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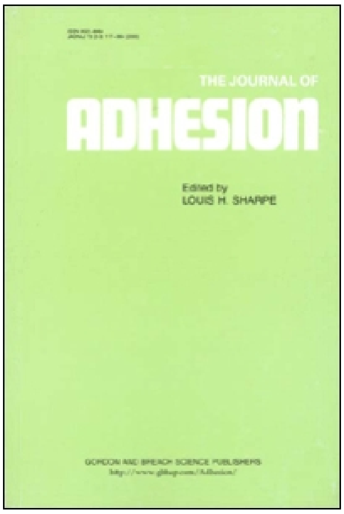

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Spreading of Viscous, Well-Wetting Liquids on Plane Surfaces

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A semi-empirical equation has been developed to describe the wetting kinetics for the spreading of viscous sessile drops. The model has been successfully applied to polystyrene melts over a wide temperature range (150–240°C) as well as a significant molecular weight range ($\overline{M}_w$ from 10,000 to 353,000). Current literature models were found to be inadequate as a complete description of wetting kinetics. The present model and experimental results corroborate earlier predictions by Smith and by VanOene concerning the time dependence of the rate of spreading of a viscous liquid when surface tension effects are negligible. The present method has also been successfully applied to two other viscous liquids, glycerol and silicone oil. The model indicates the strong influence of melt viscosity on wetting kinetics.

INTRODUCTION

The formation of an adhesive bond between a liquid adhesive and a surface depends on the development of maximum interfacial contact and the displacement of air from surface irregularities. To obtain extensive contact between the adhesive and the surface, the adhesive must wet the surface. Hence a study of the kinetics of wetting can reveal information critical to the adhesion process.

Considerable attention has been given both to the thermodynamics of wetting and to the study of adhesive forces, and with limited success,

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numerous current models [1-6] have been developed which attempt to describe the wetting process. This inability to predict completely polymer flow behavior has led us to postulate a semi-empirical model for wetting which we have successfully applied to polystyrenes of various molecular weights and molecular weight distributions over a relatively wide temperature span. The model can be used as a practical tool in predicting polymer flow properties. The present work concerns the results of experiments on the spreading of viscous polystyrene melts on a plane, soda-lime glass surface over a wide temperature and molecular weight span. The experiments were aimed at determining the main physical parameters influencing the spreading rate of the melt. The model was also successfully applied to two entirely different viscous fluids, silicone oil and glycerol, at room temperature.

MATERIALS AND PROCEDURES

The polystyrenes used in this study were of both narrow and broad molecular weight distributions. The polystyrenes of narrow molecular weight distribution were obtained from Pressure Chemical Co. Four of the remaining broad molecular weight distribution polystyrenes were synthesized (free radical) and purified in this laboratory using standard techniques. Two commercial broad distribution polystyrenes were used in an "as is" condition. Molecular weight characterization was performed by gel permeation chromatography (GPC) and the results are summarized in Table I. GPC analysis of the samples after the experimental heat cycling showed negligible molecular

TABLE I

Polymer characterization data

Polymer	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$
PS 10,000[a]	9,600			< 1.06
PS 20,400[a]	20,200			< 1.10
PS 37,000[a]	37,000			< 1.06
PS 8,879[b]	8,900	24,500		2.76
PS 10,996	11,000	25,600	56,000	2.33
PS 17,255	17,300	32,200	53,000	1.86
PS 31,733	31,700	86,600	173,000	2.73
PS 104,000	104,000	353,000	1,245,000	3.39
PS 132,000[b]	132,000	310,000	574,000	2.35

Source: [a] Pressure Chemical Co. [b] Monomer Polymer Laboratories weight changes due to possible thermal degradation of the melt under experimental conditions. This result is consistent with those of Blanchard and coworkers[7] for similar molecular weights and temperatures.

The glass surfaces (Esco 25 x 75 mm microscope slides) were cleaned in the following manner:

1) Mild detergent soak in an ultrasonic cleaner, followed by a distilled water rinse.

2) 10 minute soak in 0.5% Na_4EDTA solution.

3) Three distilled water rinses in an ultrasonic cleaner.

4) Hot air dry for a minimum of 30 minutes.

Slides cleaned in this manner resulted in good wetting behavior. In contrast, Corning glass slides (#2947), cleaned in the same fashion, showed systematic surface defects which prevented symmetrical spreading of the sessile drop of the polymer melt.

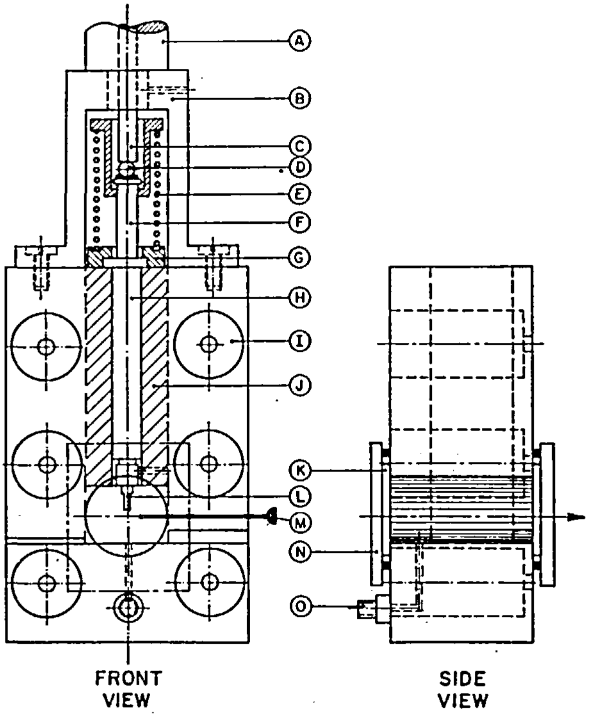

FIGURE 1 Experimental dropping apparatus. A—micrometer barrel; B—micrometer support; C—micrometer plunger; D—ball bearing; E—syringe return spring; F—syringe plunger; G—syringe barrel retainer; H—syringe barrel; I—plug heater; J—syringe barrel guide and surround; K—plane glass window; L—syringe tip; M—thermocouple; N—window retainer; O—nitrogen gas inlet.

The dropping apparatus developed in this laboratory and reported previously[8] was improved to minimize vacuum contamination and thermal gradients. Upon careful examination,[9] a nonvacuum system was found to be more suitable and a new dropping apparatus using a nitrogen atmosphere, Figure 1, was designed which used ordinary 2 ml glass syringes and a precision micrometer to achieve excellent drop control. The temperature of the system was controlled to within ±2°C with respect to the temperatures of the melt prior to dropping, of the surrounding nitrogen atmosphere and of the glass substrate. This method of using thermally equilibrated pendant drops for wetting can be contrasted to that used by Schonhorn, Frisch and Kwei,[1] or Johnson and Dettre,[10] where solid pellets of the polymer were heated to temperature in a thermostated environment. The present method is felt to minimize thermal gradients within the melt and their effects on the wetting behavior.

The wetting behavior was recorded on 35 mm film using a motorized (9 fps) single lens reflex camera. The contact angle and drop dimensions were measured using a 70× microscope with a goniometric eyepiece and a precision X–Y travelling stage. Accuracy of the angle measurements was ±2° while the accuracy of the drop dimensions was $\pm 1 \times 10^{-4}$ cm.

The polymer was first packed into the glass syringe and premelted in a vacuum oven to eliminate any entrapped gas bubbles. The syringe was placed tip upwards in the vacuum oven and the temperature raised above the polymer's glass transition temperature. After this pretreatment, the appropriate dropping tip (a stainless steel tip carefully cut and polished) was attached and the syringe could be inserted into the dropping apparatus.

RESULTS AND DISCUSSION

i) Preliminary analysis using two current models

The method and model of Lau[11] were first used to analyze the spreading data. Lau's model for wetting was based on the premise that the driving force, F, for wetting could be expressed as:

$$F = \gamma_{SV} - \gamma_{LS} - \gamma_{LV} \cos \theta_d \tag{1}$$

where γ_{ij} represents the thermodynamic interfacial energies. At equilibrium, Young's equation was invoked and it was consequently shown that

$$F = \gamma_{LV}(\cos \theta_s - \cos \theta_d) \tag{2}$$

where θ_s represented the static (equilibrium) angle and θ_d, the dynamic contact angle. The rate of spreading was then proportional to this driving force as:

$$\frac{dA}{dt} = k\gamma_{LV}(\cos \theta_s - \cos \theta_d) \tag{3}$$

The strong static contact angle-temperature relationship that was previously observed for polystyrenes of differing molecular weight was not observed in the present analysis. Rather, the contact angles measured after a suitably long time period fell into a narrow band regardless of molecular weight or temperature, as shown in Figure 2. A re-examination of Lau's method, shown in Figure 3, revealed nonlinearities which prevented its use for the present well wetting system. The improved thermal characteristics of the present system and the elimination of vacuum contamination were felt to be mainly responsible. A coating was detected on the glass surface (by water wettability tests) whenever polystyrene was present above the glass substrate. This coating however, did not impede the wettability of the melt as had been thought previously.

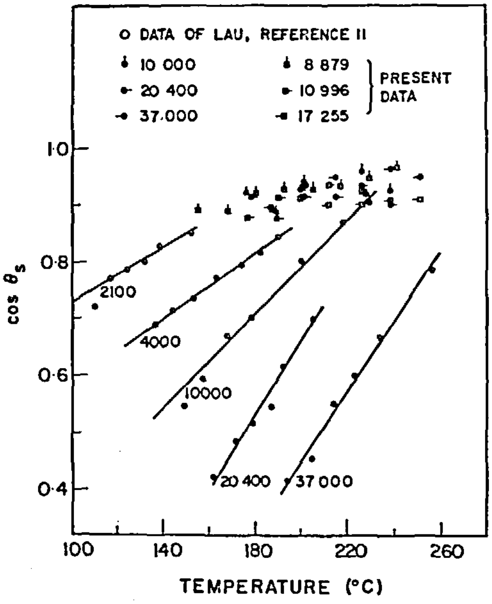

FIGURE 2 Comparison of static contact angle (cos θ_S) with temperature, Lau's data and present data.

The form of Lau's model is superficially similar to that proposed by Arslanov.[5] Arslanov considered that the moving force of spreading could be identified with the decrease of surface free energy of the system and would be resisted by the viscous resistance of the drop mass. A similar approach was taken by Yin[4] earlier but his mathematical method has been questioned.[12] Arslanov also questioned the appropriate geometry which should be used in the description of the sessile drop and observed in his experiments that a cone was better suited than the spherical segment which typically had been used by other workers. His equivalent model for spreading can be expressed as:

$$\frac{dA}{dt}=\frac{4\pi\gamma_{LV}}{\eta}\left(\frac{3V}{\pi}\right)^{1/3}(\cos\theta_e-\cos\theta_d)\tan^{2/3}\theta_d \qquad (4)$$

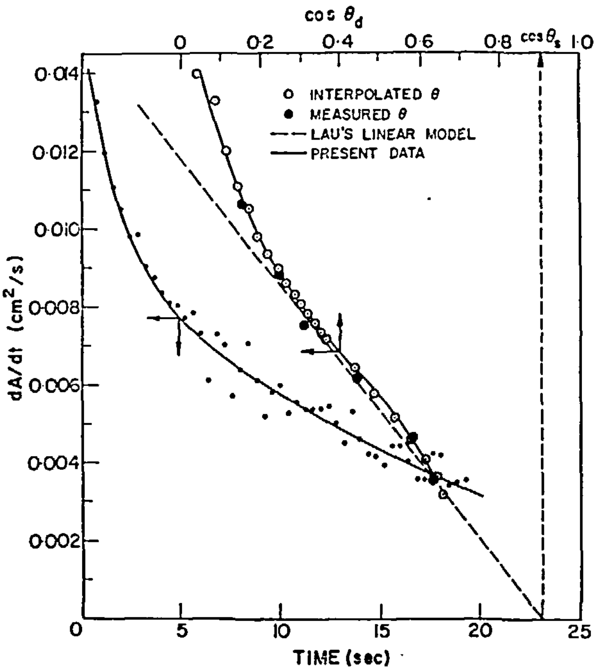

FIGURE 3 Experimental data showing the relationship of dA/dt with time and with $\cos\theta_d$ for PS 10,000 at 188°C.

In the present work an analysis of the drop profile did not indicate that a cone profile better fitted the spreading phenomenon. This was further illustrated by examining the relationship of Eq. 4 and plotting dA/dt versus $\cos\theta_d\tan^{2/3}\theta_d$ which would be expected to be linear. Deficiency of Arslanov's model as equilibrium was approached can be observed in Figure 4 when the present data were evaluated in this manner.

ii) Subsequent analysis of spreading area as a function of time

These preliminary results led us to develop a semi-empirical model for wetting. A shift factor approach was used to analyze the data since it fitted the data well and had been used by numerous authors to correlate time- and temperature-dependent behavior of polymers above their glass transition temperatures. It is quite generally known, for example, that the temperature dependence of the viscosity of polymer melts obeys a WLF or Vogel type equation.

In the present case, spreading data have been correlated by plotting A/A_{90} which represents a spreading ratio of the contact area, A (at any time t) with the area of the sessile drop at the 90° contact angle condition, with time on a log–log basis. Data for PS 8879 are shown in Figure 5 at various temperatures. A series of almost parallel lines is observed over an extensive range of spreading times and temperatures. At very small times curvature does occur; similarly at extremely long times curvature would be expected as equilibrium is approached. The present data do not indicate that equilibrium was being reached under the time scale of examination (usually less than 1 hour). However, a similar analysis using glycerol (Figure 6) showed a linear

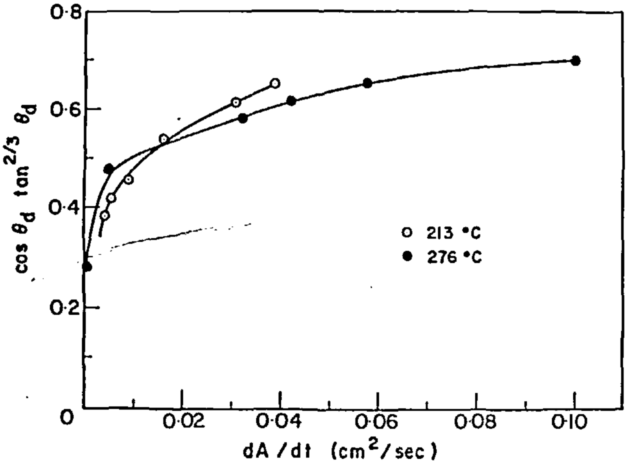

FIGURE 4 Test of Arslanov's model for spreading using present data for PS 10,000 at 213 and 226°C.

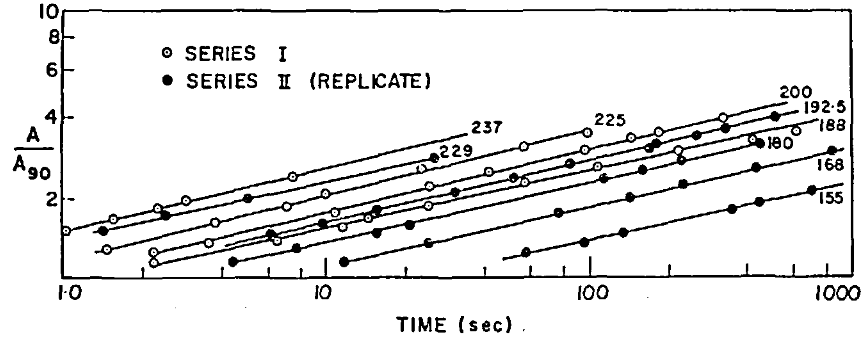

FIGURE 5 Flow curves for PS 8,879 at various temperatures.

behavior to a spreading ratio of ~ 9 or, in other words, the flow curve described wetting adequately from the 90° contact angle to a contact angle approaching 2–3°.

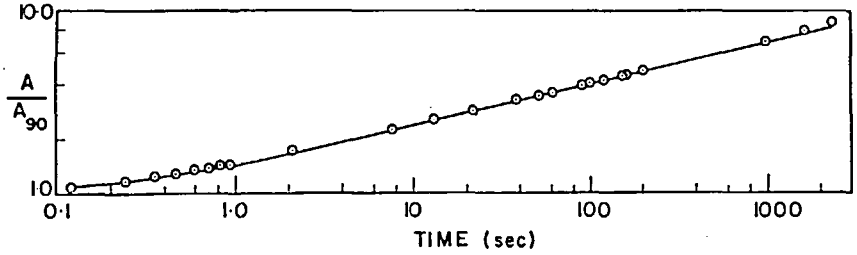

FIGURE 6 Flow curve for glycerol at room temperature (23°C).

The similarity of the data of Figure 5 suggested a data reduction or shift factor technique similar to that of Schonhorn[1] or VanOene.[13] The reduced flow curves for the polymers studied can be seen in Figures 7 and 8. Two shift factors were defined which effectively allowed the wetting behavior of the polystyrene examined to be predicted from a single universal flow curve. The temperature shift factor, α_T, reduced the flow curves to a common temperature (238°C) for a given molecular weight, and a molecular weight shift factor, α_M, reduced the flow curves with respect to the different molecular weights relative to PS 10000 at 238°C which was selected as the reference flow curve for polystyrene.

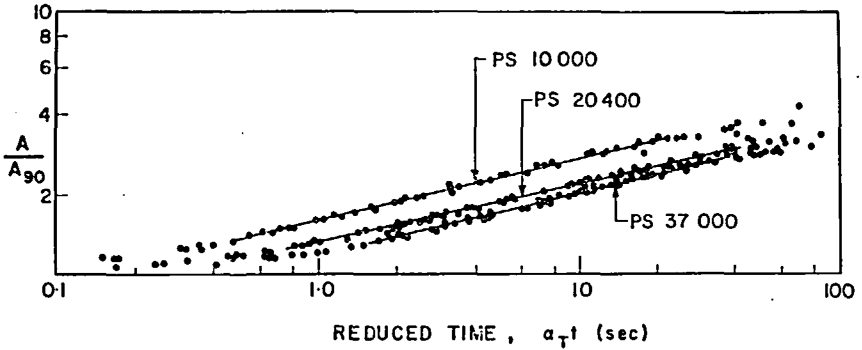

FIGURE 7 Reduced flow curves for polystyrenes having narrow distributions of molecular weights.

The shift factor can be related to the basic physical parameters of the spreading polymer system. Since the shift factor was experimentally defined through the time ratio necessary to reduce a particular flow curve to the reference flow curve, this time ratio can be interpreted as a viscosity ratio. Since polymer viscosity may be represented by an Arrhenius-type relationship for $T > T_g + 100$, it follows that the shift factors are related to the viscosity of the polymer melt and hence an Arrhenius-type expression involving α_T versus inverse temperature would be expected. A plot of log α_T versus

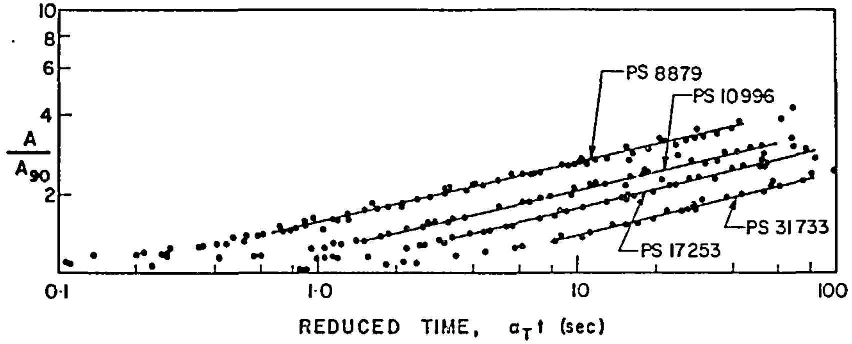

FIGURE 8 Reduced flow curves for polystyrenes having broad distributions of molecular weights.

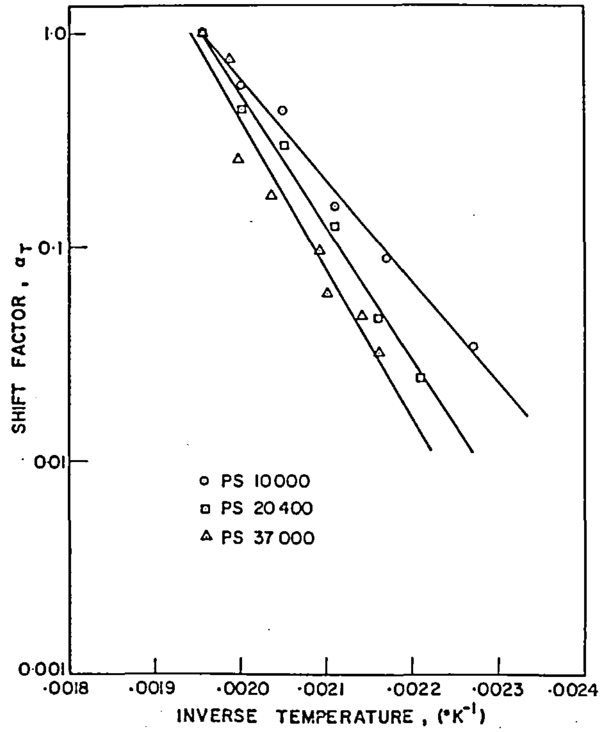

FIGURE 9 Variations of the temperature shift factor (α_T) with the reciprocal of the absolute temperature for polystyrenes having narrow distributions of molecular weights.

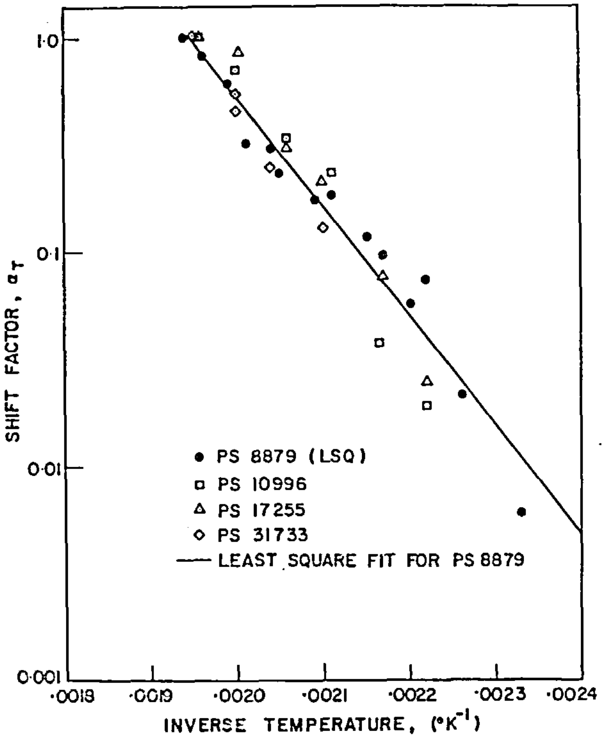

FIGURE 10 Variation of the temperature shift factor (α_T) with the reciprocal of the absolute temperature for polystyrenes having broad distributions of molecular weights.

inverse temperature is shown in Figure 9 for polystyrenes of narrow molecular weight distribution and in Figure 10 for polystyrenes of broad molecular weight distribution. These figures corroborate the Arrhenius-type relationship of shift factor with temperature with an activation energy similar to that of the activation energy of viscous flow predicted by other methods.

It is interesting to note that the shear rates for the free spreading of viscous polymer drops have been estimated[13] to be quite small and hence an appropriate melt viscosity must also be considered in this interpretation of spreading parameters. Shear viscosity is dependent upon shear rate so that, as the condition of zero shear rate is being approached, the appropriate zero shear viscosity must be considered as the dominant variable. A comparison was then made with various literature values of viscosity for polystyrenes of similar molecular weights using these values of zero shear viscosity whenever possible. The viscosity ratios and experimental shift factors were then compared as functions of inverse temperature. Activation energies for the various molecular weights were evaluated. A typical comparison of the viscosity ratio data and the present shift factor data is shown in Figure 11.

A comparison of the activation energies determined by the two methods is shown in Table II. The activation energies calculated by the shift factor method are very similar to those calculated by the viscosity ratio method and substantiate the expected strong effect of temperature on polymer viscosity and hence wetting behavior.

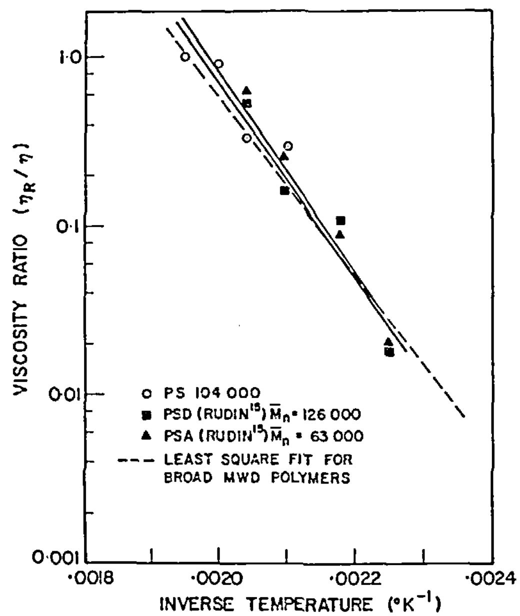

FIGURE 11 Variation of the viscosity ratio (η_R/η) with the reciprocal of the absolute temperature for polystyrenes having broad distributions of molecular weights for the data of Rudin (T_{ref} = 237°C).[15]

The molecular weight shift factor, α_M, was successfully correlated with the glass transition temperature, T_g, of the particular polystyrene. This correlation is shown in Figure 12 and emphasizes the effect of molecular weight on the melt viscosity.

Based on the extended linearity of the spreading ratio flow curve and since ln–ln coordinates were used for the flow curves, a power-law relationship of the form $y = aX^m$ was considered for the linear portion of the flow curve. Linearity was normally assumed for $A/A_{90} > 1.2$. The exponent "m" was evaluated by measuring the slopes of all the experimental flow curves and taking the arithmetic average. An average slope of 0.2314, std deviation =

TABLE II

Comparison of activation energies for polystyrenes of narrow and broad molecular weight distribution by different researchers and methods

	Narrow MWD		Broad MWD		
Reference	Molecular weight	Activation energy (kcal/mole)	Molecular $\bar{M}_n$	$\bar{M}_w$	Activation energy (kcal/mole)
Fox and Flory[14]	25,700	35.4			
	32,000	34.2			
	80,000	31.1			
	134,000	35.6			
Rudin[15]	51,000	34.8	126,000	302,000	26.3
	92,000	23.9	63,000	225,000	27.0
	411,000	25.6			
Rudd[16]	41,700	25.5			
	96,300	23.0			
Present study	10,000	24.25	8,879	24,472	26.06
	20,400	28.71	10,996	25,630	
	37,000	31.59	17,255	32,165	
			31,733	86,558	

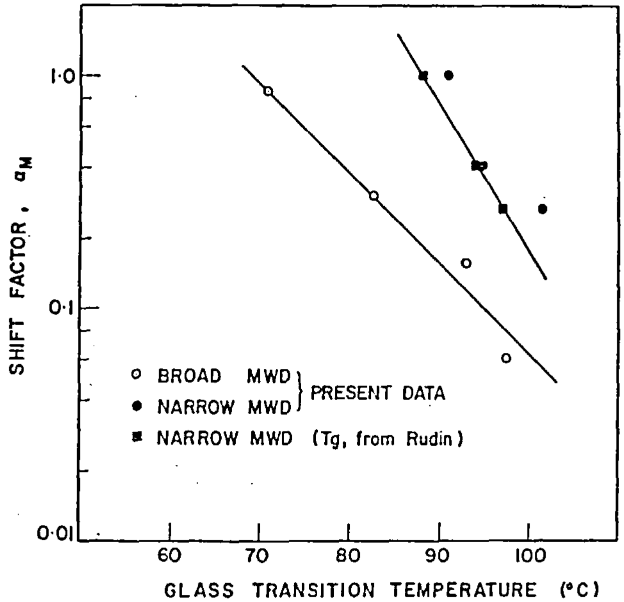

FIGURE 12 Variation of the molecular weight shift factor (α_M) with the glass transition temperature of the different polystyrenes. (Rudin's data are taken from reference 17.)

.0166, was obtained, for drops having an A_{90} range of $0.10\,\text{cm}^2 < A_{90} < 0.20\,\text{cm}^2$. The final form of the model was

$$\frac{A}{A_{90}} = 1.58(\alpha_T \alpha_M t)^{0.2314} \tag{5}$$

or

$$A = 1.58 A_{90}(\alpha_T \alpha_M t)^{0.2314} \tag{6}$$

Since the temperature shift factors α_T were shown to follow Arrhenius type expressions, these factors may also be generalized as constituting an equation of the form

$$\alpha_T = Ke^{-E_a/RT}$$

with the parameter K and E_a selected from the following experimentally determined data:

PS	E_a (kcal/mole)	K
10,000	24.25	2.52×10^{10}
20,400	28.71	1.86×10^{12}
37,000	31.59	2.50×10^{13}
All broad molecular weights	26.06	1.41×10^{11}

Similarly, the molecular weight shift factor α_M was reduced to an analogous form involving the glass transition temperature for the particular polymer and was of the form

$$\alpha_M = Be^{-DT_g}$$

with the parameters B and D selected from the experimentally determined data:

PS	D (°C^{-1})	B
Narrow	0.1465	3.96×10^5
Broad	0.0930	6.62×10^2

And where T_g is the glass transition temperature in °C.

Using these semi-empirical parameters, the flow curves for all the polystyrenes examined were calculated and compared with the actual flow data. Typical comparisons are shown in Figures 13 and 14 for two polymer samples.

The agreement was found to be excellent in most cases and the deviations at lower temperatures (see Figure 14, $T = 180°C$, $T = 155°C$) were probably not due to experimental inaccuracies but to the use of the Arrhenius-type expression for the shift factor in its nonlinear region, i.e., $T < T_g + 100$. This low temperature sensitivity does not preclude the applicability of the model over the more normal range of experimental conditions.

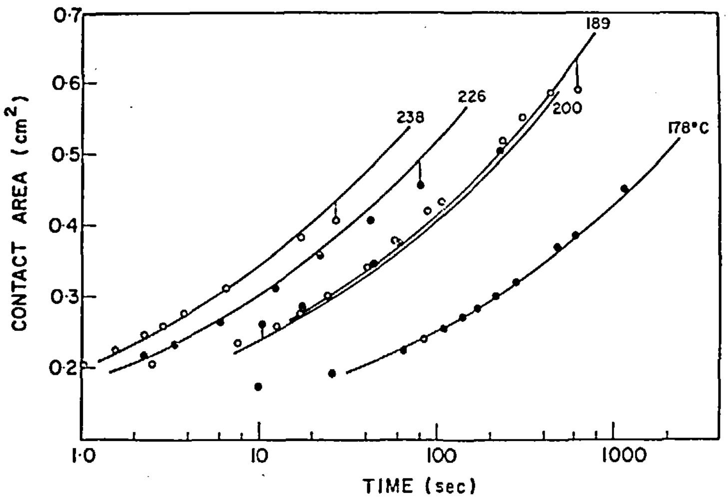

FIGURE 13 Comparison of the actual flow data and the curve predicted by the semi-empirical model for PS 20,400 (narrow MWD).

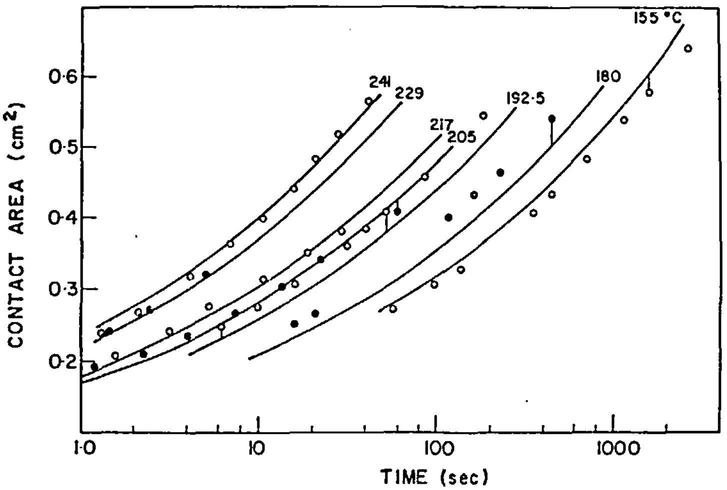

FIGURE 14 Comparison of the actual flow data and the curve predicted by the semi-empirical model for PS 8,879 (broad MWD).

iii) Corroboration of Smith's theory

It has recently come to our attention that the present data may also substantiate an exact mathematical treatment by Smith[18] who examined the development of a wave motion in a thin sheet of viscous fluid. In one particular solution he considers the spreading of a constant volume of liquid that is initially concentrated at the origin and examines the velocity as it slowly spreads over a flat bed. For the specified boundary condition and when surface tension effects have become negligible (in his case for wetting angles smaller than about 30°) Smith's theory has been calculated by VanOene[19] to yield for the rate of spreading,

$$\frac{d(r/R_0)}{dt} = 0.13(gR_0/v)^{1/8}t^{-7/8} \tag{7}$$

where t is time.

If the present empirical solution to spreading is considered where

$$\frac{A}{A_{90}} = 1.58(\alpha_T\alpha_M)^{0.2314}t^{0.2314}$$

which may be rewritten

$$\left(\frac{r}{R_0}\right)^2 = 1.58(\alpha_T\alpha_M)^{0.2314}t^{0.2314}$$

or

$$\frac{r}{R_0} = \sqrt{1.58}(\alpha_T\alpha_M)^{0.12}t^{0.12}$$

From this expression one can obtain for the rate of spreading

$$\frac{d(r/R_0)}{dt} = 0.12\sqrt{1.58}(\alpha_T\alpha_M)^{0.12}t^{-0.88}$$

$$= 0.15(\alpha_T\alpha_M)^{0.12}t^{-0.88}$$

This agreement with Smith's exact results (including both the viscosity term and the time term) provides an interesting interpretation of the spreading process. This result suggests that what is observed is the gravitationally induced viscous collapse of a viscous sheet, initially confined at the origin of the co-ordinate system. The question remains why the surface tension forces are negligible. As shown by VanOene *et al.*[13] the spreading rate is proportional to $\gamma \cos \theta/\eta R_0$ where γ is the surface tension and R_0 the initial radius at $\theta = 90°$ of the spreading droplet. The magnitude of this term can be understood by examining the physical properties of the present system. In general, melt viscosities are very high while drop sizes are small (~ 0.18 cm $< R_0 <$ 0.26 cm). However, the combinations are such that the surface tension forces are still small relative to the gravitational forces, allowing the agreement with Smith's results. For the term $\gamma \cos \theta / \eta R_0$ to become large with respect to the gravitational forces in dealing with polymer melts, then, the drops would need to be extremely small.

SUMMARY AND CONCLUSIONS

Wetting kinetics have been successfully described by a semi-empirical, experimentally accessible, equation which appears to have general applicability to viscous liquid systems of macroscopic size when surface tension effects are negligible. Current spreading models, which incorporate a spreading coefficient relating only simple free energy changes, show deficiencies in well wetting systems. The present spreading model shows the dominant effect of melt viscosity on the wetting behavior of polymer melts in well wetting systems. This model is consistent with Smith's theory as amplified by VanOene and these data are in remarkably good agreement with their theoretical predictions.

Acknowledgement

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