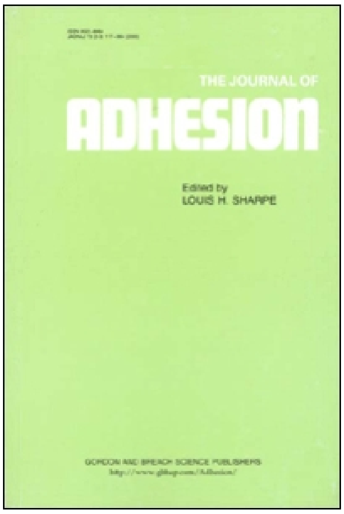

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Profiles of Spreading Sessile Drops of Viscous Polymer Melts

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The profile or shape of spreading drops of viscous polymer melts has always raised some questions regarding the basic forces inherent in and controlling the wetting phenomenon. The occurrence and nonoccurrence of "projecting feet" for spreading sessile drops has puzzled experimentalists for some time. Recent work for a homologous polymer series, differing only in molecular weight and molecular weight distribution and examined over a wide temperature range, has emphasized that an advancing projecting foot does occur and is dependent upon the molecular weight of the polymer material. The projecting feet can be interpreted as an effect resulting from the viscoelastic response of the material which can occur when the molecular weight of the polymer is higher than the characteristic critical molecular weight of entanglement of the material. For low molecular weight polymers the strong interfacial forces are not impeded by the bulk viscous response of the material whereas the present evidence indicates that, for high molecular weight material, the elastic or entangled component of the polymer may retard complete bulk flow or the redistribution of the polymer in harmony with the advancing interface. Previous inconsistencies in the literature regarding the observations of projecting feet may be explained by this model.

INTRODUCTION

The occurrence or non-occurrence of "projecting feet" for spreading sessile drops of viscous liquids has puzzled experimentalists for some time. We wish to present recent evidence[1] which indicates that the molecular weight and the molecular weight distribution of the material may be important in predicting the occurrence of this phenomenon.

The importance of good wetting to basic adhesion studies has resulted in the examination of wetting kinetics in an attempt to predict the wettability behavior of a surface by a molten polymer. Numerous mathematical models for wetting[2–8] have been developed and various mechanisms postulated. The

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spreading of the sessile drop is also concerned with the dynamic contact angle at any time and ultimately with the equilibrium contact angle of the drop. Spreading is normally considered to be promoted by capillary or interfacial forces, acting at the periphery of the drop while being resisted by the viscous nature of the fluid itself. Schonhorn, Frisch and Kwei[2] have pointed out that if spreading is strictly a viscous phenomenon and normal scaling laws are applicable, then drop profiles similar to that shown in Figure 1(a) would be evident with a projecting foot preceding the bulk of the drop. However, they observed drop profiles without the projecting feet as shown in Figure 1(b). The possibility of the formation of a thin duplex film of melt extending beyond the normal drop periphery was considered but no evidence of the film was detected.

The majority of the data reported in the literature has indicated that drop profiles similar to Figure 1(b) are common. This result has given rise to a spherical segment approach in models of the kinetics of wetting and also to the importance of the three-phase interface in controlling wetting behavior.

Later work by Johnson and Dettre[9] showed that a projecting foot could occur for certain viscous systems and that the drop profile was most probably the dominant result of the interaction between interfacial forces and the

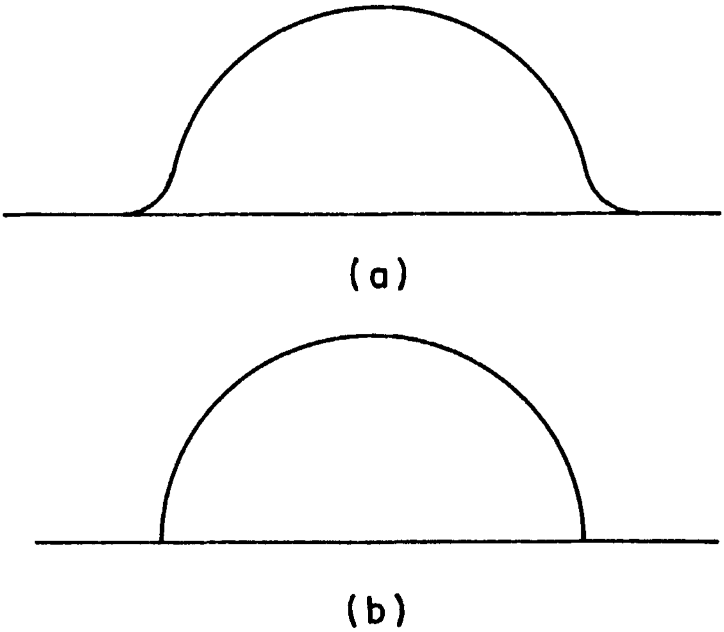

FIGURE 1 Profiles of spreading sessile drops (a) with projecting foot, (b) without projecting foot.

viscous nature of the fluid concerned. Arslanov[10] also observed that the drop profile was not that of a spherical segment for highly viscous polymer melts, but in his interpretation he used a "conical profile" to model the spreading drop. Previous work in this laboratory[11] indicated neither projecting feet, perfect spherical cap segments, nor conical shapes. No definite regular geometric shape could be assigned to the profile of the spreading drop.

EXPERIMENTAL

In the course of present studies of the wetting of plane soda-lime glass by viscous polystyrene melts of various molecular weights and molecular weight distributions over a wide temperature range two systems were observed to exhibit projecting feet. Polystyrenes of molecular weight $\bar{M}_n$ 104,000, $\bar{M}_w/\bar{M}_n$ 3.39 and of molecular weight $\bar{M}_n$ 132,000, $\bar{M}_w/\bar{M}_n$ 2.35 both exhibited projecting feet over a wide variety of temperatures. Other polystyrenes of lower molecular weight did not exhibit the projecting feet. The polystyrene of molecular weight 104,000 was prepared and purified in this laboratory while the polystyrene of molecular weight 132,000 was a commercial product (Monomer-Polymer Laboratories) and was initially used in an "as is" condition.

The apparatus used in this work as well as the substrate cleaning technique has been described earlier.[8] The polymer was heated to isothermal conditions prior to dropping to the preheated glass substrate. Temperature control of the system was $\pm 1°C$ to ensure that the melt and substrate were at thermal equilibrium prior to contact. In contrast, both Schonhorn,[2] and Johnson and Dettre[9] used solid polymer pellets which were brought to temperature in a thermostated environment and had to melt while flow was occurring.

The possibility of polystyrene degradation was considered, but after examination by gel permeation chromatography degradation was found to be negligible over the range of temperature and time studied (155–300°C; 5 hour total time-temperature history). A summary of all the polymers examined, the temperature range over which spreading was studied and the occurrence of projecting feet is shown in Table I.

Spreading profiles for PS 31,733 are shown in Figure 2 for comparison purposes. These can be contrasted to Figure 3 and Figure 4 which show the spreading profiles for PS 104,000 and PS 132,000 respectively. The projecting feet were most prominent for polystyrene of molecular weight 132,000.

The possibility that the projecting foot was a result of very low molecular weight species in the melt acting as the precursor of flow was considered, especially for PS 132,000 which was not prepared in this laboratory. This polymer was subsequently purified (dissolved in cyclohexane, precipitated in

TABLE I

Polystyrene melts studied

Polymer	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/M_n$	Temperature range, °C	Projecting feet
PS 10,000[a]	9,600			< 1.06	176–238	no
PS 20,400[a]	20,200			< 1.10	178–238	no
PS 37,000[a]	37,000			< 1.06	189–253	no
PS 110,000[a]	108,000			< 1.06	198–260	slight
PS 8,879[b]	8,900	24,500		2.76	155–241	no
PS 10,996[c]	11,000	25,600	56,000	2.33	176–238	no
PS 17,255[c]	17,300	32,200	53,200	1.86	177–251	no
PS 31,733[c]	31,700	86,600	173,000	2.73	190–252	no
PS 104,000[c]	104,000	353,000	1,250,000	3.39	202–276	yes
PS 132,000[b]	132,000	310,000	574,000	2.35	251–299	yes
†PS 69,000	69,300	171,000	348,000	2.47	260–287	yes
†PS 174,000	174,000	346,000	575,000	1.99	260–285	yes

† Polymer fraction obtained from PS 132,000.
[a] Pressure chemical.
[b] Monomer-Polymer Laboratories.
[c] Prepared in our laboratory.

hexane, and vacuum dried) and the two resulting fractions were subsequently examined. Both fractions exhibited projecting feet with the most prominent projecting foot occurring for the polystyrene of higher molecular weight, *i.e.* PS 174,000. Polystyrene of molecular weight 110,000, narrow molecular weight distribution, was also examined and only a very slight projecting foot was detected.

DISCUSSION

Johnson and Dettre's conclusion that bulk viscous forces offer significant resistance to spreading and that this imbalance of spreading forces leads to the formation of a projecting foot at the base of a drop must be modified somewhat in view of the present observations. The present study has shown that projecting feet do not occur for melts of low molecular weight even at low temperatures which would give rise to a high melt viscosity condition.

Similarly, projecting feet were observed for high molecular weight melts at all temperatures even when the melts at the higher temperatures would have resulted in relatively lower viscosities. Therefore, to consider polymer viscosity without considering polymer molecular weight or molecular weight distribution seems too simple.

The present study indicates that molecular weight and molecular weight distribution factors are important when considering the projecting feet. The data suggest that the "critical molecular weight of entanglement" may play a significant role in determining the rate of spreading and the subsequent drop profile. The critical molecular weight of entanglement for polystyrene has been estimated [12–14] at about 35–40,000. It was observed that, for polymers having molecular weights greater than the critical value and of broad molecular weight distribution, a projecting foot could be expected. The critical molecular

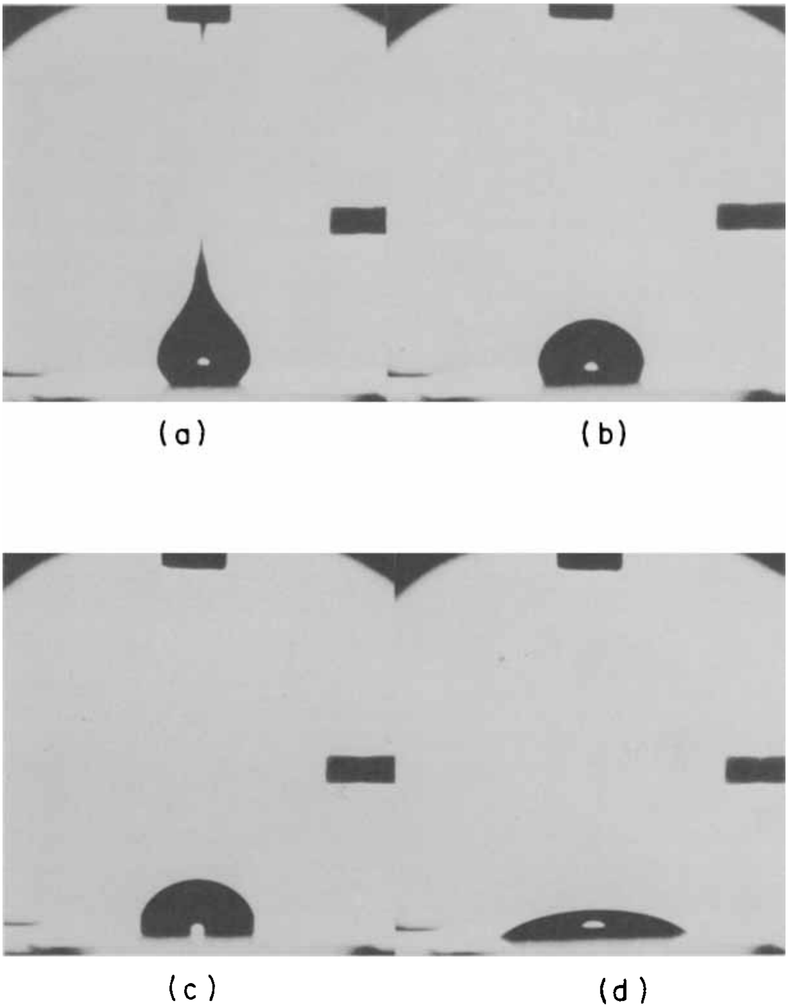

FIGURE 2 Spreading profile of PS 31733 at 203°C after (a) 131.51 s, (b) 98.20 s, (c) 57.50 s, and (d) 1664.53 s. For Figures 2, 3 and 4, the time is assigned a value of 0.00 s when the contact angle is 90°.

weight is thought to represent the molecular weight beyond which polymer entanglements became serious enough to contribute heavily to the viscosity. Single polymer molecules no longer diffuse separately, but drag along neighbors.

Closer examination of Figures 3 and 4 reveals that the projecting feet are most pronounced at the initial stages of wetting where strong solid–liquid interfacial interactions are inducing flow near the interface but the bulk response of the sessile drop retards the flow and shape redistribution

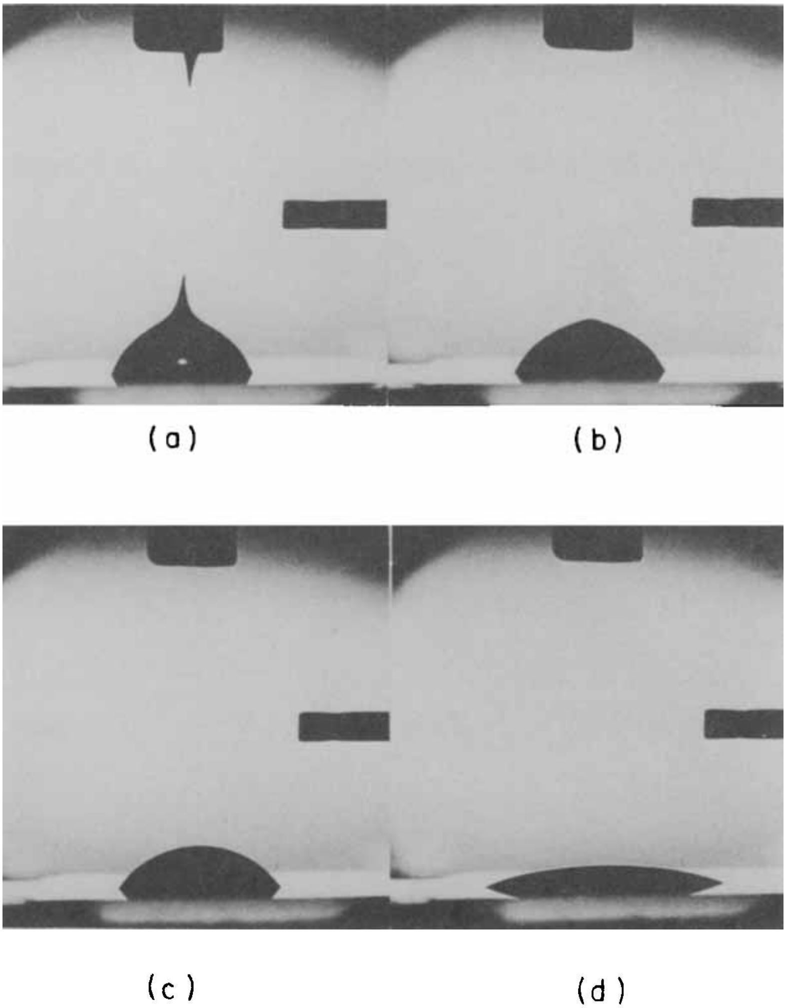

FIGURE 3 Spreading profile of PS 104,000 at 202.5°C after (a) 41.39 s, (b) 55.98 s, (c) 83.78 s, and (d) 1156.99 s.

phenomena. The leading edge of the polymer drop is believed to be spreading from the surface interactions but the bulk of the drop cannot respond as rapidly, and resists immediate rearrangement due to viscoelastic retardation. This mechanism results in the development of the projecting foot. In time, however, the viscoelastic nature of the drop responds and the bulk of the drop redistributes and "catches up" to the interface resulting in the normal, nearly spherical segment after a sufficient length of time.

In conclusion, the authors feel that the data and observations for molten

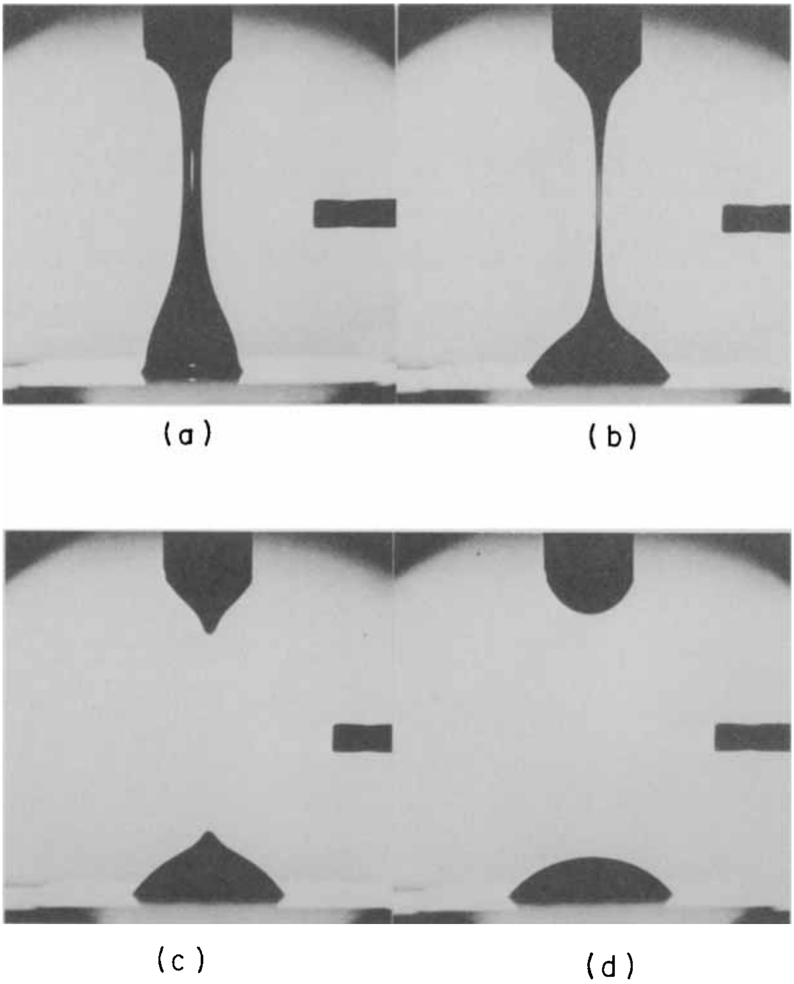

FIGURE 4 Spreading profile of PS 132,000 at 251°C after (a) 10.74 s, (b) 113.84 s, (c) 159.70 s, and (d) 273.97 s.

polymers reported in the literature fall into one of the categories of molecular weight which accounts for the occurrence or non-occurrence of the projecting feet. We believe that projecting feet may be observed under isothermal conditions only above the critical molecular weight of entanglement of the polymer.

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