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# THE MELT RHEOLOGY OF A-B BLOCK COPOLYMERS WITH SPHERICAL MICRODOMAINS

presented by

Ekong A. Ekong

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Ph.D. degree in Chemical Engineering

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# THE MELT RHEOLOGY OF A-B BLOCK COPOLYMERS WITH SPHERICAL MICRODOMAINS

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Ekong A. Ekong

### A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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### ABSTRACT

### THE MELT RHEOLOGY OF A-B BLOCK COPOLYMERS WITH SPHERICAL MICRODOMAINS

By

Ekong A. Ekong

A kinetic network model for polymeric melts that contain spherical microdomains is presented and compared with experimental results of poly(styrene-b-butadiene), ( $\bar{M}_n = 232,000-10,000$ , % wt PS = 94.1). A novel form for the segment distribution in the matrix with a constraint at the point of attachment to the domains is developed. Consistent expressions are developed for the rate of creation and destruction as a function of deformation in flows. A key parameter in this development is the degree of repulsion between segments in the interfacial region.

Transient and steady stresses are derived for uniaxial extensional flows and compared with an ABS melt data in the literature. At low Hencky strain rates (made dimensionless with a characteristic relaxation time) an apparent yield stress is predicted dependent on the range of repulsion parameter which correlates with the composition of the rubbery component.

Computations were done with this model also to obtain steady and transient stresses in uniaxial shear flows. These predictions were compared with melt rheology data gathered in this work over a temperature range of  $120^{\circ}$ C to  $175^{\circ}$ C. The shear viscosity data above  $150^{\circ}$ C indicate homopolymer-like behavior; the data at  $130^{\circ}$ C indicate the presence of a two-phase structure. The dynamic shear viscosity as well as the steady shear viscosity data show trends similar to those reported by Ghijsels and Raadsen (1980) with triblock copolymer melts at low strain rates. The observed stress growth curves show a stress overshoot at strain rates as low as 0.01 sec<sup>-1</sup> with a strain at peak stress of about 0.5. Estimation of parameters in the theory and the sensitivity of predicted stress behavior to different parameters is discussed. While the theory is able to predict observed low strain rate behavior in steady and dynamic testing, it does not predict an overshoot in stress growth curves at such low strain rates.

In the evergreen memory

of

Kokomma Bassey-Ubong Ekong

Archibong Akpan Udoh Ekong

and

Phillip Akpabio Ekong

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### NOMENCLATURE

$A(\underline{R},N)$	Helmoltz free energy
A <sub>ij</sub>	As defined in Equation (1.16)
ā	Adjustment constant (Acierno model)
ã	Constant (in Johnson and Segalman model)
a	The repulsion range parameter (in non-Gaussian) network model of this work
$\mathbb{B}_{\widetilde{\mathbb{R}}}(\texttt{t};,\texttt{t})$	Finger strain tensor for the deformation $t' \rightarrow t$ , the components are given by $B_{rc} = \Sigma(\partial x_r/\partial x_i)(\partial x_c/\partial x_j)$
	where $x_i^{\dagger}$ and $x_i^{\dagger}$ are rectangular cartesian coordinates
	of places occupied at times t' and t by a typical particle of the macroscopic continuum
b <sub>≋</sub> i	Configuration tensor (Giesekus, 1982)
С	Constant creation rate coefficient, $\sec^{-1}$
₽	The deformation rate tensor, $(\nabla \underline{V} + \nabla \underline{V}^{T})$
<u></u> [(t',t)	Strain measure (Johnson and Segalman)
f <sub>in</sub> (R,t)	Distribution function of an i-type strand with n links.
$f(\underset{\sim}{R},t)$	Distribution function of the "most probable" network segment
f <sub>e</sub> (o,N)	Segment distribution function at equilibrium
G(R,N)	Rate of creation function = $L_j$ (R,N)
G <sub>j</sub>	Modulus (Dynes/cm <sup>2</sup> ), Acierno model
Go	Modulus of rubber elasticity, n <sub>o</sub> kT
G <mark>O</mark>	Plateau modulus, dynes/cm <sup>2</sup>
G(t)	Relaxation modulus, dynes/cm <sup>2</sup>

Η(λ)	Material relaxation spectrum
H <sub>n</sub>	The effective Hookean spring constant
H <sub>n</sub> (R)	Non-linear spring modulus (Yamomoto theory)
h(I <sub>1</sub> ,I <sub>2</sub> )	Scaler damping function in (Wagner model) where $I_1$ and $I_2$ and first and second invariant of the finger strain tensor
h <sub>kl</sub> (Γ,τ')	Factorized memory damping function of the N G
h <sub>kl</sub> (γ,τ')	Newwork model
I ≈	Identity matrix
<sup>I</sup> 1, <sup>I</sup> 2	Integral kernel's defined in Appendix A
i	Strand complexity index
i	√-I (in Chapter V)
J <sub>e</sub> <sup>o</sup>	Steady-state recoverable compliance
k	Boltzman's constant
К <sub>о</sub>	Normalized constant
F	Deformation gradient, $\nabla \underline{V}$
L*	Effective deformation gradient $\nabla V - \xi \underline{D}$
L <sub>in</sub> (Ŗ)	Creation rate of the ith strand withn links
Мо	Molecular weight of the primitive chain (DE theory)
₩ ₩	Weight average molecular weight
<sup>M</sup> n	Number average molecular weight
m(t',t)	Memory function (Lodge's Network Theory)
N	Number of subunits in the "most probable" network segment with statistical length, 1
Ñ	Number of beads in Kramer's chain
N j	Total concentration of j-segments at time t (Jongshaap)



Equilibrium value of N <sub>j</sub>
Steady and transient first normal stress difference
Number of equivalent random links (Gaussian network model)
Initial concentration of network segments, C/ $\beta_{\rm o}$
Extra stress tensor = $\underline{S}$
Ensemble averaged end-to-end vector for a typical network segment
Velocity of the network segment
End-to-end vector of macromolecule at equilibrium
End-to-end vector of an active network segment (defined in Chapter III)
r/N1, where N1 is the extended length of the segment
Radius of cone-and-plate platens
Radius of inner cylinder (Mooney bob)
Radius of outer cylinder (Mooney cup)
Extra stress tensor = $P(t)$
Tangential transient shear stress during shear growth
Steady state tangential shear stress
Relaxation stress after the cessation of shear
Structural parameter (Acierno model)
Macroscopic material coordinate (Cartesian)
Temperature
Transformation matrix equation (6.2)
Present time

u	= sin ωt
V(x,t)	Polymer velocity at the position vector $\underline{x}$ and time t
x,y,z	Cartesian components of the dimensionless end-to-end segment vector, $\underset{\sim}{R}$
Z(R,N) ~	Configuration partition function
Greek Symbols	5

β( <b>R,N)</b>	Destruction coefficient of the most probable network segment
β <sub>o</sub>	Destruction rate constant, $\sec^{-1}(=1/\lambda_{o})$
β <sub>c</sub>	Chain constraint exponent
Υ <sub>o</sub>	Oscillatory strain amplitude
Ŷ	Magnitude of shear rate
Ý ≋	Rate of strain tensor
Ŷ	Dimensionless shear rate $\gamma$ $\beta_{_{O}}$
Г	Magnitude of strain rate
Γ	Dimensionless strain rate = $\hat{\Gamma}/\beta_{o}$
ε	Destruction rate constant (N $\cdot$ G $\cdot$ Model)
€ <sub>B</sub>	Link bension coefficient
ζ, ζ	Drag and tensorial drag coefficient
η	Steady shear viscosity, Poise
n <sub>E</sub> *	Non-dimensional elongational viscosity
η <mark>*+</mark> Ε	Non-dimensional transient elongational viscosity
η <sub>o</sub>	Zero shear viscosity, poise
n*	Complex viscosity
ñ	Normalized steady shear viscosity, $S_{xy/n_O} k T \tilde{\check{Y}}$

ῆ <b>',</b> ῆ''	Dimensionless dynamic and loss viscosities respectively
ñ*	Dimensionless complex viscosity
θ	Gap angle
λ <sub>o</sub>	Characteristic relaxation time
$\lambda_{in}$	Destruction coefficient of the ith strand with n links
$\lambda_j^0$	Destruction coefficient due to thermal motion (Wagner Model)
ξ	Slip coefficient (Phan-Thien and Tanner)
ξ <sub>i</sub>	Microscopic cartesian coordinates (Johnson and Segalman)
<u>ρ</u> (ρ,η,z)	Transformed coordinate frame where $\mathbf{R} = \mathbf{T}_{\underline{x}} \cdot \mathbf{p}_{\underline{x}}$
τ	Dimensionless present time, $\beta_0 t$
τ'	Dimensionless elapsed time $\beta_0(t-t')$
T	Torque generated in the shearing gap
τ <sub>d</sub> (t',t)	Loss coefficient associated with the survivability of strand at the elapsed time of deformation
τj	Relaxation time of the Acierno model
φ	Phase shift
ψ1, 0	Zero shear first normal stress difference. Dynes/cm <sup>2</sup>
ω	Frequency of oscillation
ũ	Normalized frequency of oscillation
<del>)</del> <b>i</b> t	Partial time derivative
<u>δ()</u> δt	Contravariant time derivative $\equiv \frac{d}{dt}() - \nabla \underline{V} \cdot () - ()$
	• ⊽ <u>V</u> '



### CHAPTER I

#### INTRODUCTION

#### 1.1 Material Background

In recent years there has been an increasing attention to formulation of composite polymeric materials which combine desirable properties of their components. However, it is often difficult to blend polymers because of the incompatibility of polymeric chains of different polymeric molecular structure. This problem has been overcome by sequentially polymerizing different constituents to obtain block or graft copolymers. Since its first theoretical conception by Mark (1953), and its first commercial production by Shell in 1965 (Holden et al., 1969), the possible practical applications of block copolymers have been many and varied. Block copolymers such as poly (styrene-butadiene-styrene), SBS undergo a phase separation consisting of the thermoplastic polystyrene block linked by its ends to an elastomeric butadiene block to generate a polymeric network structure in which the endblocks serve as physical reversible multifunctional crosslink sites.

These systems, without vulcanization have rubber-like properties akin to rubber vulcanizates, but are moldable at temperatures above the glass transition of the thermoplastic component (Van Breen and Vlig, 1966; Bishop and Davison, 1969). High resilience, high

1



tensile strength, highly reversible elongation and abrasion resistance may be obtained in triblock copolymer solids with careful choice of monomers and block length. Diblock copolymers are finding increasing use as a ternary component to mix highly incompatible homopolymers of low molecular weight, by emulsification (Ramos and Cohen, 1977). They may be used also for recovery and reuse of polymeric waste products such as polyolefin mixtures.

Styrene block polymers can be manufactured by anionic polymerization reaction. Styrene-butadiene, SB, diblock, Styrenebutadiene-styrene, SBS and butadiene-styrene-butadiene, BSB, triblocks are produced by the reaction of styrene molecules in the presence of a lithium catalyst to form polystyrene-lithium complex which disintegrates on further addition of the component butadiene to form a diblock of S-B or a triblock S-B-S if more styrene is added into the mixture. Phase separation occurs between the blocks leading to the formation of microdomains that are responsible for the specific properties of the block copolymer. As illustrated by Matsuo et al. (1968), (see Figure 1.1) with SBS samples, the molecular weights of the different blocks determines the overall morphology of this polymeric system. Uniform spherical domains are formed when the low M.W. component is 20 wt% or less. As the amount of this component increases, the spheres do not grow in diameter beyond a certain size, but instead, are transformed to uniform cylinders. At a still higher fraction of elastomer, the cylinders become platelets, while at midrange compositions (40-60 wt%) of each component, the material

2



Figure 1.1.--Variation of block copolymer morphology with composition (a) SBS-1 (20%B); (b,c) SBS-3 (40%B); (d,e) SBS-5 (60%B). Polymers cast from toluene solution, and stained with 0S04, so that the polybutadiene phase is black and the polystyrene phase is white (Matsuo et al., 1968.



consists of alternate lamallar of styrene and butadiene. As the percentage of elastomer is increased still further (not shown in the figure), the phase structure goes through the same changes in reverse --with the elastomer now constituting the continuous phase.

Theories based on statistical thermodynamics of microphase separation have been proposed to predict the effect of molecular parameters such as block length and thickness of interphase between the blocks, on copolymer structure; these have been reviewed by Folkes and Keller (1973). The present study deals with the mobility of segments in block copolymer melts. To data no rheological theories have been advanced to predict highly non-linear behavior observed in block copolymer melts. Such studies are essential in establishing processing conditions for these materials.

A number of rheological characterization studies have been done on block copolymeric systems (Arnold and Meier, 1970; Kraus and Gruver, 1967; Holden et al., 1969; Chung and Gale, 1976; and Ghijels and Raadsen, 1980). The major results of these works are: (1) block copolymer melts, especially triblocks with glassy domains, show an apparent yield stress at shear rates,  $\dot{\gamma} << 1$ ; (2) at low shear rates or stresses, the viscosity of block copolymers is greater than that of either homopolymer; (3) the Cox-Merz rule does not hold, in general, for block, copolymer melts. In general, it is observed that the complex viscosity,  $|n^*|$  is higher than the steady shear viscosity at  $\omega = \dot{\gamma}$ ; (4) at large deformation rates, the dynamic shear moduli, steady shear viscosity, and first normal stress difference

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values approach those of their homopolymeric counterparts with comparable overall  $\bar{M}_n$ . This complex rheological behavior is mainly attributed to the persistence of the two-phase structure of block copolymers into the melt state.

In this study we seek to extend the transient network theory framework described in the following section, to block copolymers by regarding regions of the dispersed phase as temporary junction sites that impart a three-dimensional structure to block copolymers. This allows us to develop a constitutive equation for viscoelastic flow properties of block copolymers. Despite an inherent weakness of failing to use all available structural information obtainable from non-rheological techniques of characterization (e.g., MW and MWD), network theories are useful phenomenological models taking into account the evolution of the microstructure. It is in describing this evolution of microstructure that most of the available network models differ; we proceed to discuss the description of microstructure.

#### 1.2 Evolution of the Microstructure

#### 1.1.1 Gaussian Network Theory

Following the theoretical formulation of constant connectivity of network models for elastomeric materials by Green and Tobolsky (1946), Lodge (1954, 1956, 1968) and Yamamoto (1956, 1957, 1958) extended the network theory to include polymer melts and concentrated solutions visualizing them as a temporary network formed by transient junctions or entanglements. All the Gaussian network theories stem from the following two equations.

Stress Tensor:

$$\underline{P}(t) = \Sigma_n H_n \Sigma_i \langle \underline{R}\underline{R} \rangle_{in}$$
(1.1)

Strand distribution function f<sub>in</sub>:

$$\frac{\partial f_{\text{in}}}{\partial t} = -\nabla \cdot (\dot{R}_{\text{in}} f_{\text{in}}) + L_{\text{in}} (R,t) - f_{\text{in}} / \lambda_{\text{in}}(t)$$
(1.2)

The distribution function,  $f_{in}(\tilde{R},t)$  is defined such that  $f_{in}(\tilde{R},t) d\tilde{R}$ if the concentration at time t of strands of complexity i and composed of n equivalent random links (of length 1) with ensembleaveraged end-to-end vectors with the range  $\underline{R}$  to  $\underline{R}$  + d $\underline{R}$ . The term  $H_n = 3KT/nl^2$  is the effective Hookean spring constant of an n-link strand, such that  $H_n R$  can be interpreted as a force on the strand. The terms  $L_{in}$  are the strand creation rates and  $f_i/\lambda_{in}$  denote strand destruction rates, with a strand destruction coefficient given as  $\lambda_{in}^{-1}$ . Angular brackets indicate an average value calculated with respect to f<sub>in</sub>. The success of rheological constitutive equations have been mainly based on how well the terms  $\dot{R}$ ,  $L_{in}$  and  $1/\lambda_{in}$  approximate the true microstructure dynamics occurring in the polymeric medium. The original ideas on how these terms may be modelled were laid down by Lodge (1954), in deriving the Lodge rubber-like model. In this review it will be useful to state them, in general, and focus on how several researchers have modified these assumptions to achieve useful constitutive equations.



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Assumption 1: Ensemble-average positions of junctions move affinely and can be identified with particles of the equivalent macroscopic continuum. In particular, if the melt is given a time-dependent homogeneous deformation, we have

$$\dot{R} = R \cdot \nabla V$$
(1.3)

where  $\mathbb{R}$  denotes an ensemble-average strand end-to-end vector, and V(x,t) denotes the polymer velocity at the place of the position vector <u>x</u> and time, t. The superior dot denotes a time derivative.

- <u>Assumption 2</u>: At any instant t, the set of network strands in a unit volume may be regarded as mutually exclusive, mutually independent subsets. The probability per unit time that any strand shall leave the network is a function  $1/\lambda_{in}(t)$  say at t, i, and n.
- <u>Assumption 3</u>: (i,n) strands are created with spherically symmetric distribution of R vectors, i.e., at a rate which can be expressed as  $\tilde{a}$  function  $L_{in}(R,t)$  of i, n,t and the magnitude R alone. Furthermore, at the instant of creation, all (in,) strands have the same distribution as that of a set of free n-Gaussian strands.

Using equations (1.1) to (1.3), the constant volume condition  $(\nabla \cdot \underline{V} = 0)$  and  $L_{in}(\underline{R})$  expression based on the Gaussian chain assumption, a general constitutive equation may be written of the form:

$$P(t) = \int_{-\infty}^{t} m(t,t') B(t,t') dt'$$
(1.4)

where the memory function m(t,t') is given by

$$m(t,t') = kT_{\Sigma\Sigma}\hat{L}_{in}(t') exp(-\int_{t'}^{t} dt'' |\lambda_{in}(t''))$$
(1.5)

and


$$\hat{L}_{in}^{(t)} = \frac{4\pi}{3} \int_{0}^{\infty} R^{4} L_{in}(R,t) dR$$

Here B(t,t') is the Finger strain tensor for the kinematic deformation from past time t' to the present time t.

If all the creation and loss rates are constant, i.e., all strands have the same complexity, Lodge's "rubberlike liquid model" results. This model predicts a frequency dependent dynamic shear moduli, but fails to show the dependence of steady shear viscosity on the shear rate or a non-zero second normal stress difference.

In order to correct these imperfections, several workers, as will be shown in this section, have proposed empirically different choices of the creation and loss rates, but leave intact the assumption that the microstructure flows affinely.

If creation and loss rates are functions of instantaneous values of <u>strain rate</u> invariants, various equations including those of Meister (1971) and Careau (1972) are obtained. If the creation and loss rates are functions of the instantaneous values of <u>stress</u> invariants, we obtain the equation of Kaye (1966). These and other related equations have been tabulated elsewhere in a common notation (Lodge, 1974). Most of these equations, usually characterized by many adjustable parameters, predict steady shear viscosity dependency on the shear rate and show a second normal stress difference. However, they fail to reduce to the appropriate constitutive equation of linear viscoelasticity at low deformation rates. The next integral constitutive equations are the straindependent (K-BKZ type) equations in which the memory function includes a scalar function of strain depending on the elapsed time,  $t' \rightarrow t$  as a factor. Recent step-strain data have given compelling evidence for such a "strain/time" factorization (at least in the terminal zone of the relaxation spectrum) (Osaki et al., 1971; Laun, 1978). Out of this class of equations is the Wagner model (Wagner, 1979a; Wagner and Stephenson, 1979b) with a memory function of the form

$$m(t,t') = Kt_{\Sigma}L_{j}h(I_{1}(t',t), I_{2}(t',t))exp(t'-t)/\lambda_{j}$$
(1.6)

where  $\Sigma$  is written as an abbreviation for  $\Sigma\Sigma.$  j

In this model, assumption (2) is replaced by two independent mechanisms for strand loss, one due to thermal motion with constant loss probabilities  $1/\lambda_j^0$  and the other the survivability of strand at the elasped time of deformation denoted by  $1/\tau_d(t',t)$ .

Since thermal motions determine  $\lambda_j$  and not  $\tau_d(t',t)$ , then  $\lambda_j^0$  and  $\hat{L}_j$  would depend on the microstructure of the material, but the  $\tau_d$  would be structure independent. The loss process is thus given by

$$\frac{1}{\lambda_{j}}(t',t) = \frac{1}{\lambda_{0}} + \frac{1}{\tau_{d}}(t',t)$$
(1.7)

Equation (1.6) is obtained by combining equation (1.7) and (1.5) and by taking



$$h(I_1, I_2) = \exp \int_{t}^{t'} \frac{dt''}{\tau_d(t'', t)}$$
(1.8)

The damping function h is chosen empirically to fit stress relaxation data for single-step strain experiments and stress growth data in step-function elongation rate experiments. The resulting h-expression with two adjustable parameters gave a good description of data from a variety of experiments in shear and elongation. A functional of the h-factor was further proposed by Wagner and Stephenson in order to better predict recovery following elongation at constant rates.

One major drawback as to the use of two times in  $\lambda(t',t)$  in the Wagner model is that it is not in general possible to find an equivalent differential form for the constitutive equation. For some applications, it appears helpful to have a differential equation for the stress tensor.

A fairly successful constitutive equation for polymer melts and concentrated polymer solutions proposed by Acierno et al. (1976) expressed the creation and loss processes as functions of structural variables that describe how far the microstructure deviated from equilibrium. This structural variable is governed by an independent kinetic equation of the form

$${}^{\tau}j \frac{dx_{j}}{dt} = 1 - \bar{x}_{j} - \bar{a}\bar{x}_{j}(trP_{=j}/2\bar{G}_{j})^{\frac{1}{2}}$$
(1.9)

where  $P'_{=j}$  is the non-equilibrium part of the jth contribution to the extra stress tensor, <u>P</u> given by



$$\underline{P}_{j}^{t} = \underline{P}_{j} - \int_{-\infty}^{t} m_{j}(t,t') dt' I_{\approx}$$
(1.10)

 $\underline{P}_{j}$  is computed from a Maxwellian-type constitutive equation  $\underline{P} = \Sigma \underline{P}_{j}$ 

$$P_{=j}/\bar{G}_{j} + \tau_{j} \frac{\delta}{\delta t} \left(\frac{P_{=j}}{G_{j}}\right) = 2\tau_{j_{\approx}^{\star}}$$
(1.11)

Interconnection between this model and the fundamental balance law was made clear by Jongschaap (1981) who noted that the segment loss probability function  $1/\lambda_{j}$  in this network model is given by

$$\frac{1}{\lambda_{j}} = \frac{1}{\tau_{j}} (\bar{a} \sqrt{\frac{\text{tr}_{j}^{p}}{2G_{j}}} - \frac{1}{\bar{x}_{j}} + 2)$$
(1.12)

Both sides of Equation (1.12) are multiplied by  $x_j$ . The result is combined with Equation (1.9),  $\bar{x}_j$  is replaced by  $N_j/N_{jo}$  and the result multiplied by  $N_{jo}$  to obtain

$$\frac{dN_{j}}{dt} = \frac{N_{j}}{\tau_{j}} - \frac{N_{j}}{\lambda_{j}}$$
(1.13)

Here  $N_j = \int f_j(R,t) d^3R$  is the total concentration of j- segments at time t, and  $N_{j0}$  is the equilibrium value of  $N_j$ . If in Equation (1.13)  $N_j/\tau_j$  is identified with the creation rate  $\tilde{L}_j(t) = \int L_j(\tilde{R},t) d^3\tilde{R}$ , then



$$\frac{dN_{j}}{dt} = \tilde{L}_{j} - \frac{N_{j}}{\lambda_{j}}$$
(1.14)

which is the integral of Equation (1.2) over all configuration space. Thus the differential equations for the structural variable of Acierno et al. are directly related to the fundamental balance law of the Network theory. The Acierno model is seen to allow for the segment creation and loss rates to depend on the deformation through the trace of the non-equilibrium part of the stress tensor. In the context of the Network theory, it is not evident why the particular form of the destruction process was chosen and why it is successful.

### 1.2.2 Non-Affine Motion Assumption

The Network model of Phan-Thien and Tanner (1977) and Phan-Thien (1978) also allow the function creation and loss rates to depend on  $\operatorname{tr}_{\mathbb{Z}_j}'$ , but in a more logical manner. More importantly, the Thien and Tanner model altered affine motion assumption of Network theory (see Assumption 1) allowing the network junction to "slip" with respect to an equivalent continuum specified by the macroscopic velocity gradient  $\nabla Y$ . In so doing, Phan Thien and Tanner introduced an empirical "slip tensor" to describe non-affine motion of the network functions and postulated it to be a linear function of the rate of deformation tensor  $\mathbb{Q} \equiv \frac{1}{2} (\nabla Y + \nabla V^{\mathsf{T}})$ . Consequently, Equation (1.3) is reformulated as

 $\dot{R} = (\nabla \underline{V} - \xi \underline{D}) \cdot \underline{R}$ (1.15)



in which the parameter  $\xi$  is the slip coefficient.

At the same time, Johnson and Segalman (1977) developed a continuum theory of viscoelasticity which allows non-affine deformation. Two deformation histories were defined. One was the deformation history  $\underline{\alpha}(t)$  observed at macroscopic level; the other,  $\underline{\beta}(t)$ , a history of microstructure deformation was allowed to be non-affine with the macroscopic motion. A relationship between these two motions,  $x_i$  and  $\overline{\xi}_i$  at the present time t, in Cartesian coordinates was given by

$$A_{ij} = \partial \bar{\xi}_{i} / \partial \bar{\xi}_{j} = (\frac{\tilde{a}+1}{2}) \dot{x}_{i,j} + (\frac{\tilde{a}-1}{2}) \dot{x}_{j,i}$$
(1.16)

where  $\tilde{a}$  is a constant. They then defined a strain measure  $\mathop{\mathbb{E}}_{\approx}(\texttt{t,t'})$  governed by

$$\frac{\partial E}{\partial t}(t,t') = \bigwedge_{\infty}^{A}(t) \mathop{\mathbb{E}}_{\infty}^{E}(t,t')$$

$$\underbrace{\mathbb{E}}_{\infty}^{E}(t',t') = \underbrace{\mathbb{E}}_{\infty}^{E}$$
(1.17)

and substituted this measure of strain into the Lodge network expression to obtain

$$\mathbb{P}(t') = \int_{-\infty}^{t} m(t,t') \mathbb{E}(t,t') \mathbb{E}(t,t')^{\mathsf{T}} dt' \qquad (1.18)$$

As with the Thien and Tanner model, the Johnson and Segalman model predicts a variety of non-linear rheological behavior well, particularly, the viscosity is found to decrease with the shear rate. The



Phan Thien and Tanner model contains two dimensionless constants  $\varepsilon$ and  $\xi$  that are determined through elongational flow and viscometric flow experiments respectively. For shear flows, Phan Thien showed that the Thien and Tanner model was identical to Johnson and Segalman's if  $\xi = 1-\tilde{a}$ .

The choice of the range of " $\tilde{a}$  (0 <  $\tilde{a}$  < 1) as reported by the authors through comparison with experiment was not easily perceived until the work of Lau and Schowalter (1980). They explained the fundamental basis of both models by pointing out that these were objective constitutive equations that can be formulated with a strain measure derived from appropriate linear combinations of the rate of change of material coordinates in the material fixed (corotational) reference and the space-fixed reference (code formational) frames. They chose a strain measure related to the combination  $\phi$  expressed in component form as

$$\phi_{ij} = (1 - \frac{c}{2}) V_{i,j} - \frac{c}{2} V_{j,i}$$

Then a strain tensor  $\tilde{\underline{\underline{E}}}(\underline{x}, t, t')$  was defined by

$$\frac{d}{dt} \tilde{\underline{E}} (\underline{x}, t, t') = \Phi(\underline{x}, t) \underline{E}(\underline{x}, t, t')$$

and 
$$\underline{\underline{E}}(x,t',t') = \underline{\underline{I}}$$

If  $c = (1 - \tilde{a})$ , the Johnson and Segalman model is obtained while the Thien and Tanner's model results when  $c = \xi$ . Such a rate of deformation measure can also be used to construct anisotropic fluid models



associated with dilute solutions (Gordon and Showalter, 1972). A weakness in both models is that they predict damped oscillations in shear stress at large deformation rates.

### 1.2.3 The Yamamoto Network Theory

Yamamoto (1956, 1957, 1959) presented a more fundamental network theory (cf. Lodge's theory) for concentrated polymer solutions and melts. The general form of the microstructure dynamics equation (Equation [1.2]) was originally proposed in the first of three papers in which the creation rate function and chain breakage coefficient are functions of the end-to-end distance and orientation of the segments in the flow field. Unlike Lodge's theory, the network is considered as non-Gaussian with the result that the free energy of the network segment is a function of the end-to-end distance. Thus Equation (1.1) can be written as

$$\underline{P} = \Sigma_{N} H_{N}(R) \underline{R} \underline{R} f(\underline{R}, t) d\underline{R}$$
(1.19)

It is to be noted that the spring modulus  $H_N(R)$  is allowed to depend on the deformation of the segment so that non-linear springs may be conceived. Yamamoto has shown that physically plausible assumptions about the segment creation rates and loss probabilities lead to viscosity that decrease with shear rate, a negative second normal stress coefficient, and an elongational viscosity that first increases with the elongational rate, goes through a maximum and then decreases at higher elongation rates. If the destruction coefficient is made



independent of the segment extension, the ensuing strain measure in steady elongational experiments is an exponential that increases with time in the orientation of the chains. At a critical rate of strain, the chains are elongated infinitely without breakage leading to an infinite elongational viscosity. Yamamoto then argued that in actual systems, the chains will break down at finite elongations and the destruction coefficient should be a function of the segmental extension. In this lies the germ of ideas behind recent network models which avoid an infinite elongational viscosity by assuming deformation dependent destruction coefficients.

Further studies on the Yamamoto theory, especially the non-Gaussian aspect, have been minimal with regard to modelling viscoelastic fluids. Generally, the theory does not give constitutive equations in an explicit form devoid of summations and integrations over molecular variables. However, non-Gaussian network models are receiving increasing attention in the study of rubber elasticity (Chompff, 1977). Recently, Fuller and Leal (1981) have evaluated a form of non-Gaussian distribution function obtained by a Kuth and Grühn type perturbation of the Gaussian distribution function. They reported no trend in their results different from those of a Gaussian network model. In the present work, a non-Gaussian distribution function will be presented that yields strikingly different predictions.

The Yamamoto network theory offers clearly a direction in formulating viscoelastic models of various polymeric systems if an accurate description of its segment distribution function is found.



In the Lodgean theory one has no choice but to assume that the Gaussian distribution of the chains prevails. This has been successful for homopolymeric melts especially at small deformation rates, confirming the theory that homopolymeric entanglements are a result of weak secondary forces between primary chains, and occupy a length scale of the order of a statistical subunit. This distribution does not represent the microphase structure that determines copolymer melt properties at small deformations.

### 1.2.4 The Reptation Theory

Failure to incorporate molecular variables into the network theory still stands out as one of the major weaknesses of the several versions of the model posed above. Recently, the entanglement concept has been viewed in quite a different light by Doi and Edwards (1978a, 1978b, 1978c). The idea that entangled chains rearrange their conformations by reptation, i.e., curvilinear diffusion along their own contours was first introduced by DeGennes (1971). Doi and Edwards have formulated a theory (DE), relating the dynamics of reptating chains to mechanical properties in concentrated polymer liquids. They assumed that reptation would be the dominant motion in a medium of linear long chains. Employing equations from the theory of rubber elasticity, they calculated the contribution of individual chains to the stress following a step strain and related the subsequent relaxation of stress to conformational rearrangement via reptation (1978b). Without further assumptions, notably the "independent alignment approximation." IAA, they arrived at a

constitutive equation of the BKZ type good for aribtrary deformation histories. In particular, they showed that for monodisperse entangled linear chain polymer liquids, the plateau modulus, zero-shear viscosity and steady state recoverable compliance were functions of chain properties as

$$n_{0} \propto M^{03}$$

$$J_{e}^{0} \propto M^{0}$$
(1.20)

 $G_{n}^{0} \alpha M^{0}$ 

where M<sup>O</sup> is the molecular weight of the primitive chain. These relations agree fairly well with observed data (Graessley, 1980). The only parameters present in this theory are the reptation tube diameter "a" and a monemeric friction coefficient. Due to the constraining nature of domains in the block copolymer systems, it is not very evident how the reptation theory can be applied to block copolymer rheology.



## CHAPTER II

### BLOCK COPOLYMER MELT PROPERTIES AND THEORIES

# 2.1 Previous Rheological Studies

In this chapter we wish to examine in detail data collected on the melt rehological properties of block copolymers and rubber modified polymers to identify molecular variables affecting their behavior.

	Percent S	Viscosity¢
PolymerD		
80B	0	3.2
6S-81B-6S	13	13
10S-53B-10S	27.5	29
16S-52B-16S	39	118
19S-31B-19S	53	36.5
24S-25B-24S	65	31
33S-18B-33S	80	28
835	100	5.5

TABLE 2.1.--Viscosity of block copolymers<sup>a</sup> vs. homopolymers

 $^{\rm a}{\rm Note}$  that at 175°C a lot of the domains have been destroyed (Chung and Gale, 1976).

<sup>D</sup>Molecular weights of blocks in thousands

<sup>C</sup>At shear stress of 2 x  $10^5$  dynes/cm<sup>2</sup> and a temperature of 175°C (Holden et al., 1969).



Table 2.1 summarizes the steady shear melt viscosity data at a constant stree, reported by Holden et al. for several different samples of S-B-S triblock copolymer as well as the homopolymers, polystyrene, and polybutadiene with the same order of overall molecular weight. It is readily seen that the styrene content affects the melt viscosities of the triblocks. On the other hand, it has been shown by Matsuo that the M.W. of the individual blocks affects the morphology of the block copolymer system. Holden explained the large viscosities exhibited by the block copolymers as due to the two phase structure persisting into the melt. Looking at Figure 1.1 we note that randomly distributed cylinders of polystyrene domains in a polybutadiene matrix is the morphological structure of SBS with 39%S content which has an anamolously large viscosity. Again cylindrical domains of polybutadiene is the projected morphology for the SBS with 65%S content, but has a lower viscosity. It can, therefore, be concluded using Holden's data that viscosity of block copolymer melts is strongly dependent on the morphology of the respective blocks, block length (M.W.) of the thermoplastic block and chemical nature of the center block.

Arnold and Meier (1970) presented the dynamic viscoelastic data for various samples of SBS melts at low frequencies as shown in Table 2.2. We note that the 22-50 sample has an S content of about 35% by weight while the 14-50 sample has about 31%S. They deduced that the difference of the slope d log  $n'/d \log \omega$  between the two samples was due to the presence of semicontinous domain phase



SBS Sample	Nominal block mol. wt. <sup>a</sup>	Slope of log η' vs log ω
10-50	10-50-10	-0.36
14-50	14-50-14	-0.40
22-50	22-50-22	-0.66
14-60	14-60-14	-0.36
14-70	14-70-14	-0.36
MDPS/97 <sup>b</sup>	97	0

TABLE 2.2.--SBS Samples

<sup>a</sup>In thousands

<sup>b</sup>Monodispersed polystyrene, M.W. = 97,000

of polystyrene in the former sample as opposed to "dispersed polystyrene domains" in the latter case. They further proposed a qualitative rheological theory for block copolymers system, stating that at very low deformation rates, the molecular network is essentially intact. At intermediate deformation rates, the three-dimensional network will be disrupted and the system behaves as large starshaped aggregates. Finally, at high deformation rates, these aggregates will, in turn, be disrupted and the system will behave as an assemblage of individual non-aggregated molecules.

While Arnold and Meier's dynamic data agree fairly with those of Holden et al., it is to be noted that method of sample preparation used in their study, crumbs may have affected the results. Ghijsels and Raadsen have found that the use of crumbs leads to less reproducible results, especially at low deformation rates than the use of compression moulded samples.



They also observed that  $|\eta^*(\omega)| > \eta(\dot{\gamma})|_{\dot{\gamma}=\omega}$  for all these block copolymers the disparity being greater for block copolymers terminating in polystyrene. They attributed these to the disruption of the domain network structure which must occur in steady flow, but not necessarily in small amplitude oscillations. A further explanation of the phenomenon observed above is that the presence of domains in block copolymers disallows some conformation, which would have deen available to chains through entanglement slippage. This, then, tends to increase the elastic free energy of the chains as well as the resulting modulus.

The two phase structure can also be manifested in block copolymer solutions depending on the choice of the solvent (Kotaka and White, 1973). When a good solvent for both components is used, triblock and diblock copolymers solutions behave as homopolymeric solutions. When a poor solvent for one component is used, e.g., SBS or SB in decane, a two-phase structure of insoluble PS in a solution of PB in decane results. The observed rheological behavior is, however, different for triblock and diblock copolymers. In SBS, the PB component dissolved is connected at both ends to the insoluble PS component thus creating a three-dimensional network structure even at a low concentration of the copolymer. In the diblock, there is no formation of a three-dimensional network, but rather a micelle structure in which the PS segments form a rigid core. Upon increasing the polymer concentration, the number of such micelles increases and eventually they would be arranged in a regular three-dimensional



array. The morphology of such mesormophic structures have been revealed by electron microscopy studies of Gallot (1978). From Kotaka and White's findings, these mesomorphic structures can be classified as elastic gels that can undergo a complete breakdown in structure by continuous shearing.

Another strong influence on viscoelastic properties of block copolymers is the interphase region existing at domain boundaries containing segments of both blocks. Statistical thermodynamic theories of Meier (1974) and Leary and Williams (1973) indicate that the volume fraction occupied by the interphase and, therefore, the degree of compatibility increase with decreasing molecular weight. With increasing temperature, a continuous increase in miscibility would also be anticipated involving growth of the interphase at the expense of the two pure phases, subsequent complete disappearance of the domain phase and then the continuous phase and, ultimately, complete homogeneity. Such predictions have been confirmed experimentally by Chung and Gale (1976) through rheological studies. Using moderate M.W. samples of SBS with spherical polystyrene domains, they noted that at high temperatures, the melt experiences a transition from a multiphase structure to a homogeneous structure. The flow behavior above this temperature is characterized by a Newtonian viscosity at low deformation rates and by low elasticity. Such behavior has been observed also by Kraus (even with high M.W. diblocks and Holden et al. using triblocks).

Kraus and Rollman (1976) have predicted the volume fraction of the mixed interlayer for various M.W. triblock copolymer samples,



using the theory of Meier. They then correlated dynamical mechanical moduli as a function of temperature with the results of Meier. The composition,  $\phi$  of the domain phase segments changes continuously from zero to unity within the range of the interlayer. It was assumed by Meier that the volume fraction of domain phase segments follows a symmetric profile over the interlayer, thus fixing an average composition of the interlayer by domain phase segments at 0.5. This enables one to compute the normalized volume distribution function,  $\overline{V}(\phi)$  of domain phase content in the interlayer. The planar complex moduli,  $E_E^{\star}$  of the composite for lamellar morphology was obtained by applying the principle of volume additivity as:

$$E_{E}^{\star}(t) = v_{B} E_{B}^{\star}(T) + v_{S} E_{S}^{\star}(T) + v_{IL} \int_{0}^{1} E_{B}^{\star}(T') \overline{V}(\phi) d\phi \qquad (2.1)$$

where  $v_B$ ,  $v_s$  and  $v_{IL}$  are the volume fractions of pure PB, pure PS, and mixed interlayer respectively;  $E_B^*$ ,  $E_s^*$  are the complex moduli for pure PB and pure PS respectively. Kraus and Rollman, on the other hand, assumed the mole fraction of domain phase segments follows a symmetric profile over the interlayer. They were able to correlate the dynamical mechanical moduli better. Both of these arguments have no factual basis and were formulated for the sake of mathematical convenience. Thus a complete understanding of block copolymer mechanical and rheological behavior will be dependent on the development of a statistical thermodynamic theory for the precise mathematical form of the interlayer composition profile.

Gouinlock and Porter (1977) working with SBS samples identical with that of Chung and Gale generated master curves of linear viscoelastic functions using the frequency-temperature superposition principle as shown in Figure 2.1. Each curve (reduced dynamic viscosity,  $\eta_p^{\prime}$  and reduced dynamic storage modulus,  $\textbf{G}_p^{\phantom{\prime}})$  has two branches at certain reduced critical frequencies. The low temperature data fall on the upper branches and signify the prevalence of the two phase structure. The high temperature results occur on the lower branch suggesting a homogeneous structure. It is further observed that the critical reduced frequency where branching occurs in  $G'_{\rm D}$  data are larger than the critical frequency for  $\eta_p^{\prime}$ . It is to be noted, therefore, that modification of the elastic property by domain structure is considerably more pronounced than the effect on dynamic viscosity. Moreover, experiments indicate in contrast to the deformation theory of Meier presented earlier, that domain disruption increases with decreasing frequency. In light of this, the extraction of segments from the domains would be expected to involve longrange configurational rearrangements accompanied by long relaxation times. They then concluded that domain disruption in dynamics measurements as in steady state deformation should depend principally on the strain, i.e., strain amplitude, not on frequency, and that it should occur preferentially, if at all, at lower reduced frequencies, where an effect on the dynamic properties attributable to the domain structures as such is alone inferred to exist. Another significance of the results of Gouinlock and Porter is that the relaxation time





Figure 2.1.--Reduced dynamic viscosity and elastic modulus vs. reduced frequency for SBS 7-43-7. Reference temperature is 138°C. Data of Gouinlock and Porter (1977).



associated with long-range motion of the chains of these block copolymers is not characterized by the peak of the loss modulus G''( $\omega$ ) but at a lower critical frequency where domain phase behavior dominates.

Perhaps the most detailed account of rheological study performed on block copolymers is the IUPAC commission study of SBS melt compiled by Ghijsels and Raadsen. Steady, dynamic, creep and elongational flows were conducted. The SBS specimen under study consisted of cylindrical polystyrene domains (18% wt) dispersed in the polybutadiene matrix. The effects of pressure, temperature, and time between measurements on material properties were also tested. Their results can be summarized as follows.

- The melt viscosity of the triblock copolymer is much higher than that of otherwise similar random copolymers of same composition and molecular weight.
- The viscosity at low shear is very sensitive to shear history.
- In the low shear region, the complex viscosity is as much as three times higher than the steady-shear viscosity at equal values of frequency and shear rate.
- A residual shear stress depending on previous shear conditions is observed in shear stress relaxation experiments.

Similar flow behavior, especially at low shear rates has been reported by Cogswell and Hansen (1975) with ethylene polypropylene


copolymer melt and Mundstedt (1981) with ABS graft copolymer melt.

#### 2.2 Optical Studies

Electron microscopy and x-ray difraction have become invaluable tools in structure elucidation of block copolymer systems. Since the method of sample preparation is known to affect rheological results, a brief review will be outlined on how various workers have utilized the above techniques to identify factors affecting the morphology property relationships of block copolymers.

Pedemonte et al. (1975a and b) have performed a detailed study of the dependence of their morphology and stress properties on the preparation of samples. For Kraton 1101 (SBS with 33%S), they have compared the original copolymer with films cast from toluene solution at two different evaporation rates (ca. 20 and 0.5  $cm^3/h$ ), compression moulded films, and extruded and extruded-annealed specimens. From annealing studies, it has been concluded that the original material contains rod-like polystyrene domains. From the comparison of the electron micrographs and stress-strain curves of both extruded and extruded-annealed samples, the following conclusions have been drawn. The high values of the Young modulus are caused by a high degree of orientation of the polystyrene rods along the extrusion axis; the yield point is explained by the presence of many dislocations and thin ties which link consecutive cylinders. In the case of solution cast films, the morphology of samples prepared at a high evaporation rate does not show any regular arrangement of the



polystyrene which seem to have a rod-like shape, while for low rates, a morphology similar to that of the original annealed samples is observed. In moulded films, the polystyrene chains form rod-like domains in a rubber matrix, but no particular orientation of the cylinders exists. But Lewis and Price used X-ray diffraction and electron microscopy to compare two Kraton 1101 samples--one, prepared by compression-moulding and another, a film cast from dilute benzene solution. They observed an anisotropy of mechanical properties with the former samples and an isotropy for the latter samples.

Kawai et al. (1968, 1969) have studied films of SI copolymer of different composition obtained by evaporation of about 5% toluene solution. Electron micrographs of sections perpendicular to the film surface have revealed five types of morphology: (1) spheres of PI randomly distributed in a PS matrix for a PS content of 73 wt%; (2) cylinders of PI randomly distributed in a PS matrix for a PS content of 65%; (3) a rather disordered lamellar structure for PS content of 49% and 43%; (4) cylinders of PS randomly distributed in a PI matrix for a ps content of 33%; and (5) spheres of PS randomly distributed in a PI matrix for the PS content of 18%. The authors have also studied the effect of the nature of the solvent using one good solvent for polystyrene (MEK) and four good solvents of polyisoprene (cyclohexane, CCl<sub>3</sub>, n-hexane and iso-octane). With the copolymer in such solvents, electron microscopy has revealed disordered structures. These results contradict those obtained by slow evaporation of the solvent (MEK, dimethyl ketone and toluene) from



mesophase of SI and SIS copolymers (Gallot et al., 1969) of both lamellar and cylindrical type. A possible explanation of the disordered structure observed by Kawai would be a too high evaporation rate fixing the disordered structure in the dilute solution.

Kawai et al. (1968) have also tried to relate the composition of SIS copolymers to their morphology and mechanical properties. Polystyrene spheres were found dispersed in a polyisoprene matrix for a polystyrene content of 9.5%, slightly curved PS rods arranged nearly parallel in the PI matrix for an S content of 23%, a rather disordered lamellar structure for a PS content of 47%, PI domains of various shapes and orientations in a PS matrix for a PS content of 72%. Kawai et al. have also observed a systematic change in the stress-strain behavior with the copolymer composition, a change ranging from the behavior of a soft rubber vulcanizate to that of a carbon-filled rubber vulcanizate and finally to that of a hard, but toughened, plastic exhibiting a well defined yield phenomenon when the PI content of the copolymer increases.

To explain the existence of three types of domain structures (spherical, rodlike, and lamellar) in SI, SIS, and ISI block copolymers cast from dilute solution, Kawai et al. (1969, 1977) have assumed the formation of micellar structures at a critical concentration during solvent casting. They have proposed an analysis of formation of three types of domain structure and the size of the domains taking into account thermodynamic and molecular parameters such as incompatibility between the PS and PI blocks, total chain length and



weight fraction composition of the copolymer, solvation of the blocks and temperature. They conclude that the block segments are preferentially oriented along the direction perpendicular to the interface between the two phases and they postulate that the micelles formed at a rather low concentration maintain their structure in the solid state without reorganization. During evaporation, the micelles shrink in the direction perpendicular to the interface between the domains. Spherical micelles shrink isotropically while rodlike and lamellae micelles shrink anisotropically. In rheological experiments increasing attention to sample preparation and morphological characterization are being given as attested by the works of Kraus and Rollman, Gouinlock and Porter and Ghijsels and Raadsen.

All these studies tend to illustrate the basic feature of block copolymers, i.e., the additional complication that arises from the constraints that restrict the components to separate regions in space. A more complex picture is further introduced by the geometry of these domains which may contribute to anisotropic deformation. We avoid the latter difficulty by choosing a block copolymer with spherical domains and treat them as elastic barriers.



#### CHAPTER III

# A TRANSIENT NETWORK MODEL FOR POLYMERIC MATERIALS WITH SPHERICAL MICRODOMAINS

## 3.1 Objectives

On the basis of rheological experimental observations presented in the previous chapter, we undertook to formulate and test a kinetic network model based on network theory for block copolymer melts with spherical microdomains, incorporating realistic and tractable rate terms for attachment, and detachment of segments (flexible sub-chain) and domains. The resulting segment distribution is non-Gaussian so that a general expression proposed by Yamamoto is required to calculate the macroscopic stress. In the following chapters, this model will be tested for uniaxial extensional, simple shear, and oscillatory flows in both steady and unsteady conditions. Next rheometric data shall be presented on a well characterized diblock copolymer sample --poly(styrene-b-butadiene) whose morphological structure is known and the material functions will be compared with model results.

# 3.2 The Rate Terms

Figure 3.1 depicts spherical, rubbery domains uniformly distributed in a soft, continuous phase. The position  $\underline{\rho}$  is referred to a fixed origin while the position  $\underline{r}$  is referred to the end of a segment which may or may not be at a domain; <u>R</u> denotes the nondimensional



×

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Figure 3.1.--A polymer network with rubbery domains.



position r/N1 where N1 is the extended length of the segment with N subunits. An active network segment in this representation is a flexible strand bridging rubbery domains and/or entanglement junctions in the soft phase. A segment distribution function  $f(\underline{R}, N, t)$  may be defined such that  $fd^3\underline{R}$  is the number of elastic segments in the network with an end to end vector in the range  $\underline{R}$  to  $\underline{R} + d\underline{R}$  at time t and composed of N subunits. This function obeys the evolution equation of Yamamoto

$$\frac{\partial f}{\partial t} + \nabla \cdot (\underline{R}f) = G(\underline{R}, N) - \beta(\underline{R}, N)f \qquad (3.1)$$

where  $G(\underline{R},N)$  and  $\beta(\underline{R}, N)$  denote the rate of creation and the coefficient of destruction of segments with N subunits;  $\underline{R}$  denotes the velocity of such segments which may be expressed following Phan-Thien and Tanner as

$$\underline{\mathbf{R}} = (\underline{\mathbf{L}} - \underline{\boldsymbol{\xi}}\underline{\mathbf{D}}) \cdot \underline{\mathbf{R}}$$
(3.2)

where  $\underline{L}$  is the velocity gradient and  $\underline{D}$  the deformation rate tensor in the fluid;  $\xi$  is a slip coefficient.

A flexible segment in this representation may be constrained by impenetrable barriers at one or both of its ends, as in a diblock or triblock copolymer melt. Hesselink (1971), Napper et al. (1975), and Edwards and Dolan (1975) have derived one dimensional equilibrium distribution functions for such segments, taking the presence of these barriers into account by imposing the boundary condition



$$f_e(\underline{r} = 0, N) = 0$$
 (3.3)

at the domain boundary. With spherical domains, the spherically symmetric form satisfying Equation (3.3) proposed by Chompff may be used.

$$f_{e}(r,N) \sim \exp\left[\frac{-a^{2}}{r^{2}/N\ell^{2}}\right] \exp\left[-\frac{3}{2}\frac{r^{2}}{N\ell^{2}}\right]$$
 (3.4)

This distribution is originally attributed to Reiss (1967) and Yamakawa (1968) who proposed a general expression for the total potential energy, E, of the configuration of a free polymer chain as

$$E = \sum_{v=1}^{N-1} u_{i,i+1} + \frac{1}{2} \sum_{i \neq j} v(r_{ij})$$
(3.5)

Here the monomers constituting the chain are treated as hard spheres distinguishable by their positions in the sequence constituting the polymer and are held in place by assigned potentials  $u_{i,i+1}(r_{i,i+1})$ . The spherically symmetric interaction potential between monomer i and monomer j is represented by  $v(r_{ij})$  where  $r_{ij}$  is the distance between the centers of monomers i and j and N represents the number of monomers in the polymer. The configurational partition function for a polymer molecule whose first monomer (segment) is fixed with its center at the origin assumes the form

$$Z = \int \dots \int \exp(-E/_{kT}) d\tau_2 d\tau_3 \dots d\tau_N$$
 (3.6)

where  $d\tau_2$ ,  $d\tau_3$ , etc. are the volume elements for the second and third segments, etc. The integrals extend over all space. The configurational partition function for a polymer molecule whose Nth segment has its center fixed a distance r away from the fixed first segment assumes the form

$$Z(R) = \int \dots \int \exp(-E/kT) d\tau_2, d\tau_3 \dots d\tau_{N-1}$$
 (3.7)

where in the integration it is understood that the first and last segments are a distance r apart.

The authors then calculated for the configuration probability of a free chain in which one end is fixed and is constrained so as to decouple the many body problems. This can be represented as

$$P \sim \exp(\frac{-3r^2}{2N1^2}) \exp(\frac{\Phi_N(r)}{kT})$$
 (3.8)

Here the function  $\phi_N(r)$  represents a spherically symmetric external field (centered on the first segment to which the Nth segment is subject and clearly depends on  $r_N$ . The spherically symmetric form of  $\phi_N(r)$  of Equation (3.4) adopted by Chompff predicted very well the stress-strain relationship of rubber vulcanizates at high extensions. For block copolymer systems, the parameter "a" in Equation (3.4) describes the range of repulsion between continuous elastic segments and the domain to which they are attached. If the number of segments attached to a domain is small so that the range of repulsion between segments is less than the maximum end-to-end distance of the segment,



a < 1. The creation rate expression G chosen in this study is patterned on Equation (3.4) and written as

G (R,N) = C 
$$\frac{e^{2a}}{1+2a} \left(\frac{3N}{2\pi}\right)^{3/2} \exp\left[-\frac{a^2}{NR^2} - \frac{3NR^2}{2}\right]$$
 (3.5)

where C is a constant rate coefficient. The symbols r and R denote magnitudes of the vectors <u>r</u> and <u>R</u> respectively. The shape of the distribution in Equation (3.5) is shown for several values of a in Figure 3.2. With increasing a, the peak shifts to higher values of R, i.e., the end-to-end distance of most probable segment is increased. From the previous discussions, the repulsion coefficient "a" is an inverse function of temperature. The applicable region of temperature for G is  $T_g < T \leq T_t$  where  $T_g$  and  $T_t$  are the block copolymer glass transition temperature and transition temperature to a single phase respectively. Here "a" has a range of  $1 < a \leq 0$ .

A consistent expression for the rate coefficient of destruction  $\beta$  is obtained from the relation

$$\beta (\mathbf{R},\mathbf{N}) = \beta_0 [1 + \varepsilon (\mathbf{A}(\mathbf{R},\mathbf{N}) - \mathbf{A}(\mathbf{O},\mathbf{N}))/kT]$$
(3.6)

where the leading term is the contribution from Browian motion and the second term is associated with the change in entropic free energy A of a segment in the network by flow and repulsive interaction (Acierno et al., 1976). Writing the configurational partition function Z in accord with Equation (3.4) as

$$Z(R,N) = K_0 \exp \left[-\frac{3}{2}NR^2 - a^2/NR^2\right]$$
 (3.7)





Gxb[-3NK<sub>5</sub>\5 - 9<sub>5</sub>\NK<sub>5</sub>]



and using

$$A = -kT \ln Z \tag{3.8}$$

where kT is the Boltzmann's temperature, we obtain

$$\beta(\underline{R},N) = \beta_0 (1 + \frac{3\varepsilon NR^2}{2} + \frac{\varepsilon a^2}{NR^2})$$
(3.9)

The rate of destruction is  $\beta f$  so that at R = 0,  $\beta f$  = 0, since f is an exponential function of  $1/R^2$  while  $\beta$  is a polynomial of  $1/R^2$ . Thus the rate expression is well behaved. The initial distribution of segments is given by

$$f(R,N,t=0) = G(R,N)/\beta(R,N)$$
 (3.10)

The moment integrals are considerably simplified if it is assumed following Fuller and Leal that  $\epsilon$  << 1 so that

$$f(\underline{R}, N, t=0) \stackrel{\sim}{\rightarrow} G(\underline{R}, N) / \beta_0$$
(3.10a)

with  $\varepsilon << 1$  and a < 1, the third term in equation (3.9) is clearly much smaller than the other terms.

The rate expressions outlined here should be appropriate for a block copolymer or a filled polymer melt containing spherical domains or particles with low surface density of segments and high interpenetration in the continuous polymer phase. The elastic free energy of the network is largely in the flexible segments of the continuous phase.



### 3.3 The Macroscopic Stress Tensor

As already mentioned in the preceding section, the rate expressions chosen here will lead to a non-Gaussian segment distribution f; so a general equation of Yamamoto is used to find the macroscopic stress  $S_{\rm e}$  in the network

$$\underline{S} = \int \frac{1}{R} \frac{dA}{dR} (\underline{R}, N) \underline{R}\underline{R}f(\underline{R}, N, t) d\underline{R}$$
(3.11)

or

$$\underline{S} = \langle \frac{1}{R} \frac{dA}{dR} \left( \frac{R}{R}, N \right) \underline{R} \underline{R} \rangle$$
(3.11a)

Combining (3.7), (3.8), and (3.11a) yields

$$\underline{S} = 3NKT < \underline{RR} - 2a \, \underline{RR} \\ \overline{3N^2}R^4$$
(3.12)

The validity of this model is examined in the following two chapters with detailed stress calculations for uniaxial extensional, simple steady shear and oscillatory shear flows.



### CHAPTER IV

# PREDICTED STRESS BEHAVIOR IN EXTENSIONAL FLOWS

# 4.1 Uniaxial Steady Extensional Flow

The kinematics of this flow are described by

$$V_1 = \Gamma_X, V_2 = -\frac{\Gamma}{2}y, V_3 = -\frac{\Gamma}{2}z$$
 (4.1)

where  $\Gamma$  is the magnitude of the strain rate. The steady deformational rate tensor <u>L</u>\* is given by

$$\underline{L}^{*} = \Gamma \begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & -\frac{1}{2} \end{bmatrix}$$
(4.2)

where  $\hat{\vec{\Gamma}}$  is the magnitude of the effective strain rate experienced by the network  $\hat{\vec{\Gamma}} = \Gamma$  (1- $\xi$ ). Since  $\underline{L}^*$  is a diagonal tensor independent of  $\underline{R}$ , segment evolution equation of (3.1) becomes

$$\frac{\partial f}{\partial t} + \hat{f}_{X} \frac{\partial f}{\partial x} - \frac{\hat{f}}{2} y \frac{\partial f}{\partial y} - \frac{\hat{f}}{2} z \frac{\partial f}{\partial z} = G(R,N) - \beta(R,N)f \qquad (4.3)$$

This hyperbolic first order partial differential equation has three characteristic lines as shown:

$$x = x_{0} \exp \left(\hat{\Gamma}t\right)$$
  

$$y = y_{0} \exp \left(-\frac{\hat{\Gamma}}{2}t\right)$$
  

$$z = z_{0} \exp \left(-\frac{\hat{\Gamma}}{2}t\right)$$
  
(4.4)



Using the macroscopic equation of stress, (3.12), the primary normal stress difference N<sub>1</sub> in uniaxial extension then turns out to be

$$N_{1} \equiv S_{xx} - S_{yy} \equiv 3NkT \left[ < x^{2} (1 \frac{2a^{2}}{3N^{2}R^{4}}) > - < y^{2} (1 - \frac{2a^{2}}{3N^{2}R^{4}}) > \right]$$
(4.5)

The two moment integrals in (4.5) may be evaluated using transformations described in Appendix A, similar to those employed by Fuller and Leal. Defining non-dimensional time, strain rate and elapsed time

$$\tau = \beta_0 t; \quad \hat{\Gamma} = \Gamma/\beta_0 \quad \tau' = \beta_0 (t-t') \quad (4.6)$$

we may write

$$N_{1}(\tau) = \frac{n_{0}kT}{1+2a} \{ [I_{1}(\tau) - I_{2}(\tau)]e^{-\tau} + \int_{0}^{\tau} e^{-\tau'} [I_{1}(\tau') - I_{2}(\tau')]d\tau' \} (4.7)$$

where  $n_0 \equiv C/\beta_0$ ; and  $I_1$ ,  $I_2$  are integrals over space in spherical polar coordinates as noted in Appendix A. The integration over one of the angular coordinates,  $\psi$  is carried out numerically, avoiding a singularity at  $\psi = \pi/2$  with a generalized Gauss-Legendre quadrature formula of Krylov (1962), for  $I_2$ .

## 4.2 Results

4.2.1 Steady State Stress

At steady state equation (4.7) reduces to

$$N_{1} = \frac{n_{0}kT}{1+2a} \int_{0}^{\infty} e^{-\tau} (I_{1}-I_{2})d\tau$$
 (4.8)



Both  $I_1$  and  $I_2$  depend on the two parameters a and  $\varepsilon$ . If both a and  $\varepsilon$ are set to zero, Lodge's rubber like liquid model is recovered. With a alone set to zero, equation (4.8) may be written with a damping function  $h(\Gamma,\tau)$  and a strain measure  $B(\Gamma,\tau)$  in the form proposed by Wagner (1979a)

$$N_{1} = n_{0}KT \int_{0}^{\infty} d\tau' e^{-\tau'} h(\dot{\Gamma}, \tau) B(\dot{\Gamma}, \tau') \quad (a=0)$$
 (4.9)

with

$$h(\Gamma,\tau') \equiv (1 + \frac{\varepsilon}{\Gamma} (1 - e^{\Gamma\tau'}))^{-2} (1 + \frac{\varepsilon}{2\Gamma} (e^{2\Gamma\tau'} - 1))^{-3/2}$$
(4.10)

and

$$B(\Gamma,\tau') \equiv e^{2\Gamma\tau'} - e^{-\Gamma\tau'} + \frac{\varepsilon}{2\dot{\Gamma}} (2e^{2\Gamma\tau'} + e^{-\Gamma\tau'} - 3) \qquad (4.11)$$

Such a factorization is not possible for the case where both a and  $\epsilon$  are nonzero, and the distribution is non-Gaussian.

The normal stress difference  $N_1$  may be scaled with  $n_0kT$ --a shear modulus--to compute a dimensionless elongational viscosity at steady state

$$n_{\rm E}^{\star} = \frac{N_{\rm l}/n_{\rm 0}kT}{\Gamma} = \frac{N_{\rm l}/\hat{\Gamma}}{\eta_{\rm 0}}$$
 (4.12)

Figure (4.1) presents a comparison of elongational viscosity plots against strain rate calculated with a fixed value of  $\varepsilon$  = .01 and several





Figure 4.1.--Normalized extensional viscosity vs. dimensionless strain rate. Effect of repulsion parameter "a" with  $\epsilon$  = 0.01.



values of "a." With a = 0, the elongational viscosity levels off around a dimensionless strain rate of 0.1 to a value of 3--the Trouton ratio between the low strain rate values of extensional and shear viscosities. As the value of a is increased, an upturn in viscosity is noted in the lower range of strain rates; an apparent yield stress may be identified at the lower strain rates on each of the plots with a  $\neq$  0. It is worthwhile to point out here that in the limit of zero strain rate, N<sub>1</sub> is zero and the elongational viscosity is finite; this must be true of kinetic network models such as the one discussed in this work. An analytical expression may be obtained for the apparent yield stress at low strain rates by simplifying equation (4.8) for  $\dot{\Gamma} << 1$ .

$$\frac{N_{y}}{n_{0}kT} = \frac{4}{5} \frac{a}{1+2a} \left(1 + \frac{5}{2} \epsilon\right) \quad (\Gamma << 1, \Gamma \neq 0)$$
(4.13)

It is readily seen from equation (4.13) that with  $\varepsilon << 1$ , the apparent yield stress is much more sensitive to the parameter a. Recalling that the value of a is directly related to the range of expulsion between segments attached to a domain, this relationship between the apparent yield stress and the parameter a is reasonable. The significance of this parameter is further illustrated with the elongational viscosity data reported by Munstedt (1981) on ABS block copolymers at 190°C with various concentrations of butadiene, the rubbery component. The apparent yield stress N<sub> $\gamma$ </sub> from the data is tabulated against rubber concentration in Table 4.1 along with the non-dimensional yield stress


% Butadiene in ABS	Observed Yield Stress Ny (Pa)	N <sub>Y</sub> /G*	Estimated a
20	$2.0 \times 10^3$	.004	.005
30	$5.0 \times 10^3$	.010	.013
43	$1.5 \times 10^4$	.030	.038

Table 4.1.--Model parameter "a" from data of Munstedt

 $*G_0$  Plateau Storage Modulus of 0% Butadiene in ABS.

and the corresponding values of the parameter storage modulus obtained from Figure 20 of Munstedt's paper as  $5 \times 10^5$  Pa. This table shows that increasing rubber concentration in the copolymer is described by increasing values of a in the present model, so that the segment distribution is increasingly non-Gaussian with higher concentrations of the rubbery domains.

The effect of the other parameter  $\varepsilon$  is more noticeable in the peak elongational viscosity attained at dimensionless strain rates of order 1. This peak is lowered and moved to lower strain rates with increasing values of  $\varepsilon$ , as shown in Figure 4.2, where plots of elongational viscosity are presented with a fixed at 0.05, but with several values of  $\varepsilon$ . This trend is understandable since  $\varepsilon$  is a measure of the dependence of function destruction on the deformation. Data are not available on peak elongational viscosities for block copolymers to verify this trend or allow a quantitative comparison. The effect of a on the peak value is only slight; increasing a leads to a small reduction in this value as seen in Figure 4.1.









#### 4.2.2 Stress Transients

The development of stress in experiments with a sudden step in elongational strain rate,  $\Gamma$  may be predicted with the help of equation (4.7) at several values of  $\Gamma$ . The results are plotted in  $N_1(\tau)/n_0 kT\Gamma$  against  $\tau$  in Figures 4.3-4.5. In Figure 4.3 a ratio a is set to zero and at  $\Gamma$  = 1 and  $\Gamma$  = 10, increasing  $\epsilon$  leads to reduced overshoot. Figure 4.4 presents the transient elongational viscosity at  $\Gamma$  = 0.1 with  $\varepsilon$  = 0.01 and several values of a. As a is increased, the trnasient viscosity is increased at all times. At  $\Gamma = 1$ , however, as shown in Figure 4.5, the transient elongational viscosity curve changes only slightly as a is increased. The data of Lobe and White (1979) on carbon black filled polystyrene melts at 170°C (see Figures 5-7 of their paper) show similar trends with concentration of filler at low elongation rates of 0.0063 sec<sup>-1</sup> and 0.02 sec<sup>-1</sup>, increasing carbon black content leads to higher transient elongational viscosity at all times. Once again, the value of a in the present model correlates directly with the concentration of filler in the material.









Figure 4.4.--Normalized transient viscosity vs. dimensionless time as a function of strain rate. Effect of the repulsion parameter "a," with 1 = 0.1 and  $\varepsilon = 0.01$ .

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Figure 4.5.--Normalized transient viscosity vs. dimension-less time. Effect of the repulsion parameter "a" with  $\dot{\Gamma}$  = 1 and  $\varepsilon$  = 0.1.



#### CHAPTER V

### PREDICTED STRESS BEHAVIOR IN SIMPLE SHEAR FLOWS

# 5.1 Simple Steady Shear

In uniaxial steady shear flows, the effective deformation rate tensor is given by

$$L^{\star} = \dot{Y} \begin{bmatrix} 0 & 2-\xi & 0 \\ -\xi & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$
(5.1)

where  $\dot{\gamma}$  is the magnitude of steady shear rate. For convenience, this tensor is diagonalized by introducing a tensor  $T_{\approx}$  such that  $T_{\approx}^{-1}L^{*}T_{\approx} = V_{\approx}$  where  $V_{\approx}$  is a diagonal and

$$T_{\approx} = \frac{1}{\sqrt{2(1-\xi)}} \begin{bmatrix} -i(2-\xi)^{\frac{1}{2}} & i(2-\xi)^{\frac{1}{2}} & 0 \\ \xi^{\frac{1}{2}} & \xi^{\frac{1}{2}} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$
(5.2)

Next a coordinate transformation leads to a new frame  $\rho = \rho(\rho, n, z)$ such that  $R = T \cdot \rho$ . The diagonalized tensor  $V_{\approx}$  is composed of the eigen values of the tensor  $L^*$  and expressed as



$$\bigvee_{\approx} = \frac{i\tilde{m}}{2} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$
(5.3)

where

$$\tilde{m} = \gamma [\xi(2-\xi)]^{\frac{1}{2}}, i = \sqrt{-1}.$$

The evolution equation for segment distribution becomes

$$\frac{\partial \mathbf{f}}{\partial \mathbf{t}} + i\tilde{\mathbf{m}}\rho\frac{\partial \mathbf{f}}{\partial \rho} - i\tilde{\mathbf{m}}n\frac{\partial \mathbf{f}}{\partial \eta} = \hat{\mathbf{G}}(\rho, \mathbf{N}) - \hat{\boldsymbol{\beta}}(\rho, \mathbf{N})\mathbf{f}$$
(5.4)

where

$$\widehat{G}(\rho,N) = G(\underbrace{T}_{\approx} \cdot \rho,N)$$
(5.5)

$$\hat{\beta} \left( \underset{\approx}{\rho}, \mathsf{N} \right) = \beta(\underset{\approx}{\mathbb{T}}, \underset{\approx}{\rho}, \mathsf{N})$$
(5.6)

In terms of the transformed coordinates

$$\mathbf{x} \cdot \mathbf{x} = \rho \cdot \mathbf{x}^{\mathsf{T}} \cdot \mathbf{x} = \rho \cdot \mathbf{x}^{\mathsf{T}} \cdot \mathbf{x} + \rho$$
(5.7)

i.e.,

$$R^2 = x^2 + y^2 + z^2 = \rho^2 - 2W\rho\eta + \eta^2 + z^2$$

where

$$W = (1 - \xi)^{-1}$$



The characteristic lines for Equation 5.4 in terms of  $\rho(\rho,\eta,z)$  coordinates are

$$\rho = \rho_0 e^{i\tilde{m}t/2}$$

$$\eta \quad \eta_0 e^{-i\tilde{m}t/2}$$

$$z = z_0$$
(5.8)

Applying the macroscopic equation of stress given in (3.12) for a non-Gaussian segment distribution function f, tangential and first normal stress difference relations can be generated in terms of moments in cartesian coordinates as

$$S_{xy} = 3NKT < (1 - \frac{2a^2}{3N^2R^4}) xy > (5.9)$$

$$N_1 \equiv S_{xx} - S_{yy} \equiv 3NkT [\langle (x^2 - y^2) (1 - 2a^2/3N^2R^4) \rangle]$$
 (5.10)

Necessary cartesian components of the stress tensor can be evaluated from the transformed coordinates  $f(\rho, \eta, z)$  using the expression

$$\underline{x}\underline{x} = \varrho \cdot \underline{\underline{T}}^{\mathsf{T}}(\underline{\underline{I}} \cdot \underline{\rho})$$
(5.11)

The cartesian moments are related to the moments of the transformed frame by the multiplicative factor, det(T) and these are expressed as:

$$\langle xy \rangle = \frac{\tilde{m}}{2\dot{\gamma}} \frac{\sqrt{\xi(2-\xi)}}{(1-\xi)^2} \langle \rho^2 - \eta^2 \rangle$$
 (5.12)



$$\langle x^{2} - y^{2} \rangle = \frac{\tilde{m}}{\gamma(1-\xi)^{2}} \langle \rho^{2} - 2(1-\xi)\rho\eta + \eta^{2} \rangle$$
 (5.13)

Moment integrals in transformed coordinates are solved in Appendix B, first by evaluating Equation (5.4) through the use of transformations prescribed by Fuller and Leal.

## 5.2 Results

Results of steady state dimensionless viscosity  $(\tilde{S}_{xy}/\dot{\gamma})$  and first dimensionless normal stress difference,  $\tilde{N}_1$  obtainable from Equations (5.9) and (5.10) can best be discussed with and without "a" equal to zero.

With "a" equal to zero, a case where the initial distribution of segments is Gaussian the steady shear viscosity and the first normal stress difference are obtainable from Equations (5.19) and (5.10) as:

$$\tilde{\eta}(\tilde{\dot{\gamma}}) = \frac{-i\xi(2-\xi)}{\tilde{\dot{\gamma}}(1-\xi)^2} \int_0^{\infty} e^{-\tau'} \frac{d\tau'(sinm\tau' - \frac{\varepsilon}{m}(cosm\tau' - 1))}{(1+\frac{2\varepsilon}{m}sinm\tau' - \frac{2\varepsilon^2}{m^2}(cosm\tau' - 1) - (\frac{1+\varepsilon\tau}{1-\xi})^2)^{3/2}}$$
(5.13)

$$\widetilde{N}_{1}(\widehat{\gamma}) = \frac{2}{(1-\xi)} \int_{0}^{\infty} e^{-\tau} \frac{d\tau'(-\xi(2-\xi))^{\frac{1}{2}}(1+\epsilon\tau' - \cos m\tau' - \epsilon/m \sin m\tau')}{(1+\frac{2\epsilon}{m} \sin m\tau' - \frac{2\epsilon^{2}}{m^{2}} (\cos m\tau' - 1) - (\frac{1+\epsilon\tau'}{1-\xi})^{2})^{3/2}} (5.14)$$

$$m = \left(\xi(2-\xi)\right)^{\frac{1}{2}} \tilde{\dot{Y}}$$

Here  $\widetilde{n}$  and  $\overset{\sim}{N}_1$  are defined as



$$\tilde{\eta} \equiv \frac{S_{xy}'\dot{\gamma}}{N_{o}kT/\beta_{o}}$$

$$\widetilde{N}_{1} \equiv \frac{N_{1}}{n_{0}kT}$$

where  $\tilde{\dot{\gamma}} \equiv \dot{\gamma}/\beta_0$  is the dimensionless shear rate,  $n_0$  is the initial concentration of network segments and  $\tau'$  denotes the dimensionless elasped time,  $\beta_0(t-t')$ .

Further, if  $\varepsilon$  is set to zero in Equations (5.14 and 5.15), viscometric material functions similar to those of the Phan-Thien and Tanner model, [see Equations (30) and (31) of Phan-Thien and Tanner, 1978] result

$$\tilde{\eta} = \frac{(1-\xi)}{1 + \xi(2-\xi)\tilde{\gamma}^2}$$
(5.16)

$$\tilde{N}_{1} = \frac{2(1-\xi)\tilde{\dot{\gamma}}^{2}}{1+\xi(2-\xi)\tilde{\dot{\gamma}}^{2}}$$
(5.17)

The non-linear dependence of shear viscosity on shear rate in most polymeric systems is accounted for in this model through the slip mechanism,  $\xi$ . In Figure 5.1, the effect of the destruction coefficient  $\varepsilon$  on dimensionless viscosity is presented as a result of computing (5.13) using a 40-point Simpson's composite formula. This result shows that " $\varepsilon$ " does not affect the trends in viscosity vs. shear rate, but merely changes the scaling factor,  $n_0 kT/\beta_0$ . Similar









conclusions have been arrived at by Phan-Thien and Tanner as well as Fuller and Leal. Since the value of  $\varepsilon$  affects only the scaling factor, subsequent curves of viscosity are plotted only for  $\varepsilon$  < 0.01 so that  $n_0 kT/\beta_0$  coincides with the zero shear rate viscosity.

For the non-Gaussian model (a  $\neq$  0), steady shear viscosity and first normal stress difference expressions are derived from Equations (5.9) and (5.10) as

$$\tilde{\eta}(\tilde{\dot{\gamma}}) = \left(\frac{e^{2a}}{1+2a}\right) \begin{cases} \left(-\frac{\xi(2-\xi)}{(1-\xi)^2}\right)^{\frac{1}{2}} \\ \left(1-\xi\right)^2 \tilde{\gamma} \end{cases} \int_{0}^{\infty} e^{-\tau'} \left(-h(\tilde{\dot{\gamma}},\tau') B_{10}(\tilde{\dot{\gamma}},\tau')\right) \\ \\ \end{bmatrix}$$

+ 
$$\frac{6\varepsilon a^2}{m(1-\xi)^2} h_1(\tilde{\dot{\gamma}},\tau') B_{11}(\tilde{\dot{\gamma}},\tau') d\tau'$$
 (5.18)

where

$$h(\tilde{\dot{\gamma}},\tau') = \frac{(\xi(2-\xi))^{\frac{1}{2}}}{(1+2\frac{\varepsilon}{m}\sin \pi\tau' - \frac{2\varepsilon^2}{m^2}(\cos \pi\tau'-1) - (\frac{1+\varepsilon\tau'}{1-\xi})^2)^{3/2}}$$

$$B_{10}(\tilde{\dot{\gamma}},\tau') = \operatorname{sinm}\tau' - \frac{\varepsilon}{m} (\operatorname{cosm}\tau'-1)$$

$$B_{11}(\tilde{\dot{\gamma}},\tau') = 1 - \xi(2-\xi) \operatorname{cosm}\tau' - (1-\xi)^2 \operatorname{cos}^2 m\tau' - m\tau' \operatorname{sinm}\tau'$$

$$h_{1}(\dot{\gamma},\tau') = \frac{1}{(1+2\frac{\varepsilon}{m} \operatorname{sinm}\tau' - \frac{2\varepsilon^{2}}{m^{2}}(\operatorname{cosm}\tau'-1) - (\frac{1+\varepsilon\tau'}{1-\xi})^{2}} (\dot{\gamma},\tau')$$



$$C(\tilde{\dot{\gamma}},\tau') = 1+2 \frac{\varepsilon}{m} \sin m\tau' + \frac{8\varepsilon^{2}}{m^{2}} \left[ \xi \frac{(2-\xi)}{(1-\xi)^{2}} \cos m\tau' - \cos 2m\tau'/2 - 3/2 + (1-\xi)^{-2}(1+\frac{m^{2}\tau'^{2}}{2}) + \frac{m\tau' \sin m\tau'}{(1-\xi)^{2}} \right]$$
$$\hat{N}_{1}(\tilde{\dot{\gamma}}) = \left(\frac{e^{2a}}{1+2a}\right) \frac{2}{(1-\xi)} \int_{0}^{\infty} d\tau' e^{-\tau} (h(\tilde{\dot{\gamma}},\tau') B_{20}(\tilde{\dot{\gamma}},\tau') + 8\varepsilon) a^{2}$$

× 
$$(1-\xi)h_1(\tilde{\dot{\gamma}},\tau)B_{21}(\tilde{\dot{\gamma}},\tau'))$$
 (5.19)

where

$$B_{20}(\tilde{\dot{\gamma}},\tau') = 1 - \cos m\tau' - \frac{\varepsilon}{m} (\sin m\tau' + m\tau')$$

$$B_{21}(\tilde{\dot{\gamma}},\tau') = \frac{\tau \cos m\tau}{(1-\xi)^3} - \tau' - \sin m\tau' \left(\frac{1}{(1-\xi)^3} + \frac{(\cos m\tau'-1)}{1-\xi} - 1\right)$$

The second term in (5.19) is an additional contribution to the stress level of newly formed chains with respect to the degree of their repulsion from the domains. Again using a 40-point Simpson's composite formula Equations (5.18) and (5.19) are computed. In Figures 5.2 and 5.3, the viscosity and first normal stress difference are presented with  $\varepsilon = 0.005$  and various values of "a." For a  $\neq 0$  Figure 5.2 shows an apparent yield stress and a quick decay of viscosity to a "plateau" at dimensionless shear rates of order .01. At large shear rates the model then yields the power law behavior. The general shape of the curves in Figure 5.2













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are in good agreement with flow curves of block copolymer melts and even with those of triblock melts. There is sharper upturn of shear viscosity at low  $\dot{y}$  with increasing "a" and experimentally a sharp upturn of shear viscosity is also noted at higher fractions of the domain phase. Thus "a" correlates directly with the concentration of the domain phase. The upturn in shear viscosity results is not as drastic as those shown in the extensional flows. This is attributed to functions controlling their strain measure  $e^{\Gamma \tau}$  for extensional flows and sin  $m_{\tau}$ ' for shear flows. The effect of the slip factor as shown in Figure 5.3 is to change the power law behavior of the material that occurs at large deformation rates. The model does not predict any new trend in first normal stress difference except a slight increase in magnitude at all shear rates, as compared with the Gaussian model. The large difference with high slip ratios at large shear rates (see Figure 5.3) are predicted even with a = 0. The trend in normal stress-shear rate relationship predicted by the model awaits further evaluation by experimental data. However, literature is devoid of such data for block copolymers mainly due to general difficulty in collecting reliable normal stress data in conventional rheometers. The normal stresses of all melts of high M.W. is difficult to measure due to the compliance of the instrument at high shear rates. Such problems encountered also in this study will be discussed in the experimental section. From the results of extensional and shear flows, the contribution of the non-Gaussian nature of chains occurs at small chain extensions. It





Figure 5.4.--Normalized transient viscosity function. Effect of the repulsion parameter a,  $\varepsilon$  = 0.005,  $\xi$  = 0.05.




Figure 5.5.--Normalized transient viscosity function. Effect of the repulsion parameter "a,"  $\dot{\gamma}$  = 3,  $\epsilon$  = 0.005,  $\xi$  = 0.05.





Figure 5.6.--Normalized transient first normal stress difference function a = 0.0,  $\varepsilon$  = 0.005,  $\xi$  = 0.05.



is worthwhile to emphasize here that the ensuing newtwork model is mainly applicable to the low deformation region.

Transient stresses are computed by using time dependent moments as developed in Equation (B.9) in the stress expressions of equations (5.9) and (5.10). The results are plotted as  $\widetilde{\eta}^{+}$  ( $\tau)$  and  $\tilde{N}_1 \textbf{+}$  ( $\tau\textbf{)}$  vs. dimensionless time  $\tau$  in Figure 5.4 to 5.6. Figure 5.4 shows the shear growth viscosity at low shear rate as a function of time. The magnitude of this material function increases strongly as the parameter "a" increases, growing monotonically with time until it reaches the steady state value. In contrast to the IUPAC data on SBS melts, no stress overshoot is predicted by the model until shear rates of the order 1 as shown in Figure 5.6. In these data stress overshoot was noticed at shear rates as low as 0.01 s<sup>-1</sup>. The strain at stress peak,  $\dot{\gamma}t_{max}$  has average value of 3 at  $\dot{\check{\gamma}}$  ~ 0(1) and increases linearily to 6 for instance at  $\tilde{Y}$  = 30. As  $\xi$  approaches 0.2,  $\dot{\gamma}_{t_{max}}$  stays fairly constant at 3. Many workers, Osaki et al. (1967), Graessley et al. (1977) have correlated this data to the total strain on the material. An experimental value of  $\dot{\gamma}t_{max}$  = 3 have been reported by the former researchers on homopolymeric melts. Regardless of the value of a, the stress growth curve predicted is oscillatory when the slip ratio  $\xi > 0.1$ . More recent experiments (Osaki et al.) have discountenanced the presence of the undershoot after an initial overshoot.



# 5.3 Oscillatory Shear Flow

In oscillatory shearing,  $\underline{\underline{L}}^{\star}$  is given by

$$L_{\approx}^{\star} = \frac{\dot{Y}_{0}}{2} \cos_{\omega} t \begin{bmatrix} 0 & 2-\xi & 0 \\ -\xi & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$
(5.20)

where  $\dot{\gamma} = \omega \gamma_0$ 

and  $\omega$  is the frequency of oscillation and  $\gamma_{0}^{}$  is the strain amplitude.

Exactly the same coordinate transformation used for steady shear flows is applied here to obtain the specific evolution equation as

$$\frac{\partial f}{\partial t} + \frac{i\tilde{m}_{o}}{2} (\cos\omega t) (\rho \frac{\partial f}{\partial \rho}) - \frac{i\tilde{m}_{o}}{2} (\cos\omega t) (\eta \frac{\partial f}{\partial \eta}) = \hat{G}(\rho, N) - \hat{\beta}(\rho, N) (5.21)$$

where

$$\tilde{m}_{0} = \omega \gamma_{0} \sqrt{\xi(2-\xi)}$$

We next make a domain transformation in the independent variable t to u such that u =  $\sin_{\omega}t$  to obtain the characteristic lines as shown in (5.21). This simplifies the computation of f as described in Appendix C.

$$\rho = \rho_{o} e^{i\tilde{m}_{o}u/\omega}$$

$$\eta = \eta_{o} e^{-i\tilde{m}_{o}u/\omega}$$

$$z = z_{o}$$
(5.22)



An oscillatory shear stress can be obtained through the macroscopic stress equation of (3.12) in terms of moments in the cartesian coordinate as

$$S_{xy} = 3NKT < (1 - \frac{2a^2}{3N^2R^4}) xy >$$
 (5.23)

We note the velocity gradient is varying sinusoidally with time; hence, the shear stress varies sinusoidally after transients have died down and may be represented as

$$S_{xy} = Re \{S_0 e^{i\omega t}\}$$
 (5.24)

where  $S_{0}$  is in general a complex function. For small strain amplitudes a strain independent complex viscosity  $\eta^{\star}(\omega)$  may be defined as the limit

$$\lim_{\gamma_{O} \to 0} |\eta^{\star}(\omega, \gamma_{O})| = \lim_{\gamma_{O} \to 0} S_{O} / \omega \gamma_{O} = |\eta^{\star}(\omega)|$$
(5.25)

where

The real part of the complex viscosity,  $\eta'$  (the dynamic viscosity) is associated with energy dissipation and the imaginary part  $\eta''$ ,  $\omega\eta'' = G'$  is associated with energy storage; these are the so-called linear viscoelastic moduli and are related to the oscillatory shear stress by



$$S_{xy} = n'\dot{\gamma}cos\omega t + \dot{n}''\dot{\gamma}_{o}sin\omega t$$
 (5.26)

Upon computing the moment integrals encountered in equation (5.22) as shown in Appendix C, we obtain the following expressions.

$$\widetilde{\eta}'(\widetilde{\omega},\gamma_{0}) = \left(\frac{e^{2a}}{1+2a}\right) \xi \frac{(2-\xi)}{(1-\xi)^{2}} \int_{0}^{\infty} d\tau' e^{-\tau'} \left[h_{0}(\widetilde{\omega},\tau')B_{0}(\widetilde{\omega},\tau') + 6a^{2}h_{1}(\widetilde{\omega},\gamma_{0},\tau') B_{1}(\widetilde{\omega},\tau')\right]$$

$$(5.27)$$

$$\tilde{\eta}^{"}(\bar{\omega},\gamma_{0}) = \left(\frac{e^{2a}}{1+2a}\right) \xi \frac{(2-\xi)}{(1-\xi)^{2}} \int_{0}^{\infty} d\tau' e^{-\tau'} \left[h_{0}(\tilde{\omega},\tau') B_{2}(\tilde{\omega},\tau') + 6a^{2}h_{1}(\tilde{\omega},\gamma_{0},\tau') B_{3}(\tilde{\omega},\tau')\right]$$
(5.28)

where

$$\tilde{\omega} = \omega/\beta_0 \qquad \tilde{\eta}' = \beta_0 \eta'/n_0 KT \qquad \tilde{\eta}'' = \beta_0 \eta'/n_0 kT$$

$$h_{0}(\tilde{\omega},\tau') = \frac{(-\xi(2-\xi))^{\frac{1}{2}}}{C(\tilde{\omega},\tau')^{3/2}}$$

$$C(\tilde{\omega},\gamma_{0,\tau'}) = \frac{1 - (1+\epsilon\tau')^{2}/(1-\xi)^{2}}{1 - \frac{(1+\epsilon\tau')^{2}}{(1-\xi)^{2}} + \frac{4\epsilon^{2}}{m_{0}^{2}\tilde{\omega}^{2}}(\tilde{\omega}\tau'(1-\frac{m_{0}^{2}}{2}) + \frac{m_{0}^{2}}{2}\sin\tilde{\omega}\tau')^{2}}$$



$$B_{0}(\tilde{\omega},\tau') = 1 - \cos \tilde{\omega}\tau' + \frac{\varepsilon}{\tilde{\omega}}(\tilde{\omega}\tau' - \sin \tilde{\omega}\tau')$$

$$h_{1}(\tilde{\omega}, \gamma_{0}, \tau') = \frac{(-\xi(2-\xi))^{\frac{1}{2}}}{C(\tilde{\omega}, \tau')^{\frac{1}{2}}(1 + \tilde{\omega}\tau'(2-m_{0}^{2}) + m_{0}^{2} \sin \tilde{\omega}\tau')}$$

 $B_{1}(\tilde{\omega},\tau') = (\tilde{\omega}\tau'\cos\tilde{\omega}\tau' - \sin\tilde{\omega}\tau')(1 + \frac{2\varepsilon\tau'}{(1-\xi)^{2}})$ 

 $B_2(\tilde{\omega},\tau') = \sin \tilde{\omega} \tau' + \frac{\varepsilon}{\tilde{\omega}} (1 - \cos \tilde{\omega} \tau')$ 

$$B_{3}(\tilde{\omega},\tau') = (1-\tilde{\omega}\tau'\sin\tilde{\omega}\tau' - \cos\tilde{\omega}\tau')(1 + \frac{2\varepsilon\tau'}{(1-\xi)^{2}})$$

Equations (5.26 and 5.27) involve  $m_0 = \gamma_0 \sqrt{\xi(2-\xi)}$  in their second term making  $\tilde{\eta}'$  and  $\tilde{\eta}''$  dependent on the strain amplitude. However, numerical analysis of these function at  $\gamma_0 < 0.1$  showed no significant difference from the linear results. In this region then, it is assumed the linear response applies and thus compute the complex viscosity function as

 $|\tilde{n}^{\star}(\tilde{\omega},\tilde{\gamma}_{0})| \approx |\tilde{n}^{\star}(\tilde{\omega})| = (\tilde{n}^{\prime}(\tilde{\omega})^{2} + \tilde{n}^{\prime}(\tilde{\omega})^{2})^{\frac{1}{2}}$ 

Figure 5.7 shows the result of numerical integration for the dimensionless dynamic viscosity,  $\tilde{n}'$  and dimensionless complex viscosity,  $|\tilde{n}^*|$  as functions of dimensionless frequency. For the sake of comparison, this figure also shows the normalized steady shear viscosity which was calculated in Section 5.2 using the same parameters,  $\varepsilon$ ,  $\xi$ , and a. This is to see how well the empirical Cox-Merz



rule (which states that  $\eta(\dot{\gamma})$  is equal to  $|\eta^*(\omega)|\tilde{\omega} + \tilde{\gamma}$ ) works in this constitutive equation. At low dimensionless frequencies, i.e.,  $\tilde{\omega}$  < .001, the complex viscosity is a constant and decays slowly with the shear rate. However, beyond this value the complex viscosity curve is higher than the steady viscosity curve. This deviation from the Cox-Merz rule is consistent with the data on the SBS block copolymer melt (Ghijsels and Raadsen). However, the SBS data did now show clearly a zero frequency limit or a crossover point both of which are seen in Figure 5.7, but this trend appears to be the case if more data were collected at the lower shear rate end. In the diblock copolymer data of this study, the leveling off of  $|n^*|$  is inferred at about  $\dot{\gamma} = 10^{-3} \text{sec}^{-1}$ . The experimental results, as well as the model (extension-dependent type) calculations portray the junction density (including segments) as being more responsive to total strain in copolymers than to strain rate. In homopolymers, the response in both oscillatory and steady shear modes is dependent on the rate of strain and thus occurs over a larger range. These results yield  $|\eta^*|/(\eta) \sim 2$  as compared with a value of 4 for the SBS data (Ghijsels and Raadsen), pointing out model applicability with weaker block copolymer networks such as diblocks. Comparison of model results with data of an SB diblock shall be deferred to the Discussion chapter.

The model results for stress relaxation after cessation in shear are not given because they are not substantially different from those of linear viscoelasticity. In any case since there is no







flow (i.e.,  $\dot{\gamma}$  = 0), this can easily be computed with the explicit distribution function given as

$$f(\rho,\eta,z,t) = f_{0}(\rho,\eta,z)e^{-\hat{\beta}(\rho,\eta,z,N)t} + \frac{\hat{G}(\rho,\eta,z,N)}{\hat{\beta}(\rho,\eta,z,N)}(1-e^{-\hat{\beta}(\rho,\eta,z,N)t})$$
(5.29)



## CHAPTER VI

## SAMPLE CHARACTERIZATION AND EXPERIMENTAL TECHNIQUES

#### 6.1 Material and Sample Preparation

The block copolymer employed in this investigation was a research grade poly(styrene-b-butadiene), CO326-9 (containing a small amount of an antioxidant, Ionox) generously provided to us by Dr. Lu Ho Tung of the Dow Chemical Company. Characterization information for this copolymer is provided in Tables 6.1 and 6.2.

Approximately 0.2 cm thick copolymer films were prepared for both rheological and morphological studies by the solvent casting technique (Hashimoto et al., 1977). Thin films of the copolymer were made by dissolving 20 gms of copolymer in 100 ml of toluene and the solution transferred to 10 cm Petri dishes. These solutions were then placed in a vacuum oven kept at 30°C with all port outlets closed except one connected through a valve regulator to a hood chamber to insure slow evaporation. The oven was periodically flushed with nitrogen to prevent the oxidation of unsaturated bonds in the butadiene phase. After the films were visibly dry a procedure requiring five days, they were further vacuum dried at 80°C. It was assumed that adequate drying was achieved when the decrease in weight of the sample varied by no more than 0.005 gm. Again to prevent sample degradation during weighing, the vacuum oven temperature was



TABLE	6.1Block	copolymer	characterization
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Specimen Code	Туре	B Block		S Block		
		M <sub>N</sub>	$\overline{M}_{W}/\overline{M}_{N}$	Wt. Percent B Block	M <sub>N</sub>	™ <sub>w</sub> ∕™ <sub>N</sub>
C0326-9	(S-B) <sub>1</sub>	10,000	~1.1	5.9	232,000	~1.7

TABLE 6.2.--Property of glassy continuous phase

Structure	Molecular Weight Between Entanglement M <sup>a</sup> c	Solubility Parameter (Cal/cm <sup>3</sup> ) <sup>1D</sup>	Glass Transition Tempera- ture °C
Polystyrene	33,000	(8.1) .05 <sup>C</sup>	100 <sup>d</sup>

<sup>a</sup>Value derived from Newtonian Viscosity data of linear polymer (Berry and Fox, 1968).

<sup>b</sup>Hashimoto et al., (1974).

<sup>C</sup>Solubility parameter difference between PS and PB.

<sup>d</sup>Kraus and Rollman.

Note: Polybutadiene Tg ~ -90°C

Block copolymer - liquid above 100°C.



decreased to 25°C and the sample allowed to cool in vacuum. Thereafter, the oven was brought to atmospheric pressure with the nitrogen flush. This procedure was repeated until the constant weight was achieved. The sample was further annealed at 110°C for 24 hours. The film samples were then placed in a vacuum dessicator and a representative sample was used for structure elucidation by electron microscopy.

### 6.2 Electron Microscopy

The domain structure of the film specimen was investigated by transmission microscopy in a Philips 201 electron microscope operated by K. Baker of Pesticide Research Center, M.S.U. After embedding in a Spurr resin, the film was presectioned, stained, and fixed with Osmium tetroxide,  $0s0_4$ . The specimens placed on a support were allowed to stand for about half an hour at room temperature over a 2% aqueous solution of  $0s0_4$  stabilized with a Sorensen phosphate buffer, in a small, tightly closed glass vessel. The stained films were then cooled with liquid nitrogen to approximately -150°C and cut on a Sorvall Porter-Blum, MT-2 Ultramicrotome with a diamond knife. Ultra thin sections of about  $800\frac{3}{4}$  thick were cut normal to the film surface by the ultramicrotome. Figures 6.1 and 2 show some of the typical electron micrographs of the butadiene-styrene block copolymer at different magnifications.

### 6.3 Morphology

The dark areas of Figure 6.1 are the polybutadiene phase selectivity stained by  $0s0_4$  while the white portion is the polystyrene





Figure 6.1.--Typical EM micrograph of ultra-thin section of poly(styrene-b-butadiene) specimen at x 50,000.





Figure 6.2.--Typical EM micrograph of ultra-thin sections of poly(styrene-b-butadiene) specimen at x 150,000.



phase. The absence of spherical bundles or lamellae structure indicates only spherical microdomain structure of polybutadiene uniformly dispersed in a matrix of polystyrene blocks present in the copolymer specimen. The spherical domains have an average diameter of  $350\text{\AA}$ and an average interdomain distance of  $500\text{\AA}$ . The thickness of the domain boundary interphase,  $\Delta R$  directly related to the degree of compatibility of the blocks is indeterminable by electron microscopy, but are known to be significant for low to moderate M.W. copolymers such as this specimen (Leary and Williams, 1970; Krauss and Rollman, 1976). Hashimoto et al. using SAXS studies have reported  $\Delta R$  values for S-I samples showing an overall independence of  $\Delta R$  on M.W. of their samples. On the basis of a fair agreement of micrograph of Figure 6.1 with those of Hashimoto's (1977) and a similar order of rubber block weight fraction it is inferred that a thick domainboundary interphase exists in this sample.

It can be concluded, therefore, that the structure of this particular block copolymer conforms to assumptions in theory of spherically symmetric rubbery domains with low surface coverage uniformly dispersed in a thermoplastic matrix.

#### 6.4 The Modified Weissenberg Rheogoniometer

The steady, dynamic, and transient material functions such as shear viscosity, transient, and relaxation stresses and dynamic viscoelastic functions were measured over a range of shear rates, frequencies, and time with a modified Weissenberg Rheogoniometer, WRG (Model R-16). The modification involved the removal of the axial



force servo system and the LVDT transducers and replaced by a dynamic piezoelectric load cell and a charge amplifier. This, along with the utilization of a stiff torsion bar ( $K_T = 5.8492 \times 10^5$  dyn cm/.001" deflection) similar to those employed by Meissner (1972) were made to increase axial and torsional stiffness and thereby diminish unwanted motion in the platen assembly especially during dynamic and stress growth measurements.

Figure 6.3 is a schematic of the internal structure of the WRG. A detailed description and operating procedure will not be given here as they have been reported by various authors and more recently by Cross (1983) on the WRG used in this study. A torque in the torque bar is measured with a linear variable displacement transducer, LVDT. The output voltage is sent through an amplification and low frequency filter units and is recorded on the torsion transducer meter. In event that stress histories are required, the filtered output voltage are recorded with a Honeywell Visicorder that records transient events on photographic paper. An additional clam-shell electric oven was constructed for this equipment to accommodate a Mooney platen of Diameter, D = 10 cm

Two types of plate arrangements were utilized in this study are shown in Figure 6.4.

- 1. The cone-and-plate platen with cone angles of  $\theta_0$  = .552° and 1.982° and D = 7.5 cm and 5 cm respectively.
- 2. Combined cylindrical and cone and plate platen (Mooney) with  $\theta_0$  - 0.933 Outer Cylinder diameter,  $D_0$  = 10.01 cm,





Figure 6.3.--Weissenberg Rheogoniometer internal (Sangamo Controls Ltd.).




Figure 6.4a.--Cone and plate platen.



Figure 6.4b.--Combined cylindrical and cone and plate platen (Mooney type).



inner cylinder diameter  $D_i = 9.8195$  cm. and cylinder height = 2.533cm.

Here, the inner cylinder is formed of a conical platen at the bottom and cylindrical side, the diameter of which is accurately machined to allow a radial gap equal to the gap at the edge of the cone and plate of the platen. This ensures a uniform rate of shear throughout the sample.

Values for steady and transient shear stresses can be calculated from the torque in this arrangement by noting that for "Couette" cylindrical platens, the tangential shear stresses arising in the gap is given by

$$S_{xy} = \frac{\dot{y}}{2\pi\tilde{R}^2 h}$$
(6.1)

For cone-and-plate

$$S_{xy} = \frac{3\overline{y_2}}{2\pi \tilde{R}^3}$$
(6.2)

where  $\tilde{R}$  is the platen radius, h the cylindrical height, and  $\mathscr{T}_1$  and  $\mathscr{T}_2$ are the torques developed in "Couette" cylindrical and cone-and-plate platens respectively. Since the shear rate is uniform throughout the gap

The total torque = 
$$_2(1 + 6h/D)$$
 (6.3)

The cone-and-plate platens were utilized to collect steady shear and transient shear stress data with a steady shear rate range of 0.005



 $\sec^{-1}$  to 0.1  $\sec^{-1}$  at 130°C or lower. At 150°C the range improved to  $\dot{\gamma} \leq 0.3 \sec^{-1}$ . Beyond these shear rates ranges shear instabilities were noticed and this will be discussed fully in the experimental section. The Mooney platen was useful in extending shear viscosity data up to  $\dot{\gamma} = 3 \sec^{-1}$ . Beyond this an associated error of 9-12% was noted in the viscosity of the calibration fluid (ASTM standard) of  $n(T = 25^{\circ}C) = 742.1$  poise. This error is attributed to inertial effects and non-uniform shear regime in the gap commonly associated to large size platens performing at large shear rates (Walters, 1970). Due to the limitation of the amount of sample tested with the Mooney platen were limited to the range  $0.1 < \dot{\gamma} < 3 \sec^{-1}$ .

The transient and steady first normal stress difference are important material functions normally collected with the WRG. The transient normal stress data of various polymeric melts manifests strong overshoots and sometimes double peaks (Huang, 1976) before attaining a steady state with time. Unfortunately, at the time of this study, the WRG was equipped with a dynamic piezoelectric load cell that registers transient events, but returns to the null state when the steady state is attained. In the light of these no reliable normal force data were collected for the sample. In this work signals from the piezoelectric load cell were displayed on an oscilloscope and utilized in attaining the exact required gap separation distance beween the platens. This was especially useful when using the Mooney platen since it is impossible to see the inner cylinder just touching the outer cup for gap setting purposes.



## 6.5 Sample Loading and Temperature Control

In measuring the material functions of SB block copolymer melt, the residence time of the material should be kept very short in order to minimize oxidative reaction in the polybutadiene phase. On the other hand, due to the long relaxation times of polymer melts, rather long waiting periods are required to attain the gap setting and equilibration of the sample to a stress-free initial state.

To shorten this period and insure an initial equilibrated uniform distribution of the domains, premolded samples by way of solvent cast films are helpful, with dimensions which fit the coneand-plate geometry of the test gap. Since the melt temperature is known to strongly affect sample morphology care was taken not to introduce temperature inversions by using the procedure described below. Without setting the gap, the platens are heated to a temperature of 5°C below the desired temperature in about  $1\frac{1}{2}$  hours. At this point a nitrogen purge of  $\frac{1}{2}$  to 1 lb. pressure is bled into the heated chamber until the desired temperature is attained. It was predetermined that an  $\mathrm{N}_2$  pressure less than 1.51b. does not affect gap separation nor the torsion readings. After 5 minutes on attaining desired temperature, the gap between the platens was then set, primarily by the use of the normal force measuring system. Then the oven was opened and the sample is quickly transferred from the evacuated dessicator used in storing the sample to the plate making sure that no air bubbles were trapped between. The head was then brought down and excess melt cleaned off with a blade and the thermal chamber closed again.



The sample was then allowed to heat up to the desired temperature, a procedure that took 45 to 60 minutes. The temperature controller maintained the plate temperature to within  $\pm 2^{\circ}$ C.

# 6.6 Rheometric Testing

#### 6.6.1 Oscillatory Shear Experiments

The measurements of visoelastic properties of poly(styrene-bbutadiene) block copolymer melt were carried out with the cone-andplate platens at T = 130°C, 150°C, and 175°C. The strain applied to the sample by the oscillation of the bottom plate, causes the oscillation of the top cone. Oscillatory displacements are transformed into an electrical potential by the LVDT. It is then amplified and recorded on the visicorder. The strain sinuscidal input wave is also recorded on the visicorder. A phase shift and the amplitude ratio are determined from these two waveforms to obtain the linear viscoelastic functions as

$$\eta'(\omega) = \frac{S_{xy}^{o}}{\dot{\gamma}_{o}} \quad \sin \phi$$

$$G'(\omega) = \frac{S_{xy}^{\circ}}{\gamma_{o}} - \cos \phi$$

where  $\phi$  and  $S_{xy}^{\circ}$  / $\dot{\gamma}o$  are the phase shift and the amplitude ratio respectively.



An applied strain amplitude range of 0.1 - 0.2 gave no distrotions of sinusirdal waveforms in data and this was taken as the linear viscoelastic range. For high sensitivity and small sample size, the cone-and-plate platen of D = 5 cm was mainly used in oscillatory testing. Testing was carried out with the same sample giving from low to high frequency of oscillation. A waiting time of 30-45 minutes between testings was implemented.

Oscillatory testing at 124°C with strain amplitude maintained at 0.15 resulted in nonsinusoidal torsion waveforms as shown in Figure 6.5. Such highly non-linear oscillatory behavior have been reported by Ghijsels and Raadsen and a triblock sample and is a peculiar feature with structurizing dispersed systems.

# 6.6.2 Steady Simple Shear Experiments

Low drifts were noted in the torsion head transducer meter range of 0.25 x  $10^{-3}$  in and 1 x  $10^{-3}$  in the gap. Therefore, a shift torsion bar ( $K_T = 5.8492 \times 10^5$  dynes cm/.001 in.) is utilized as it gives the highest sensitivity at the transducer range setting of 2.5 x  $10^{-3}$ in. Such choice was made to restrict the movement of the torsion head to a minimum aiding transient measurement with the chosen platen diameter and the anticipated value of the steady viscosity of the sample.

A steady shear rate range of 0.005 to 3 sec<sup>-1</sup> was attainable with the instrument using both the cone and plate and the Mooney platens. Data were obtained in the range 0.005 to 0.1 sec<sup>-1</sup> with a waiting time between measurements of 30 minutes and next with one hour.









No appreciable difference in data was noted and thus the former waiting period was implemented. An associated error of 7-10% in the material functions occurred in this range. Beyond this range and at a temperature of 130°C or less a variation of 12-20% was noted in the stress readings for different runs under the same conditions. Upon closer studies it was observed that shear instabilities, e.g., stress fracture developed in the material as can be determined in Figure 6.6a and 6.6b. Figure 6.6a illustrates the situation where the material is extruded out of the gap after a shearing time of 8 minutes. In Figure 6.6b the appearance of the material at  $\dot{\gamma} = 0.096 \text{ sec}^{-1}$  and 0.43  $sec^{-1}$  are compared for quenched samples which experienced similar shearing times. Non-uniform shear profile is likely to develop in the sample at  $\dot{\gamma} = 0.43 \text{ sec}^{-1}$  resulting in faulty stress readings. The Mooney platens have a potential range of  $0.1 < \dot{\gamma} < 10 \text{ sec}^{-1}$  as seen in Holden's data. The major advantage of this platen is that the sample is prevented from leaving the shearing gap by the guard ring. Also very little area of the material is exposed to the air minimizing errors due to oxidative degradation. However, the bulk (D = 10 cm)of this platen tends to increase the inertia head leading to inacuracies mainly in transient and oscillatory measurements. As can be seen in the viscosity flow curves (presented in Chapter 7) no appreciable error is incurred using this platen at the shear rates prescribed as data extends smoothly from low to moderate shear region, i.e.,  $(0.1 < \dot{\gamma} < 0.4)$ . The effect of inertia is, however, seen in transient measurements as will be shown shortly. For steady shear





Figure 6.6a.--Picture showing test material extruding from gap after a shearing for 8 mins;  $\gamma$  = 0.43 sec^1. Shear instability is due to stress fracture. T = 130°C.



Figure 6.6b.--Quenched sheared materials after a shearing time of 8 min. Left hand specimen sheared at  $\dot{\gamma}$  = 0.096 sec<sup>-1</sup>. Right hand specimen sheared at  $\dot{\gamma}$  = 0.43 sec<sup>-1</sup>. T = 130°C.



viscosity results an associated error of 5-7% was noted using the Mooney platen.

Using fresh samples, stress growth experiments were conducted with the two platens. After the temperature of the material has stabilized in the gap, the clutch system was quickly engaged after the motor has been running for at least 5 minutes. Stress transients were recorded on the visicorder that was calibrated with the steady state stress value obtained from the torsion head transducer meter. The time dependent stress is normalized with the steady state value. Using the Mooney platen the effect of inertia on transient measurements can be seen in Figure 6.7. An overshoot in the stress build up does not occur until at  $\dot{\gamma} = 0.914 \text{ sec}^{-1}$ . This is in sharp contrast with results using the cone-and-plate platen at the same temperature, which shows an overshoot at shear rates as low as  $0.027 \text{ sec}^{-1}$ . It is generally observed that overshoot occurs in stress-growth at high shear rates. It denotes the point at which the material experiences a maximum strain.

Transient measurements are also affected by the cone angle of the cone-and-plate arrangement. Theoretically, the assumption the cone angle,  $\theta_0$  is to be chosen such that the assumption  $\tan \theta_0 \sim \theta_0$  is valid. This insures the existence of a constant shear rate throughout the melt. Meissner and Huang noted systematic differences in transient shear stress and normal stress measurements as a function of cone angle used. However, Graessley et al. (1977) found no difference in stress growth measurements for 1°, 2°, and 4° cone.









In this study on comparing measurements as a function of the cone angle of 0.552° and 1.982° gave a variation of data of 1.8% which is well within the experimental error. It is thus presumed that the choice of  $\theta_0 = 2^\circ$  introduces no significant error in the transient measurements. The stress relaxation after cessation of shear was also collected using the visicorder on samples used in stress growth tests. The results of these experiments will be presented and analyzed in the following chapter.



# CHAPTER VII

## **RESULTS AND DISCUSSION**

# 7.1 Introduction

The material functions, dynamic viscosity, storage modulus, steady shear viscosity, shear stress growth, and relaxation stress after cessation of shear of a poly(styrene-b-butadiene) with 94.1 wt. % S have been collected as functions of the deformation rate and temperature. These results suggest that there exists a melt transition temperature demarcating the prevalence of two types of block copolymer microstructure. The occurrence of such transition temperature or region will be discussed in Section 7.2, using evidence in the experimental results. We will not use the time-temperature superposition principle in reducing data since such two-phase structure in block copolymer melt have been established (Chung and Gale, 1976; Gounlock and Porter, 1977). In Section 7.3 the rheological results showing the effect of deformation on the microstructure above transition temperature shall be presented and discussed with the view to understanding the underlying microstructure. Next, the rheological results below transition temperature is presented and discussed again with a view to verifying the block copolymer microstructure. In order to test the transient network model developed in Chapter III, two material constants are estimated using



the linear viscoelastic data. Other model parameters shall be computed by fitting model predictions with these functions. The model then will be used to predict the steady and stress growth flow behavior of the block copolymer at T below the transition. It is necessary to restate here that our major focus is on the rheological behavior of the block copolymer at low deformations. This region yields the most differentiating features of block copolymers with respect to their homopolymer and random block copolymer counterparts; it also plays a crucial role in evaluating a network model based on a more realistic chain statistic.

## 7.2 Phase Transition Temperature

The dynamic viscoelastic properties of the block copolymer sample are shown in Figure 7.1 at T of 130°C to 175°C. The reproducibility of these results is good, 5.2% at  $\omega < 0.6 \text{ sec}^{-1}$  and fair, 7-9% over 0.8  $< \omega < 3 \text{ sec}^{-1}$  with 2° cone angle and the stiff torsion bar. As usual, increase in temperature tends to decrease the moduli. At 150°C the dynamic viscosity levels off at about 0.1 sec<sup>-1</sup> but storage modulus as a function of the frequency shows a slope of 1.3 on the log-log scale. On the whole, such behavior is similar to those exhibited by homopolymers where a single phase microstructure is known to exist. At 130°C or lower, the dynamic viscosity does not level off at the lowest frequency tested and a larger deviation of the slope of the dynamic storage modulus vs. frequency from 2 is noted. Next, we evaluate the two temperature regimes for homopolymeric character by applying the Cox-Merz rule defined earlier on the viscoelastic









properties. These results are shown in Figures 7.2, 7.3, and 7.3a. At 150°C as given in Figure 7.2, the complex viscosity is found to be greater than the steady shear viscosity especially at  $\dot{\gamma}$  > 0.1 sec<sup>-1</sup>. However, at  $\dot{\gamma} < .1 \text{ sec}^{-1}$  both functions not only level off, but appear to be approaching each other. The steady shear results show a limiting zero shear viscosity of 1.4 x  $10^5$  P. This compares with a homopolymeric PS having  $\bar{M}_{W}$  = 259,000  $\bar{M}_{W}/\bar{M}_{N}$  = 2.35 at T = 200°C with  $\eta_{o}$  = 4.25 x 10<sup>5</sup> P (Mendelson, 1980). On the whole the deviation from Cox-Merz rule follow a similar trend often shown by homopolymers and random copolymers. A dissimilar deviation from the Cox-Merz rule is found when the complex viscosity, the dynamic viscosity and steady shear viscosity results at 130°C are compared as reported in Figure 7.4 and 7.3a. In Figure 7.3 the largest deviation of the two functions appear at  $\dot{\gamma} < 0.1 \text{ sec}^{-1}$ . Both functions are sensitive to the deformation rate at the low deformation rate region suggesting a more complex microstructure controlling the viscoelastic response. At  $\omega \sim 0.01$  $sec^{-1}$ , the complex viscosity appears to be levelling off even though more data (at  $\omega \sim 10^{-3} \text{ sec}^{-1}$ ) are needed to confirm this assertion. If this is the case, these results suggest the occurrence of a network structure sensitive to the imposed strain history of the material. Figure 7.3a shows the dynamic viscosity, n' to be significantly sensitive to the frequency equivalent to the shear rate range  $0.05 < \gamma$ < 0.3 sec<sup>-1</sup> where a so-called "equilibrium" shear viscosity is attained. At  $\omega < 1.5 \text{ sec}^{-1}$ , n' values are higher than those of n by 18% or less. The strong dependence of  $\eta'$  on  $\omega$  seems to lessen at





Figure 7.2.--Complex and steady viscosity of S-B at 150°C as a function of frequency and shear rate, respectively.





Figure 7.3.--Complex and steady viscosity of S-B at  $130^{\circ}$ C as a function of frequency and shear rate, respectively.








 $\omega \sim 10^{-2} \text{ sec}^{-1}$ . Further data at  $\omega < 10^{-2} \text{ sec}^{-1}$  will be very helpful in establishing whether n' levels off and how this frequency at which this occurs compares with that suggested for  $|n^*|$ .

Since the zero shear limit for 150°C is seen at shear rates comparable to that at which homopolymer  $\eta$  levels off, a single phase microstructure is suggested. For two phase structure, such a limit may be observed only at deformation rates that are order(s) of magnitude lower. Attainment of Newtonian viscosity at such low shear rates implies the prevalence of a network structure sensitive to the applied strain history, that have been attributed to diblock copolymers (Krauss et al., 1971). The transition temperature region for this diblock sample occurs at  $130^{\circ}C < T < 150^{\circ}C$ . This is attributed to a weakening and/or loss of the two-phase structure due to sharp increase in phase miscibility and/or the attainment at or above the transition temperature of an easily disruptible dispersed phase not controlling viscoelastic response and, therefore, leading to Newtonian behavior at low deformation rates. The narrowness of the transition suggests that chain miscibility is at least the major factor since, in the absence of such a phase change, the property changes would be expected to be more gradual.

## 7.3 Viscoelastic Behavior Above the Transition Temperature

Figure 7.4 shows the effect of shear rate on the steady shear viscosity at 150°C. We note here the quick decay of viscosity from Newtonian behavior at higher shear rate. Such behavior is often





Figure 7.4.--Steady shear viscosity function of S-B at 150°C.



associated with high M.W. polydisperse homopolymeric melts. The polydispersity of the continuous PS chains in the sample under study is 1.7. In Figure 7.5 the shear stress growth results are portrayed as normalized values using the constant stress value  $S_{xy/ss}$  as the normalization constant. The curve of  $\dot{\gamma} = 0.0108 \text{ sec}^{-1}$  shows points of inflection at 8 mins. and 16 mins. that are not found in the other curves. The associated error observed for this shear rate between forward and backward rotation was 3-5% at t < 2 min, 12-18% at 2 < t < 12 min. and about 5% at larger times. It is judged that this error may be caused by incomplete relaxation of the test sample in the gap. The other results reported in Figure 7.5, as well as the shear stress growth curves at 130°C had associated errors at 5-8%. On the whole, the trends in result resemble those of homopolymers. We note, however, the occurrance of significant overshoots at much smaller shear rates in contrast to homopolymeric melts (Graessley et al., 1977). Furthermore, these curves depart from linear viscoelastic behavior even at small times. The extent of this departure may be determined by evaluating a relaxation modulus G<sup>O</sup> at different strain rates from the slopes of the normalized growth curves at small times.

$$G^{o} = \lim_{t \to 0} \frac{\frac{S_{xy}^{+} / S_{xy,ss}}{t}}{t}$$

The values computed for G<sup>O</sup> ranged from 0.28 to 0.52 over the range of shear rates studied. Figure 7.6 shows normalized stress relaxation functions at 150°C.











These results showed a decay of stress relaxation to zero similar to those of homopolymers. It is concluded that an entanglement microstructure of the continuous PS chains appears to influence the block copolymer melt at 150°C or higher; however, these results do not exclude the existence of domains above this transition temperature since easily disruptable domains not controlling the viscous response might yield similar results.

The range of temperatures where a two-phase structure manifests in the material has been established at  $T < 150^{\circ}C$ . In keeping with the objective of this study, viscoelastic results of 150°C will not be compared with the transient network model. In the next section, the material functions of 130°C shall be presented and compared with the model having a nonzero "a." In this analysis the tangential shear stress shall be normalized by the constant  $G_0 = n_0 kT$ , the modulus of rubber elasticity, while the shear rate,  $\dot{\gamma}$  and present time, t are normalized by a single relaxation time  $\lambda_{0}$  ( = 1/B\_{0}). It is worth emphasizing here that our interest lies in the low deformation rate region and we seek to predict the material viscoelastic behavior at such a range. Since linear dynamic functions were not obtained at 124°C, it is not possible to predict other material functions at this temperature using our procedure. In this model evaluation we will deal mostly with normalized quantities, i.e., the normalized viscosity, normalized shear rate, in line with definitions given in Chapter V.



## 7.4 Viscoelastic Behavior Below the Transition Temperature

The complex viscosity as a function of frequency, shown in Figure 7.3 has a slope, d log  $|n^*|/dlog\omega(at \omega < 0.1 sec^{-1})$  equal to -0.26 as compared to a value of -0.5 obtained by Ghijsels and Raadson for SBS triblocks. Table 7.1 further illustrates the results of the slopes of n and n' vs.  $\dot{\gamma}$  and  $\omega$  respectively, (see Figure 7.3a).

Table 7.1.--Phase separated block copolymer melt properties

Sample	MW(×10 <sup>-3</sup> )	T°C	dlogn'∕dlogw⁄ < 1	dlogn/dlogý/ <sub>ý &lt; 1</sub>
SBS <sup>a</sup>	11-56-11	150	-0.61	-0.68
sbsb	22-50-22	170	-0.66	-0.66
SBS <sup>b</sup>	14-70-14	170	-0.36	
SB <sup>C</sup>	232-10	130	-0.43	-0.38

<sup>a</sup>Data of Ghijsels and Raadsen (1980).

<sup>D</sup>Data of Arnold and Meier (1970).

<sup>C</sup>This work.

These slopes indicate that the triblocks have more strength than the diblocks (even at higher melt temperatures). Even though the SB diblock has an MW an order of magnitude higher than the SBS triblock, from these slopes the network structure of the triblocks are stronger.

The results of steady shear viscosity of S-B melt sample as a function of shear rate at 130°C and 124°C are reported in Figures 7.7 and 7.8, respectively. The upturn in viscosity occurs at about















0.1 sec<sup>-1</sup> at both temperatures similar to an SBS melt at  $150^{\circ}$ C (Ghijsels and Raadsen). About shear rates of O(1) the viscosity is no longer strongly dependent on the shear rate, but thereafter the material seems to approach the power law region. Upon comparing these curves with the high temperature curves (T > 150°C) we see that the low shear rate response is that of a weak three dimensional micellar network in which the polybutadiene domains acting as junction sites solely influences the viscoelastic response.

Further evidence of the effect of two-phase microstructure can be seen in the shear stress growth curves of Figures 7.9 and 7.10 collected at 130°C. At small times, these curves exhibit higher transient shear stress with lower shear rates, than the corresponding curves at 150°C. It is further observed that the magnitude of the overshoot from the steady state level is higher (0.18) at  $\dot{y}$  = 0.0272  $\sec^{-1}$  than at  $\dot{\gamma} = 0.043 \sec^{-1} (0.12)$ --a feature also present in the SBS data. On comparing these curves with the high temperature counterpart (Figure 7.5), it is clearly evident that a more detailed microstructure behavior is found in such transient flows and more effort should be applied in this area for a better understanding of the microstructure mobility than at steady state conditions. No stress growth responses were obtained at 124°C due to the limitation of the amount of sample. The next curves (Figures 7.11 to 7.13) shows the stress relaxation functions at 130°C and 124°C. Here in contrast to the findings on SBS data which manifests residual stresses, these































functions at all shear rates decay to zero, but at a much slower rate than those of 150°C.

At higher shear rates ( $\dot{\gamma} > 1 \text{ sec}^{-1}$ ), polydispersity of the continuous phase in our sample makes it difficult to determine whether domain flow or entanglement disruption in the continuous phase control the viscoelastic response. Whether domains are completely disrupted by shear deformation and the point to which this occurs may be difficult to establish with rheometry alone. This may be made possible by utilizing electron microscopy with deformed samples as was performed in solid elasticity (Aggarwal et al., 1969). This is outside the scope of this study.

## 7.4.1 Estimation of Model Parameters

The non-Gaussian transient network model presented in Chapter III assumes that the continuous soft phase of the block copolymer is composed of the "most probable" network segment with N sub-units. This demands the knowledge of a single relaxation time  $\lambda_0$ , that is associated with the rate coefficient,  $\beta_0$ , ( $\lambda_0 = 1/\beta_0$ ) of the destruction rate process and the modulus of rubber elasticity,  $G_0$ , (G =  $n_0 kT$ ). In reality, in any polymer matrix, there is a distribution of N and thus multiple relaxation times obtainable from the fluid relaxation spectrum which is often constructed from functions of linear viscoelasticity, G'( $\omega$ ), G''( $\omega$ ), and G<sup>0</sup>(t). It is worthwhile to emphasize that  $G_0$  and  $\lambda_0$  are not to be considered as adjustable parameters in the model.



Even in homopolymer rheology the use of a single relaxation time in viscoelastic models can only predict data in a restricted range. Generally, a large relaxation time characterizes long time behavior and is applicable with low deformation rates predictions while a small relaxation time predicts higher order deformation rate range. Typical dynamic shear moduli of narrow M.W. distribution samples display two sets of relaxation times corresponding to two relaxation mechanisms separated in the time scale. One set of relaxation times associated with the transition in the high frequency region; another set associated with the entangelment slippage in the low frequency region which appear as a peak of  $G''(\omega)$ . A characteristic relaxation time associated with long-range motions of homopolymers is estimated by the inverse of the frequency at which the peak of the loss modulus,  $G''(\omega)$  occurs (Onogi et al., 1970). However, in polydisperse samples there is often an overlap between these sets of relaxations so that the peak in G'' appears as a plateau. Further, the slope of G'' vs.  $\omega$  is close to unity on a logarithmic scale for homopolymers. Gouinlock and Porter have identified that the departure from 1 of this slope in block copolymer melts is due to the domain morphology. Ghijsels and Raadsen also found the presence of maximum in the loss factor tan  $\delta$  (= G''/G') and related this with domain activity. These points were considered as one of the criteria in determining  ${\rm G}_{\rm o}$  and  $\lambda_{\rm o}$  . The other criterion is based on


the point where the upturn of viscosity occurs in the experimental steady shear viscosity. Such an upturn also occurs in the predicted curves based on the former criteria, but they were plotted as a function of  $\lambda_{\alpha}\dot{\gamma}$ . By comparing these points  $\lambda_{\alpha}$  can be evaluated.

Figure 7.14 shows the results of G''( $\omega$ ) and loss factor as a function of frequency. The deviation of the slope of G'' vs  $\omega$  from 1 is not very discernible but the loss factor shows a pronounced transition at 0.25 sec<sup>-1</sup>. From this we obtained the material constants shown in Table 7.2. Also using the refining criteria a second set of relaxation times are evaluated and listed in Table 7.2.

Method 1	Method 2
$\lambda_{o}(sec)$ 4	1.25
$G_0(\frac{dynes}{cm^2})$ 6.8 x 10 <sup>4<sup>b</sup></sup>	2.16 x 10 <sup>5</sup>
$a_{\lambda_0} = 1/\omega_t$	
${}^{b}G_{0} \cong  G^{\star}(\omega_{t}) $	

Table 7.2.--Material constants from experimental data

Values of the segment repulsion range parameter "a," the destruction rate coefficient " $\varepsilon$ " and the slip factor  $\xi$  for Method 1 are determined by fitting the data of complex viscosity with Equations (5.26 and 5.27). The result of the best fit with data is given in Figure 7.15. In Method 2 it was necessary to refit the data with











Figure 7.15.--Evaluation of model parameters using linear viscoelastic functions (dimensionless). o = data, --- = model fit Equations (5.26) and (5.27). T - 130°C.

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the new set of constants and the results are shown in Figure 7.16. These results are least sensitive to the parameter " $\varepsilon$ ", the range 0.001 <  $\varepsilon$  < 0.007 gave practically the same results. This parameter is best ascertained with strong flows, e.g., in uniaxial transient extensional flows.

# 7.4.2 Experimental Evaluation of the Transient Network Model

Without any further adjustments in the parameters, steady and transient shear results are predicted by using Equation (5.17) and portrayed on the accompanying plots as a normalized viscosity  $(\tilde{n} (n/G_{o}\lambda_{o}))$  as a function of normalized shear rate,  $(\lambda_{o}\dot{\gamma})$  and normalized transient shear stress  $(S_{xy}^{+}/S_{xy/ss})$  as a function of normalized time  $(t/\lambda_{o})$ , respectively.

# 7.4.3 Steady State Predictions

The model predicts correctly the overall trends of the steady shear data as shown in Figure 7.17 and 7.18. In Figure 7.17 the quantitative agreement between experimental results and theory is poor to fair in the range  $0.02 < \tilde{\gamma} < 0.18$  where a 40 - 0% deviation is noted. The theoretical prediction of the range  $0.18 < \tilde{\gamma} < 12$  is satisfactory with about 5% derivation.

On the other hand, using Method 2 having the same order of magnitude of the relaxation time as in 1 improved results significantly at the range of interest (see Figure 7.18). In the range  $0.006 < \tilde{\dot{\gamma}} < 0.1$ , the theoretical prediction of results is excellent having under 3% deviation. At moderate dimensionless shear rates of















Figure 7.18.--Comparison of steady shear viscosity with model  $\epsilon$  = 0.005,  $\xi$  = 0.05, a = 0.55,  $\lambda_o$  = 1.25 sec.



0.1 to 1, the prediction is fair to poor with 3-36% deviation and unsatisfactory at  $\tilde{\dot{y}} > 1$  with 40% deviation. The slope of viscosity as a function of shear rate at  $\dot{y} < 0.1 \text{ sec}^{-1}$  is predicted very accurately. It is concluded that the loss factor cannot serve as a guide in obtaining a characteristic relaxation time. At the large shear rate range, it is unreasonable to expect a good fit in the light of the polydispersity of the PS phase ( $\bar{M}_w/\bar{M}_n = 1.7$ ).

#### 7.4.4 Transient Predictions

Comparison of the model predictions with the data for stress growth are given in Figures 7.19 to 7.24 at low shear rates using the two procedures. Here the agreement between data and theory is rather fair, especially if we remember that all the parameters were determined from data of small amplitude oscillatory shear flow only. On the whole, the model prediction with  $\lambda_{_{\rm O}}$  = 125 sec is good at the lowest shear rates (0 - 15% deviation) and excellent at strains less than 9.001 (under 3% deviation). On the other hand, the high relaxation time model appears superior at higher shear rates for all models significant deviations occur at intermediate times. A weakness in the model is its failure to show an overshoot at low shear rates. Such overshoots are shown at higher shear rates, as illustrated in Figure 7.25 on page 132. The positions of the overshoot, t<sub>c</sub> can be correlated most directly with the total strain as many workers have noted previously. Figure 7.25 shows the strain at stress peak as a function of shear rate for both data and model predictions. Overshoots are predicted by the model only









Figure 7.20.--Comparison of stress growth at 130°C with model  $\lambda$  = 1.25; a = 0.55,  $\xi$  = 0.05 0 = data; \_\_\_\_ model.















Figure 7.23.--Comparison of stress growth at 130°C with model of  $\lambda_{\rm O}$  = 4 sec.











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at  $\dot{\gamma} > 0.25 \text{ sec}^{-1}$ . The predicted peaks occur at strains insensitive to the shear rate and are determined by the slip factor  $\xi$ .

A constant value for this strain of about three has been reported experimentally for a homopolymeric melt (Osaki et al., 1976). Graessley et al. (1977) have studied this quantity at low shear rates with homopolymer samples and indicated that insensitivity of strain at stress peak, to shear rate is associated with materials that possess a broad relaxation spectrum.

It is noted that the foregoing feature and the fact that the magnitudes of the overshoot for transient stresses at smaller shear rates are larger than those at large shear rates (which is not predicted by this model) presents a severe test for viscoelastic models. This will have to be addressed with only <u>one</u> relaxation time if the exact physics of two-phase microstructure mobility is to be comprehended.



# CHAPTER VIII

### CONCLUSION AND RECOMMENDATION

# 8.1 Conclusion

A new kinetic network model has been developed and evaluated for the rheology of block copolymer melts and polymer composites with spherical microdomains. This model involves in addition to the readily determined relaxation time  $\lambda$  and modulus G<sub>0</sub>, three parameters: "a" describes the range of repuslion between segments of matrix attached to spherical domains, " $\varepsilon$ " describes the dependence of junction destruction rate on the conformation of the continuous random phase and ( $\xi$ ) accounts for a slip between the fluid and the network junctions. The model is used to compute the material functions in uniaxial extension, simple shear and small-amplitude oscillatory shear flows. Experimental data on elongation are obtained from the literature while data on shear flows are obtained in this work.

In uniaxial extension, the model predicts the Trouton viscosity at normalized strain rates,  $\dot{\Gamma}$  of O(1) if spherical domains are absent (a = 0). This is in good accord with data of Mundstedt and Laun (1978). If spherical domains are present (i.e., a  $\neq$  0), the model predicts a non-constant elongational viscosity at the low strain rates, but a smaller maximum viscosity at higher strain rates. Comparison of these calculations with data of ABS melt (Mundstëdt)



reveals that the repulsion measure "a" determines the apparent yield stress observed at low elongation rates. The destruction rate parameter " $\varepsilon$ " determines the level of the maximum elongational viscosity at steady state as well as the stress overshoot observed at higher rates in stress growth experiments. However, no data for elongational flows at large strain rates are available to evaluate the model suitability in this region.

The viscoelastic properties of a diblock copolymer, poly-(styrene-b-butadiene) of high thermoplastic content have been studied experimentally in this work. The material is composed of uniform spherical domains of polybutadiene randomly dispersed in a polystyrene matrix as confirmed by electron microscopy on solvent cast samples. The melt for rheological study was obtained from carefully annealed solvent cast samples (toluene as solvent) leading to an associated error of 7 to 10% in material functions at low shear rates. An associated error of 12-20% have been reported by Ghijsels and Raadsen in melts starting from crumbs in this region.

Microphase separations appear to start as the temperature is lowered from 150°C. At 150°C or above the material exhibits Newtonian behavior in the steady shear viscosity and the complex viscosity at low deformation rates and appears to obey the Cox-Merz rule. At 130°C or below the complex viscosity is higher than the corresponding steady viscosity, except at very low strain rates  $(\dot{\gamma} < 0.05)$ .

At 130°C and 124°C a significant upturn of steady viscosity occurs for shear rates lower than 0.1  $\sec^{-1}$ , similar to the SBS melt;


however, the slope d log  $\eta|d \log \dot{\gamma}|_{\dot{\gamma} \to 0}$  is much less for the present SB melt. In contrast with homopolymers and random copolymers, a significant transient stress overshoot is observed in the shear growth experiments at shear rates as low as 0.02 sec<sup>-1</sup>. It is further noted that the height of this overshoot diminishes with increasing shear rates. Contrary to the SBS data, no residual shear stresses are observed in the SB data in shear stress relaxation experiments confirming the assertion that only apparent yield stresses are exhibited by the SB melt.

All model parameters have been found by fitting data of oscillatory shear experiments, using two procedures to obtain the characteristic relaxation time. The overall trends in the data have been predicted very well, in the range of interest. Quantitatively, the predicted shear viscosity is very sensitive to the choice of the single relaxation time at the low shear rate range. The model also fails to show an overshoot in stress growth at shear rates less than  $0.1 \text{ sec}^{-1}$ . These deficiencies are largely due to assuming that only a single relaxation time controls the entire material viscoelastic behavior.

## 8.2 Recommendations for Further Study

The stress constitutive equation presented in equation (3.12) is written for a single relaxation time. To take into account the distribution in N, especially in polydisperse samples, we must allow for multiple relaxation times. Since in the network theory no interchain correlation is taken into account, each active network segment

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therefore contributes to the stress additively. The overall stress then becomes:

$$\underbrace{S}_{i} = \sum_{i} \underbrace{S}_{i}$$
(9.1)

where  $\underline{S}_{i}$  replaces  $\underline{S}_{i}$ , N becomes N<sub>i</sub>, and f becomes f<sub>i</sub> in equation 3.12. The consequence of this in the specific stress relations is that G<sub>o</sub> and  $\lambda_{o}(-1/\beta_{o})$  are replaced by G<sub>i</sub> and  $\lambda_{i}$  respectively obtainable using the material relaxation spectrum H( $\lambda_{i}$ ) through these relations (Phan Thien and Tanner, 1978).

$$\lambda_{i} = \begin{cases} H(\lambda)\lambda d\lambda \\ H(\lambda)d\lambda \end{cases}$$
(9.2)

$$G_{i} = \frac{\int H(\lambda) d\lambda}{\lambda_{i}}$$
(9.3)

Here the relaxation spectrum is subdivided into intervals, such that each interval is a wedge spectrum to facilitate the numerical procedure. The relaxation spectrum can be computed from the linear viscoelastic data G'( $\omega$ ), G''( $\omega$ ) and G(t) by the standard method (Ferry, 1961). The long-time behavior of block copolymers is of utmost significance in gaining the optimum relaxation spectrum, thus it is necessary to collect G'( $\omega$ ) and G''( $\omega$ ) data at frequencies as low as  $10^{-4} \text{ s}^{-1}$ . Such ranges are achievable by using the cone-and-plate platen with several cone angles, which were unavailable at the time of experimentation.



For a complete knowledge of melt rheological behavior of block copolymers, steady and transient normal stress data is highly needed. Chung and Gale and Kraus and coworkers (1971) have associated the material exuding from the shearing gap at low deformation rates with high elasticity developed in the material, but did not report any normal stress data. In the WRG the shearing gap is significantly influenced by the lack of vertical stiffness of the apparatus. This lack of stiffness affects both steady and transient normal stress response measurements of molten polymers (Huang, 1976). Modifications to correct for this problem were given by Hansen (1974) and is recommended for this equipment. The use of Mooney platens of D < 5 cm along with a steady piezoelectric load cell is further suggested.

Curtis and Bird (1981) have presented a reptation theory for melts starting from the general phase space formalism (Bird et al., 1977). They modeled the macromolecules as Kramers freely chain (with  $\bar{N}$  beads and  $\bar{N}$ -1 rods of length a) used a nonisotropic version of Stokes law to describe the drag force on a bead as it moves through the melt. The model contains four parameters, the number of beads,  $\bar{N}$ , a drag coefficient  $\zeta$ , a link tension coefficient  $\varepsilon_{\rm B}$  and a chain constraint exponent  $\beta_{\rm C}$ . They report that the model yields  $n_{\rm O} \sim M^{3+\beta}c$ . and  $\psi_{1,0} \sim M^{6+2\beta}c$  which empares well with homopolymeric data if  $\beta_{\rm C} \sim 0.3 - 0.5$ .

Modelling of polymer molecules as beads joined by elastic or rigid, connectors is attractive for block copolymeric systems



with spherical domains. However, the Curtiss-Bird theory does not allow us to compute the relevant chain segment distribution function. A recommended route would be the concept of configuration-dependent molecular mobility tailored by Giesekus (1982). He associated a tensorial drag coefficient  $\underline{z}_i$  with the force,  $\underline{f}_i$ , experienced by an ith bead. This drag tensor does not depend on the actual configuration of the molecule, but only on the average configuration of all the molecules. After some manipulations with the excess stress relation, a configuration tensor  $\underline{b}_i$  can be defined which maps the actual molecular configuration from the equilibrium configuration as

$$< r_{i}, r_{i} > = b_{i} \cdot < r_{i}^{0}, r_{i}^{0} > = 1/3 < r_{i}^{0} \cdot r_{i}^{0} > b_{i}^{0}$$

This tensor may be understood to be a measure of deformation of an elastic continuum, note in a strict sense of a material continuum, but in a statistical sense represents only the configurational states of a polymer chain.

With this assumption one may no longer assign individual  $b_i$ and  $\zeta$  to every position vector  $\dot{r}_i$ . Instead the whole set of beads (i = 1 . . .; N) can be classified into classes (K = 1, . . . K) with  $n_K$  beads per unit volume with a common configuration tensor  $b_{K}$  and a drag tensor  $\zeta_k$  for each class. The class K = 1 leads to various Lodgean type models with appropriate assumptions on  $b_{\tilde{k}}$ , but classification of the total number of structure elements into K classes may



encompass systems such as block or graft copolymers. Here only detailed modelling of  $b_{\approx K}$  is required to generate the constitutive equation.

In this study the major focus was on spherical domain block copolymer systems, but as shown in Table 2.1 cylindrical and lamellar type systems possess superior rheological properties. Odani et al. (1977) have studied diffusion, solution, and permeation behavior for a series of inert gases in block copolymer films having these morphologies thinted that they were excellent models for understanding the relationship between the morphology and transport properties heterogeneous polymeric media. The preparative methods of these block copolymers have been much refined by the Dow Chemical Company, Midland). It is recommended that rheological and transport studies of block copolymers of higher block composition be undertaken.



APPENDICES





APPENDIX A

UNIAXIAL EXTENSIONAL FLOW--TRANSFORMATIONS AND CALCULATIONS



## APPENDIX A

# UNIAXIAL EXTENSIONAL FLOW--TRANSFORMATIONS AND CALCULATIONS

The solution of  $(4_3)$  using the method of characteristics is given by:

$$f(x, y, z, t) = f(x_0, y_0, z_0) \exp\left[-\int_0^t \beta(x_0 \exp(\hat{r} t'), y_0 \exp(-\hat{r} t'/2), z_0 \exp(-\hat{r} t'/2))dt'\right]$$

$$+ \int_0^t G(x_0 \exp(\hat{r} t'), y_0 \exp(-\hat{r} t'/2), z_0 \exp(-\hat{r} t'/2), N) \exp\left[-\int_0^t dt'' t' \right]$$

$$\times \beta(x_0 \exp(\hat{r} t'), y_0 \exp(-\hat{r} t'/2), z_0 \exp(-\hat{r} t'/2)) dt' \qquad (1-A)$$

A two-step change of variables similar to that of Fuller and Leal (1981), but for uniaxial extension is performed on (1-A) to introduce definite limits on the integrals. First t' and t'' are changed to x' =  $x_0 \exp(\hat{T}t')$  and x'' =  $x_0 \exp(\hat{T}t'')$  respectively; then x' to  $\bar{x}$ using x' =  $T\bar{x} + x\exp(-\hat{T}t)$  where T =  $1-\exp(-\hat{T}t)$ . Further,  $\bar{y} = y(x/x')^{\frac{1}{2}}$ ,  $\bar{z} = z(x/x')^{\frac{1}{2}}$ ,  $\theta' = x''/\bar{x}$  to obtain a final expression for f(x,y,z,t)as

$$f(x, y, z, t) = f_0(x exp(-\hat{r}t), y exp(\hat{r}t/2), z exp(\hat{r}t/2))$$
$$exp\left[-I_{\hat{r}}\left(\frac{\beta[(T + \theta e x p(-\hat{r}t))\overline{x}, \overline{y}, \overline{z}]d\theta}{\theta(T + \theta e x p(-\hat{r}t))}\right)$$



$$+ \prod_{\hat{T}} \left\{ \begin{array}{l} \ddot{d}\theta G \left[ \left[ \overline{T} + \theta \exp(-\tilde{\Gamma}t) \right] \overline{x}, \overline{y}, \overline{z} \right] \\ \theta \left( \overline{T} + \theta \exp(-\tilde{\Gamma}t) \right) \end{array} \right\}$$

$$\exp \left[ - \prod_{\hat{T}} \left[ \begin{array}{l} \theta \\ \beta \left[ \theta \overline{x}, \overline{y} \left( \overline{T} + \theta \exp(-\tilde{\Gamma}t) \right) \right] \right] \left( \overline{T} + \theta \exp(-\tilde{\Gamma}t) \right) \right] d\theta' \theta' \right]$$

$$(2-A)$$

 $I_1$  and  $I_2$  of equation (4.7) may be written in spherical polay coordinates as

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•

$$I_{1} = \int_{0}^{\pi} F(\psi, \dot{\Gamma}, \tau) \cos^{2}\psi \sin\psi d\psi$$
(3-A)  
$$I_{2} = \int_{0}^{\pi} F(\psi, \dot{\Gamma}, \tau) \sin^{3}\psi d\psi$$
(4-A)

where

$$F(\psi, \dot{\Gamma}, \tau) = \frac{1}{1 + 2a} \left[ \frac{3/2}{(\lambda_{1}^{4}\cos^{3}\psi + \lambda_{2}^{2}\sin^{2}\psi)} \frac{5}{2} + \frac{3a}{(\lambda_{1}^{2}\cos^{2}\psi + \lambda_{2}^{2}\sin^{2}\psi)^{2}} \frac{3a}{(\lambda_{1}^{2}\cos^{2}\psi + \lambda_{2}^{2}\sin^{2}\psi)^{2}} + \frac{2a^{2}}{(\lambda_{1}^{2}\cos^{2}\psi + \lambda_{2}^{2}\sin^{2}\psi)^{2}} \frac{1}{(\lambda_{1}^{2}\cos^{2}\psi + \lambda_{2}^{2}\sin^{2}\psi)^{2}} \frac{1}{(\lambda_{1}^{2}\cos^{2}\psi + \lambda_{2}^{2}\sin^{2}\psi)^{2}} \right] \gamma$$

$$= \frac{1}{(\lambda_{1}^{2}\cos^{2}\psi + \lambda_{2}^{2}\sin^{2}\psi)^{2}} \frac{1}{(\lambda_{1}^{2}\cos^{2}\psi + \lambda_{2}^{2}\sin^{2}\psi)^{2}} \gamma$$

$$Y = \exp -2a \left[ \frac{\lambda_{1}^{2}\cos^{2}\psi + \lambda_{2}^{2}\sin^{2}\psi}{\lambda_{3}^{2}\cos^{2}\psi + \lambda_{4}^{2}\sin^{2}\psi} \right] \frac{1}{2}$$

$$\lambda_{1} = \left[ e^{-2\dot{\Gamma}\tau} + \frac{\varepsilon}{2\dot{\Gamma}} \left( 1 - e^{-2\dot{\Gamma}\tau} \right) \right]^{\frac{1}{2}}$$

$$\lambda_{2} = \left[ e^{\dot{\Gamma}\tau} + \frac{\varepsilon}{\dot{\Gamma}} \left( e^{\dot{\Gamma}\tau} - 1 \right) \right]^{\frac{1}{2}}$$

$$\lambda_{3} = e^{-\dot{\Gamma}\tau}, \lambda_{4} = e^{\dot{\Gamma}\tau/2}$$

$$(6-A)$$

$$\tau = \beta_0 t$$
,  $\tau' = \beta_0 (t - t')$  and  $\dot{\Gamma} = \hat{\Gamma} / \beta_0$ 

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By substituting w = tan  $\psi$  in the above equations, we obtain

$$I_{1} - I_{2} = \int_{0}^{\infty} dw (2 - w) \left[ \frac{3/4}{\lambda_{1}^{2} + \lambda_{2}^{2} w} \right]_{2}^{2} (\frac{3}{\lambda_{1}^{2} + \lambda_{2}^{2} w})^{3/2} (\lambda_{3}^{2} + \lambda_{4}^{2} w) + \frac{3/2a}{(\lambda_{1}^{2} + \lambda_{2}^{2} w)^{3/2} (\lambda_{3}^{2} + \lambda_{4}^{2} w)^{2} (\lambda_{3}^{2} + \lambda_{4}^{2} w)$$

Then letting

.

$$v^{2} = \frac{1 + (\lambda_{2}/\lambda_{1})^{2} w}{1 + (\lambda_{4}/\lambda_{3})^{2} w}$$
, (8-A)

we obtain with integration by parts,

$$I_{1} = \frac{1}{\lambda_{1}^{3}} \frac{1}{\lambda_{2}^{2}} \left[ e^{-2a/\delta} + \frac{2a}{(1-\delta^{2})^{3/2}} \int_{1}^{1/\delta} \frac{(v^{2}-1)^{1/2}}{(v^{2}-1)^{1/2}} + 2a(1/v^{2}-1/2) e^{-2av} dv \right]$$

$$I_{2} = \frac{1}{\lambda_{1}} \frac{1}{\lambda_{2}^{4}} \left[ e^{-2a/\delta} + \frac{a}{(1-\delta^{2})^{3/2}} \int_{1}^{1/\delta} \frac{e^{-2av}}{(v^{2}-1)^{1/2}} \frac{(2/v^{3}+(v^{2}(2-3\delta^{2})-1))}{v} - a(1-2\delta^{2}-\delta^{2}v^{2}-2/v^{2}) dv \right]$$

$$(10-A)$$

where  $\delta \stackrel{*}{=} \lambda_3 / \lambda_1 = \left[1 + \frac{\varepsilon}{2\dot{\Gamma}} \left(e^{2\dot{\Gamma}\tau} - 1\right)\right]^{-\frac{1}{2}}$ 

The integrand in (8-A) has a singularity at v - 1; setting r - v + 1 allows us to evaluate the integral.

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APPENDIX B

SIMPLE STEADY SHEAR FLOWS--TRANSFORMATIONS AND CALCULATIONS



### APPENDIX B

## SIMPLE STEADY SHEAR FLOWS--TRANSFORMATIONS AND CALCULATIONS

The solution of eg. (5.4) by the method of characteristics, in  $\rho$  ( $\rho$ , $\eta$ ,z) coordinates is given by:

$$f(\rho, \eta, z, t) = f_{0}(\rho_{0}, \eta_{0} z, t) \exp\left[-\int_{0}^{t} dt'\hat{\beta}(\rho_{0} \exp(\frac{i\tilde{m}}{2}t'), \eta_{0} \exp(-i\tilde{m}t'/2), z, N)\right]$$

$$+ \int_{0}^{t} dt'\hat{G}(\rho_{0} \exp(\frac{i\tilde{m}}{2}t'), \eta_{0} \exp(-\frac{i\tilde{m}}{2}t'), z, N) \exp\left[-\int_{0}^{t} dt'' + \int_{0}^{t} dt' + \int_{0}^$$

An identical change of variable scheme as in Appendix A is next undertaken except that these are in the transformed coordinates  $\rho(\rho,\eta,z)$ , i.e., t' and t'' are changed to  $\rho' = \rho_0 \exp(i\tilde{m}t')$  and  $\tilde{\rho}'' = \rho_0 \exp(i\tilde{m}t'')$  respectively; then  $\rho'$  to  $\bar{\rho}$  using  $\rho' = T_p + \rho \exp(-i\tilde{m}t)$  where T = 1-exp(-i $\tilde{m}t$ ). Also  $\bar{\eta} = n(\rho/\rho')$   $\bar{z} = z$ ,  $\theta = \rho/\bar{\rho}$ and  $\theta' = \rho''/\bar{\rho}$  to obtain a generalized moment expression as



$$= det(\underline{T}) \left[ \iint_{-\infty}^{\infty} d\rho dn dzg(\rho,n,z) f_{0}(exp(-\frac{i\tilde{m}}{2}t),nexp(\frac{imt}{2},z) + exp(\frac{imt}{2},z) \right] \\ \times exp\left[ \frac{-2T}{i\tilde{m}} \int_{1}^{\infty} \beta \frac{\left[ (T + \theta exp(-\frac{im}{2}t))\bar{\rho},\bar{n},z \right] d\theta}{\theta(T + \theta exp(-\frac{i\tilde{m}}{2}t))} \right] \\ + \frac{2T}{i\tilde{m}} \iiint_{-\infty}^{\infty} d\rho dn dzg(\rho,n,z) \int_{1}^{\infty} \frac{d\theta G((T + \theta exp(-\frac{i\tilde{m}}{2}t)\bar{\rho},\bar{n},z)}{\theta(T + \theta exp(-\frac{i\tilde{m}}{2}t))} \\ \times exp\left[ -\frac{1}{i\tilde{m}} \int_{0}^{\theta} \hat{\beta}(\theta'\rho,\bar{n},\frac{(T + \theta exp(-\frac{im}{2}t))}{2},z,N) \frac{d\theta'}{\theta'} \right] \right]$$
(B-2)

All moments < $\rho^2$ >, < $\eta^2$ >, < $\rho\eta$ >, < $\rho^2/R^4$ >, < $\eta^2/R^4$ > and < $\rho\eta/R^4$ > are generated by eq. (B-2). Since in uniaxial shear flows no deformation occurs in z-direction, z is arbitrarily set to zero, then these moment integrals are evaluated as exemplified by < $\rho^2$ > integral

$$<\rho^2> = det(T) \frac{C}{\beta_0} (\frac{3N}{2\pi}) e^{-\tau} \iint_{-\infty}^{\infty} d\rho d\eta \rho^2 exp \left[ -\frac{3N}{2} (\lambda^2_1 \rho^2 - 2W\rho\eta q + \lambda_2^2 \eta^2) \right]$$

$$-\frac{2a^2/3N}{\lambda_3^2\rho^2-2W\rho\eta+\lambda_4^2\nu^2}$$



$$\int_{0}^{T} d\tau' e^{-\tau'} \iint_{-\infty}^{\infty} d\rho d\eta exp \left[ -\frac{3N}{2} (\lambda_{1}^{'2} \rho^{2} - 2Wq' \rho \eta + \lambda_{2}^{'2} \eta^{2}) - \frac{2a^{2}/3N}{\lambda_{3}^{'2} \rho^{2} - 2W\rho \eta + \lambda_{4}^{'2} \eta^{2}} \right]$$
(B-3)

Where

$$\lambda_{1} = (e^{-im\tau} + \frac{\varepsilon}{im} (1 - e^{-m\tau}))^{\frac{1}{2}}$$

$$\lambda_{2} = (e^{im\tau} + \frac{\varepsilon}{im} (e^{im\tau} - 1))^{\frac{1}{2}}, \lambda_{4}^{2} = e^{im\tau}$$

$$q = 1 + \varepsilon\tau, \lambda_{3}^{2} = e^{-im\tau}$$

$$m = \tilde{m}/\beta_{0}, \tau = \beta_{0}t \text{ and } \tau' = \beta_{0}(t - t')$$

$$\tilde{\tilde{Y}} = \tilde{Y}/\beta_{0}$$
(B-4)

It is noted here that  $\lambda$ 's in 2nd term of eq(B-2) are defined as in eq.(B-4), however, they are functions of elapsed time,  $\tau$ '.

Next the  $\rho(\rho,\eta)$  frame is transformed into cylindrical polar coordinates  $h(d,\psi)$ . On intergrating out the radical component d, eq. (B-4) becomes

$$<\rho^{2}> = \det(\underline{T})(\frac{C}{\beta_{0}})(\frac{3N}{2\pi}) \{ e^{-\tau} \int_{0}^{2\pi} I(\lambda,\psi) \sin^{2}\psi d\psi + \int_{0}^{\tau} d\tau' e^{-\tau'} \int_{0}^{2\pi} I(\lambda,\psi) \sin^{2}\psi d\psi \}$$
(B-5)



where

$$\begin{split} I(\lambda,\psi) &= \left(\frac{4a^2}{9N^2}\right) \; \frac{K_2(\mu)}{\left(\lambda_1^2 \sin^2\psi - 2Wq\sin\psi\cos\psi + \lambda_2^2\cos^2\psi\right)\left(\lambda_3^2 \sin^2\psi - 2\sin\psi\cos\psi + \lambda_4^2\cos^2\psi\right)} \\ K_2(\mu) \; \text{is a 2nd order Bessel function, and} \end{split}$$

$$\mu = 2a\left(\frac{\lambda_{1}^{2}\sin\psi - 2Wq\sin\psi\cos\psi + \lambda_{2}^{2}\cos^{2}\psi}{\lambda_{3}^{2}\sin\psi - 2W\sin\psi\cos\psi + \lambda_{1}^{2}\cos^{2}\psi}\right)^{\frac{1}{2}}$$

Since a <0(1),  $\mu$  is small from the  $\lambda$  expressions. Then the series for the Bessel function of integral order and of the 3rd kind is utilized in order to completely integrate out the coordinate variable, i.e.,

$$\begin{split} \kappa_{n}(\mu) &= \frac{1}{2} \sum_{\Sigma} (-1)^{k} \frac{(n-k-1)!}{k! (\mu/2)^{n-2k}} + (-1)^{n+1} \sum_{\Sigma} \frac{(\mu/2)^{n+2k} [\ln \mu/2 - \frac{1}{2} \Psi(k+1)]}{k=0} \\ &\quad -\frac{1}{2} \Psi(n+k+1)] \end{split} \tag{B-6}$$

where  $\Psi(.)$  is the Euler's psi function.

Thus applying eq. (B-6) to eq. (5-1) we obtain

$$\begin{split} I(\theta,\tau) &= \frac{1}{\pi} \int_{0}^{2\pi} \int_{0}^{4\pi} \frac{1}{\lambda_{1}^{2} \sin^{2}\psi - 2Wq \sin\psi \cos\psi + \lambda_{2}^{2} \cos^{2}\psi)^{2}} \\ &- \frac{a^{2}}{(\lambda_{1}^{2} \sin^{2}\psi - 2q \sin\psi \cos\psi + \lambda_{2}^{2} \cos^{2}\psi)(\lambda_{3}^{2} \sin^{2}\psi - 2W \sin\psi \cos\psi + \lambda_{4}^{2} \cos^{2}\psi)} \\ &+ 0 \left(a^{4}\right) \end{split} \tag{B-7}$$

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The first term in Eq (B-7) is analytically integrable, but the second term is integrated by the method of partial fraction to yield a final expression of  $I(\lambda)$  as

$$I(\lambda) = \frac{\lambda_2^2}{(\lambda_1^2 \lambda_2^2 - W^2 q^2)^{3/2}} - \frac{2a^2 (B_1 \lambda_2^2 - A_1 W q)}{\lambda_1^2 (\lambda_1^2 \lambda_2^2 - W^2 q^2)^{1/2}}$$
(B-8)

where

$$B_{1} = - (\lambda_{1}^{2}\lambda_{2}^{2} - \lambda_{2}^{4})/C$$
$$A_{1} = -2W(\lambda_{1}^{2}\lambda_{2}^{2} - \lambda_{4}^{2}q)/C$$

and

$$C = 4W^{2}(\lambda_{1}^{2}\lambda_{2}^{2} - q(\lambda_{2}^{2}\lambda_{3}^{2} + \lambda_{1}^{2}\lambda_{4}^{2}) + q^{2}) - (2\lambda_{1}^{2}\lambda_{2}^{2} - (\lambda_{2}^{4}\lambda_{3}^{4} + \lambda_{1}^{4}\lambda_{4}^{4}))$$

Thus the moment integral  $<\!\rho^2\!>$  is obtained as

$$<_{\rho^{2}>} = \frac{n}{3N} \left( \frac{e^{2a}}{1+2a} \right) \det(\mathsf{T}) \left[ I(\lambda) e^{-\tau} + \int_{0}^{\tau} e^{-\tau'} I(\lambda') d\tau' \right]$$
(B-9)



#### APPENDIX C

### OSCILLATORY SHEAR FLOWS--TRANSFORMATIONS AND CALCULATIONS

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#### APPENDIX C

### OSCILLATORY SHEAR FLOWS--TRANSFORMATIONS AND CALCULATIONS

The transformation to the sinusoidal domain with  $u = \sin \omega t$ after the characteristics of eq. (5.21) have been defined gives a slightly different o.d.e. of the form

$$\frac{df}{du} + \frac{\hat{\beta}f}{(1-u^2)^{\frac{1}{2}}} = \frac{\hat{G}}{(1-u^2)^{\frac{1}{2}}}$$
(C-1)

The solution of this by method of characteristics is

$$\begin{split} f(\rho,\eta,z,u) &= f_{0}(\rho_{0},\omega_{0},z_{0})exp - \int_{0}^{u} \frac{du'\hat{\beta}}{\omega(1-u'^{2})^{\frac{1}{2}}} (\rho_{0}exp(\frac{i\overline{m}_{0}u'}{2\omega}), nexp(\frac{-i\overline{m}_{0}u'}{2\omega}), z_{0}) \\ &+ \int_{0}^{\sin^{-1}u} \frac{du'\hat{\beta}}{(1-u'^{2})^{\frac{1}{2}}\omega} (\rho_{0}exp(\frac{i\overline{m}_{0}u'}{2\omega}), \eta_{0}exp(\frac{-i\overline{m}_{0}u'}{2\omega}), z_{0}) \\ &\times exp \left[ - \int_{u'}^{u} du''\hat{\beta}(\rho_{0}exp(\frac{i\overline{m}_{u'}'}{2\omega}), \eta_{0}exp(\frac{-i\overline{m}_{0}u''}{2\omega}), z_{0}) \right]$$
(C-2)

Using transformations identical to Appendix B, except the independent variable is u' instead of t'. The moment integral is obtained as


$$\langle g(\rho,\eta,z) \rangle = det(\tilde{T}) \qquad \iiint_{-\infty}^{\infty} d\rho d\eta dz g(\rho,\eta,z) f_0 \left[ \rho exp(\frac{-i\tilde{m}_0^u}{\omega}), \eta exp(\frac{-i\tilde{m}_0^u}{\omega}), z \right]$$

$$x \exp \left[ -\frac{T}{(im_{o}\omega)} \int_{1}^{\infty} \hat{\beta} \left[ \frac{(T+\theta \exp(-\frac{i\tilde{m}_{o}^{U}}{\omega})\tilde{\rho},\tilde{\eta},z) d\theta}{\theta(T+\theta \exp(\frac{-i\tilde{m}_{o}^{U}}{\omega})) \left[ 1+u^{2} - \frac{\omega \ln}{i\tilde{m}_{o}} \left( \frac{(T+\theta \exp(\frac{im_{o}u}{\omega})}{\theta} \right) 2 \right]^{\frac{1}{2}} \right]$$

$$+ \frac{T_{\omega}}{i\tilde{m}_{o}} \iiint_{-\infty}^{\infty} d\rho d\eta dz g(\rho,\eta,z) \int_{1}^{\infty} \frac{d\theta \widehat{G}((T+\theta exp(-\frac{i\tilde{m}_{o}u}{\omega})\overline{\rho},\overline{\eta},z))}{\theta(T+\theta exp(-\frac{im_{o}u}{\omega}))} \left[1+u^{2}\frac{\omega ln}{i\overline{m}_{o}} \left(\frac{(T+exp(\frac{im_{o}u}{\omega})}{\theta}\right)^{2}\right]^{\frac{1}{2}}$$

$$x \exp \left[ \frac{1}{\hat{1}\tilde{m}_{0}^{\omega}} \int_{\hat{\beta}(\theta^{\dagger},\bar{\rho},\bar{\eta})}^{\theta} \frac{(\frac{T+\theta \exp(-\frac{\hat{1}\tilde{m}_{0}^{u}}{\omega}),z,N)d\theta^{\dagger}}{\theta^{\dagger}}}{T+\theta \exp(-\frac{\hat{1}\tilde{m}_{0}^{u}}{\omega}) \theta^{\dagger}(1+\frac{\omega^{2}}{m_{0}^{2}}(1n\theta^{\dagger}/\theta-\frac{\hat{1}\tilde{m}_{0}^{u}}{\omega})^{2})^{\frac{1}{2}}} \right]$$
(C-3)

In oscillatory shear flows, the transients are allowed to die out consequently the first term in the moment expressions damps out. Pertinent moments can be derived from eq. (C-3) from the specific of choice  $\hat{G}$  and  $\hat{\beta}$ . The moment  $<\rho^2>$  will serve as an example.



$$<\rho^{2}> = \det\left(\underline{I}\right) \frac{C}{\beta_{0}} \left(\frac{3N}{2\pi}\right) \int_{0}^{\infty} d\tau' e^{-\tau'} \left( \int_{-\infty}^{\infty} d\rho d\eta \rho^{2} \right) \\ \exp\left[ -\frac{3N}{2} \left(\rho^{2} \lambda_{1}^{\prime 2} - 2\omega q' \rho \eta + \lambda_{2}^{2} \eta^{2} \right) - \frac{2a^{2}/3N}{\lambda_{3}^{2} \rho^{2} - 2W \rho \eta + \lambda_{4}^{2} \eta^{2}} \right]$$
(C-4)

where

$$\begin{split} \lambda_{1}^{2} &= \exp - \frac{i\tilde{m}_{0}}{\omega} (u - u^{*}) + \frac{\varepsilon}{2im_{0}} \int_{u}^{u} \frac{e^{-\left[\frac{i\tilde{m}_{0}}{\omega} (u - u^{*})\right]} du^{**}}{(1 - u^{**})^{\frac{1}{2}}} \\ \lambda_{2}^{2} &= \exp \frac{i\tilde{m}_{0}}{\omega} (u - u^{*}) + \frac{\varepsilon}{2im_{0}^{*}} \int_{u}^{u} \frac{e^{\left[\frac{i\tilde{m}_{0}}{\omega} (u - u^{*})\right]} du^{**}}{(1 - u^{**})^{\frac{1}{2}}} \\ \lambda_{3}^{2} &= \exp \frac{i\tilde{m}_{0}}{\omega} (u - u^{*}) \lambda_{4}^{2} = \exp \frac{i\tilde{m}_{0}}{\omega} (u - u^{*}) \\ q^{*} &= 1 + \varepsilon \tau^{*} \quad m_{0} = \tilde{m}_{0}/\beta_{0} \quad \tau^{*} = \beta_{0}(t - t^{*}) \end{split}$$

Utilizing transformation procedures and integration techniques identical to those used to obtain eq. (B-9), we obtain the ocillatory shear function as

$$Sxy = \frac{c}{\beta_{o}} \frac{e^{2\hat{a}^{*}}}{1+2a} kTdet(\tilde{z})(\frac{1}{2} \frac{\sqrt{\xi(2-\xi)}}{1-\xi}) \int_{0}^{\infty} e^{-\tau^{*}} I(\lambda) d\tau^{*}$$
(C-5)

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where

$$I(\lambda) = \frac{\lambda_{1}^{2} - \lambda_{2}^{2}}{(\lambda_{1}^{2}\lambda_{2}^{2} - q^{2}W^{2})^{3/2}} - \frac{4a^{2}}{c} (\lambda_{1}^{2} + \lambda_{2}^{2})(\lambda_{1}^{2}\lambda_{4}^{2} - \lambda_{2}^{2}\lambda_{3}^{2})$$
$$- 2W^{2}[(\lambda_{1}^{2} - \lambda_{2}^{2})W + W^{2}(\lambda_{4}^{2} - \lambda_{3}^{2})]$$
(C-6)

$$\mathring{C} = 4W^2(\lambda_1^2\lambda_2^2 - q(\lambda_2^2\lambda_3^2 + \lambda_1^2\lambda_4^2 + q^2) - W(2\lambda_1^2\lambda_2^2 - (\lambda_2^4\lambda_3^4 + \lambda_1^4\lambda_4^4))$$

In the first term

$$\lambda_{1}^{2} - \lambda_{2}^{2} = -2i \left[ \sin m_{0}(\sin \omega t - \sin(t - \tau'/\beta_{0})) + \frac{\varepsilon}{\omega m_{0}} \int_{u}^{u} \frac{\sin \tilde{m}_{0}(u - u'')}{(1 - u''^{2})^{\frac{1}{2}}} du'' \right]$$

$$(C-7)$$

In small-amplitude oscillatory shear flows,

$$\gamma_0 < 1, m_0, \tilde{m}_0 << 1$$

and thus

$$sinm_{o}(sin_{\omega}t - sin(t-\tau'/\beta_{o})) = m_{o}(sin_{\omega}t-sin_{\omega}(t-\tau'/\beta_{o}))$$

and

$$sin\tilde{m}_{o}(u-u'') = \tilde{m}_{o}(u-u'')$$
 (C-8)

also



$$sin\omega(t-\tau'/\beta_0) = sin\omega tcos\bar{\omega}\tau' - cos\omega tsin\bar{\omega}\tau'$$

where  $\bar{\omega} = \omega / \beta_0$ 

Upon integration of 2nd term in equation (C-4) we obtain

$$\lambda_1^2 - \lambda_2^2 = -2im_0 \left\{ \left[ 1 - \cos \omega \tau + \frac{\varepsilon}{\omega} \left( \omega \tau' - \sin \omega \tau' \right) \right] \sin \omega t \right\}$$

+ 
$$[-\sin\omega\tau + \frac{\varepsilon}{\omega} (1-\cos\omega\tau')] \cos\omega t$$
 (C-9).

All the other terms in equation (C-6) were analyzed with the above approximations and higher order quantities of  $\sin \omega t$  and  $\cos \omega t$  were discarded. From these, then, the final viscoelastic function expressions of equation 5.26 and 5.27 were calculated.





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