscosity at Tg (Pa sec)
A	4	235	9.32×10^7
B	11	225	1.29×10^7
C	17	221	6.00×10^6
D	20	210	4.20×10^5
E	34	195	1.66×10^6

lists the calculated viscosities at the glass transition temperature. These viscosities are considerably lower than those of amorphous polymeric materials which exhibit viscosities of about 10^{12} Pa sec at their glass transition temperatures.[17]

D. Effects of isotropic content and viscosity on mesophase domain size

The disclination structure of the carbonaceous mesophase has been discussed extensively by White and Zimmer.[18] The dynamic behavior of pitch mesophase is similar to that of conventional nematic liquid crystals.[19] Thus, the anisotropic domain size, or the average distance between disclinations in the mesophase is expected to be related to mesophase viscosity since fluidity promotes annihilation of disclinations. Therefore, the mesophase domain size would be expected to decrease with decreasing isotropic content at a standard reference temperature.

In order to determine the effects of viscosity on domain size, the five mesophase pitches were all annealed at 23°C above their Mettler softening points, the highest temperatures at which the apparent viscosities were measured. The annealing procedure involved heating the pitch quiescently for 30 minutes in an inert atmosphere.[12]

Polarized light photomicrographs of the annealed samples, taken at 250× magnifications, are shown in Figure 6. On annealing, the isotropic fraction separates as spheres uniformly dispersed throughout the mesophase. It appears that contrary to expectations, the domain size increases with decreasing isotropic content. An attempt was made to measure the domain size with the use of an Image Analyzer technique.[20] The results are shown in Table IV along with the viscosity values at the annealing temperature. Although the accurate domain size measurements are difficult to make, because of the isotropic inclusions, it appears that there is a trend for the domain size to

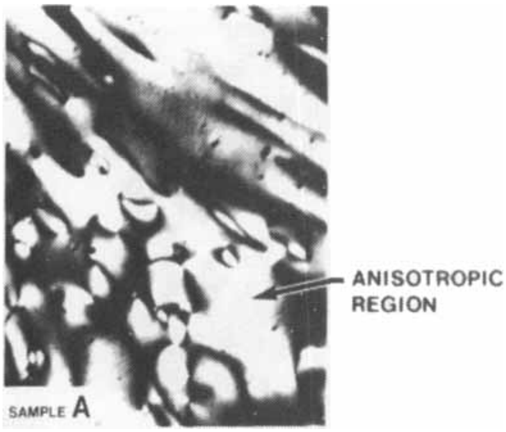

FIGURE 6a Photomicrograph of sample A (4% isotropic). Annealed at 362°C, magnification = 250.

TABLE IV

Comparison of mesophase domain size and viscosity at 23°C above the Mettler softening point with isotropic content

Pitch	Annealing temp., °C	Viscosity, Pa sec	Average domain size, μ	% isotropic
A	362	79	81	4
B	357	50	65	11
C	352	37	62	17
D	347	13	65	20
E	335	7	45	34

FIGURE 6b Photomicrograph of sample B (11% isotropic). Annealed at 357°C, magnification = 250.

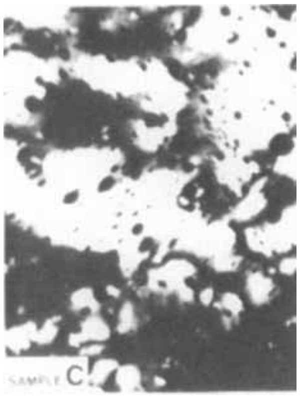

FIGURE 6c Photomicrograph of sample C (17% isotropic). Annealed at 352°C, magnification = 250.

increase with decreasing isotropic content. This result is attributed to the effect of the isotropic inclusions which seem to act as nucleation sites for the disclination loops. Therefore, the domain size is not controlled only by the absolute viscosity.

E. Application of William-Landel-Ferry (WLF) relationship to mesophase pitch

William, Landel and Ferry[21] found that: "in an amorphous polymer above its glass transition temperature, a single empirical function can describe the temperature dependence of all mechanical and electrical

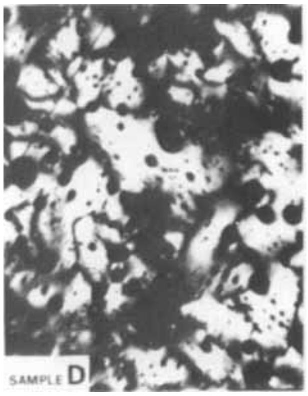

FIGURE 6d Photomicrograph of sample D (20% isotropic). Annealed at 347°C, magnification = 250.

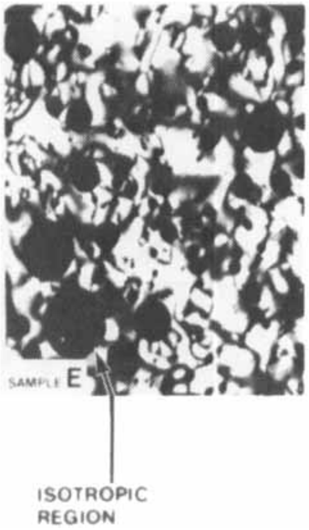

FIGURE 6e Photomicrograph of sample E (34% isotropic). Annealed at 335°C, magnification = 250.

relaxation processes." This function includes the shift factor, a_T, or the ratio of relaxation times at two different temperatures. The log (a_T) plotted against the difference in temperature from a specific reference temperature gave essentially the same curve for many polymeric systems. We have applied this relationship to the five mesophase pitches included in this study.

The shift factor, a_T, is defined as:

$$a_T = \frac{\eta\, T_r\, \rho_r}{\eta_r\, T\, \rho} \tag{4}$$

where: T, T_r = temperature, reference temperature, °K;
η, η_r = apparent viscosities at T and T_r;
ρ, ρ_r = densities at T and T_r.

Since the density of the spheres in mesophase pitches are not very different,[22,23] the density ratio ρ_r/ρ for the mesophase pitches are close to unity. The reference temperature, T_r, was chosen to be the glass transition temperature (Table I) plus 140°C and the reference viscosity was calculated using the activation energies in Table II. Following these guidelines, the WLF-type plot in Figure 7 was de-

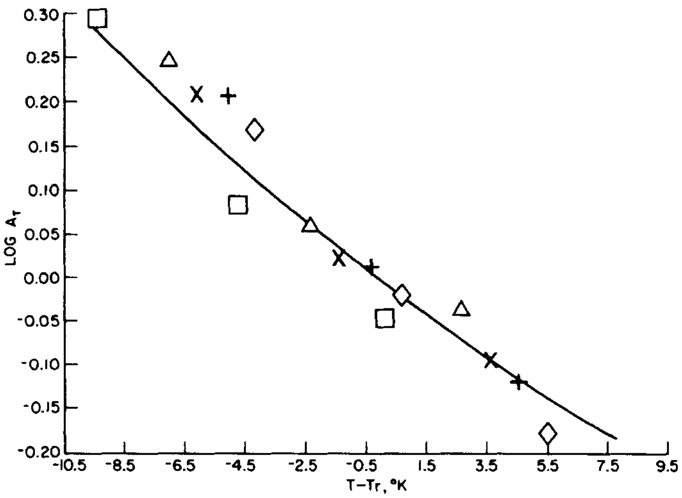

FIGURE 7 Shift factor plot for mesophase pitches. ◇ = sample A, + = sample B, × = sample C, △ = sample D, □ = sample E.

veloped for the five mesophase pitches. This plot is very similar to the published WLF plot for organic glasses and polymers.[21]

The results of our study show that mesophase pitch possesses many of the characteristics of conventional liquid crystalline and polymer systems. Because of its applicability to mesophase pitches, the WLF equation can be used to calculate viscosity or isotropic content with the use of appropriate data. For example, with the use of the transformed equation:

$$\eta_2 = \eta_1 (T_1/T_2)\,(a_{T_2}/a_{T_1}) \tag{5}$$

the viscosity of a mesophase pitch at a particular temperature can be calculated from its glass transition temperature and its viscosity at a different temperature. The relationship should hold for mesophase pitches prepared from the same precursor. Additionally, since the mesophase pitch glass transition temperature and Mettler softening point are related to the isotropic content, one can derive a relationship between the measured viscosity at a particular temperature and isotropic content (X):

$$\eta = T\mathrm{Exp}\,\frac{[4097.3 - 6.7T + 45.3X - 0.09XT - 0.07X^2]}{[-543.7 + T + 0.71X]} \tag{6}$$

We have used this equation to successfully calculate isotropic contents of mesophase pitches produced from the same petroleum pitch precursor.

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