$$\lambda_n = \lambda_n^{-\alpha} \quad (A2)$$

$$\eta_n = \eta_o \lambda_n \Big/ \sum_{n=1}^{\infty} \lambda_n \quad (A3)$$

one obtains

$$\eta' = \frac{\eta_o}{Z(\alpha)} \sum_{n=1}^{\infty} \frac{p^\alpha}{p^{2\alpha} + (\lambda\omega)^2} \quad (A4)$$

where $Z(\alpha)$ is the Riemann Zeta function. The relaxation time λ is readily obtained from Equation (A4) by a master curve technique.

The final two fluid constants m and a are determined from steady shear viscosity data. The power law slope of the viscosity-shear rate curve is m, while a is obtained again by a master curve technique.

Manuscript received October 8, 1976; revision received July 6, and accepted July 7, 1977.

Part II. Definition and Measurement of Apparent Elongational Viscosity

The collapse of a single spherical gas bubble within a large body of fluid creates a uniaxial elongational flow in the surrounding fluid. Collapse under constant bubble pressure is observed to produce nearly constant strain rate kinematics. If the steady state stress at the bubble/fluid boundary could be measured, it would be possible to estimate the elongational viscosity of the fluid.

Unfortunately the experiment does not yield the desired stress data, except in the special case of the Newtonian fluid. We are led to define an apparent elongational viscosity, and for specific constitutive models we can evaluate the deviation between the apparent and true viscosity. The experimental and theoretical work indicate that the apparent elongational viscosity provides a good estimate of true elongational viscosity for the two viscoelastic solutions studied so far.

SCOPE

The standard techniques for measuring elongational viscosity work only for highly viscous melts ($\eta_o > 10^6$ P) and at low strain rates ($\dot{\epsilon} < 10^{-1}$ s^{-1}). In many cases of practical importance in the polymer processing industry, it is desirable to have elongational flow information for concentrated polymer solutions or low molecular weight polymer melts, both of which exhibit modest viscosities. As well, elongational behavior at higher strain rates must be studied.

Collapse of a single spherical gas bubble in a sea of fluid will create a uniaxial extensional flow. For two concentrated polymer solutions of moderate viscosity ($\eta_o \sim 10^3$ P), constant strain rates of 10^{-1} to 10 s^{-1} were achieved. Through evaluation of the transient elongational flow behavior, one can determine if the fluid studied exhibits stretch thickening or stretch thinning elongational viscosity. Assuming the latter, we present an evaluation of an apparent elongational viscosity as a function of strain rate for two solutions. The assumption that the fluids are stretch thinning is consistent with the data.

CONCLUSIONS AND SIGNIFICANCE

The bubble collapse experiment can be used to estimate the elongational viscosity of a concentrated polymer solution. The actual measurement is of an apparent elongational viscosity $\eta_{e,\text{app}}$. A comparison of $\eta_{e,\text{app}}$ data to the predictions of the Tanner-Simmons Rupture model and the modified corotational (Zaremba-Fromm-DeWitt) Maxwell model was made, with good agreement exhibited for both viscoelastic solutions studied. The constitutive test was severe in that all material constants were fit using viscometric (shear flow) data prior to predicting $\eta_e(\dot{\epsilon})$.

Part I of this paper dealt with certain aspects of the transient response of a viscoelastic fluid to an elongational flow (Pearson and Middleman, 1977). The collapse of a spherical gas bubble surrounded by an infinite sea of fluid was analyzed using both purely viscous and viscoelastic constitutive models. Experiments were performed with Newtonian and viscoelastic solutions of moderate viscosity ($\eta_o \sim 1\,000$ P). Collapse of the bubble was induced by a rapid change of pressure within the bubble. From measurement of bubble pressure, and high-speed photography of bubble collapse, the dynamics and kin-

Correspondence concerning this paper should be addressed to Stanley Middleman. Glen Pearson is with Eastman Kodak Company, Rochester, New York 14650.

ematics of this elongational flow were obtained. Excellent agreement was obtained between the predicted and observed response of the Newtonian fluid studied. The observed transient data could be quantitatively modeled by the modified corotational model based on the Zaremba-Fromm-DeWitt rate equation.

The constant pressure collapse experiment is observed to yield data at constant strain rate. This opens the possibility of obtaining the steady elongational viscosity from this type of experiment, and the present paper describes the results of our attempt to do so for two viscoelastic polymer solutions. Part I describes the transient modeling, and complete details are given in Pearson (1976).

DEFINITION OF $\eta_{e,app}$

For a spherically symmetric bubble collapsing within a sea of fluid, the pressure P_G inside the bubble is related to the stress in the fluid by (Pearson and Middleman, 1977)

$$\Phi \equiv P_G - P_\infty - \frac{2\sigma}{R} = -2\int_R^\infty \frac{\tau_{rr} - \tau_{\theta\theta}}{r}\,dr \qquad (1)$$

when inertial forces can be neglected.

The rate of deformation tensor, assuming spherically symmetric incompressible flow in the external fluid, is given by

$$\mathbf{\Delta} = -\frac{2R^2\dot{R}}{r^3}\begin{bmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \qquad (2)$$

For a Newtonian fluid

$$\boldsymbol{\tau} = \eta_0 \mathbf{\Delta} \qquad (3)$$

and symmetry implies $\tau_{\theta\theta} = \tau_{\phi\phi}$, from which it follows that

$$\tau_{rr} = -2\tau_{\theta\theta}. \qquad (4)$$

Equation (1) may be integrated, for the Newtonian case, with the result

$$\tau_{rr} - \tau_{\theta\theta}\big|_{R,\text{Newt}} = -\frac{3}{2}\Phi \qquad (5)$$

The elongational viscosity is defined, subject to conditions of steady state stress and rate of strain, as

$$\eta_e = \frac{\tau_{rr} - \tau_{\theta\theta}}{(1/2)\Delta_{rr}} \qquad (6)$$

At the bubble/fluid boundary $[r = R(t)]$ we define the nominal strain rate $\dot{\epsilon}$ to be

$$\dot{\epsilon} = \frac{\partial u_r}{\partial r}\bigg|_R = \frac{1}{2}\Delta_{rr}\bigg|_R = -\frac{2\dot{R}}{R} \qquad (7)$$

Thus, for a Newtonian fluid, we may calculate η_e from

$$\eta_e = \frac{3\Phi R}{4\dot{R}} \qquad (8)$$

In general, we cannot relate $(\tau_{rr} - \tau_{\theta\theta})_R$ directly to Φ except for some particularly simple forms of non-Newtonian constitutive equations (Pearson, 1976). As a consequence, Equation (8) does not provide a generally valid relationship between elongational viscosity and measurable quantities.

We will define an apparent elongational viscosity $\eta_{e,app}$ as

$$\eta_{e,app} = \frac{3\Phi R}{4\dot{R}} \qquad (9)$$

This is analogous to the use of Poiseuille's law for definition of an apparent shear viscosity as determined from pressure/flow data in a long capillary or tube of circular cross section. However, in that case, a procedure exists [based on the Weissenberg, Rabinowitsch, Mooney equation (Middleman, 1968)] whereby the true viscosity may be determined from data on the dependence of the apparent viscosity on shear rate. So far we have been unsuccessful in deriving an analogue of this procedure for use with Equation (9). In principle, then, the relationship of $\eta_{e,app}$ to η_e is unknown, and it is not clear a priori that Equation (9) provides a useful estimate of the desired quantity η_e itself.

The deviation between apparent and true elongational viscosity is due to, and proportional to, the deviation between the normal stress difference at the bubble surface $-(\tau_{rr} - \tau_{\theta\theta})_R$ and the readily measured pressure function $3/2\Phi$. For a specific constitutive equation, it may be possible to calculate both the stress difference and the pressure function and thereby evaluate $\eta_{e,app}$ as an estimate of η_e. Such calculations have been carried out by Pearson (1976) for the generalized Newtonian fluid and for a variety of viscoelastic constitutive equations including the fluid of grade 2, the BKZ fluid, and several corotational and codeformational nonlinear Maxwell models.

We illustrate here the analysis of $\eta_{e,app}$ based on the Zaremba-Fromm-DeWitt model (Bird et al., 1974) modified to fit shear viscosity data:

$$\tau^{ij} + \lambda_{ef}\frac{\mathcal{D}\tau^{ij}}{\mathcal{D}t} = \eta_{ef}\,\Delta^{ij} \qquad (10)$$

where the corotational (or Jaumann) derivative is defined as

$$\frac{\mathcal{D}\tau^{ij}}{\mathcal{D}t} = \frac{\partial\tau^{ij}}{\partial t} + u_k\frac{\partial\tau^{ij}}{\partial x_k} + \frac{1}{2}\left(\omega^{im}\tau^{mj} - \omega^{mj}\tau^{im}\right) \qquad (11)$$

and the deformation-rate dependent relaxation time and shear viscosity are taken to be

$$\lambda_{ef} = \frac{\lambda}{1 + \lambda\sqrt{\frac{1}{2}II_\Delta}} \qquad (12)$$

$$\eta_{ef} = \frac{\eta_0}{\left(1 + a\lambda\sqrt{\frac{1}{2}II_\Delta}\right)^m} \qquad (13)$$

Some material functions of this fluid are summarized in Table 1 of part I. We refer to this model as the modified Zaremba-Fromm-DeWitt model (MZFD).

The mathematical analysis of bubble collapse becomes simpler in a moving coordinate frame suggested by Epstein and Plesset (1950):

$$t = t' \qquad (14)$$

$$1/3\,[r^3 - R^3(t)] = \xi \qquad (15)$$

Equation (1) now becomes

$$\Phi = -2\int_0^\infty \frac{\pi_{\xi\xi} - \pi_{\theta\theta}}{3\xi + R^3}\,d\xi \qquad (16)$$

where π_{ij} denotes a stress component in the moving system. Equation (16) must be solved simultaneously with the constitutive relation, Equation (10), which yields a first-order differential equation for the stress difference:

$$\frac{d}{dt'}(\pi_{\xi\xi} - \pi_{\theta\theta}) + \frac{\pi_{\xi\xi} - \pi_{\theta\theta}}{\lambda_{ef}} = -\frac{4\eta_{ef}}{\lambda_{ef}}\frac{R^2\dot{R}}{3\xi + R^3} \qquad (17)$$

In general, Equations (16) and (17) must be solved numerically.

An evaluation of the degree to which $\eta_{e,app}$ might be a

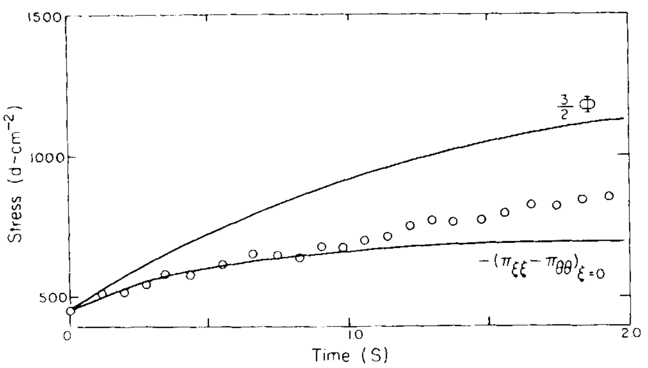

Fig. 1. **3/2 $\Phi(t)$ and $(\pi_{\xi\xi} - \pi_{\theta\theta})_{\xi=0}$ for the MZFD model compared to data for the HPC fluid, $\dot{Y}/Y = -0.29\ s^{-1}$.**

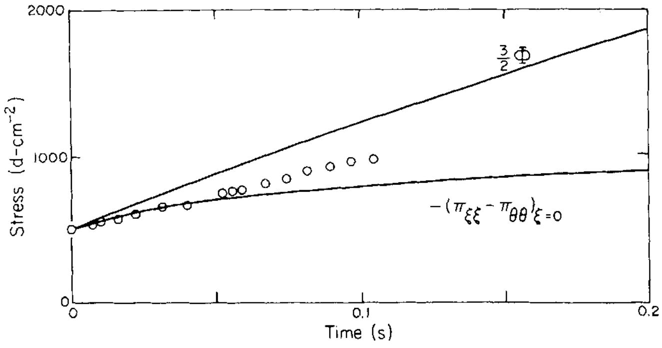

Fig. 2. **3/2 $\Phi(t)$ and $(\pi_{\xi\xi} - \pi_{\theta\theta})_{\xi=0}$ for the MZFD model compared to data for the PA fluid, $\dot{Y}/Y = -3.31\ s^{-1}$.**

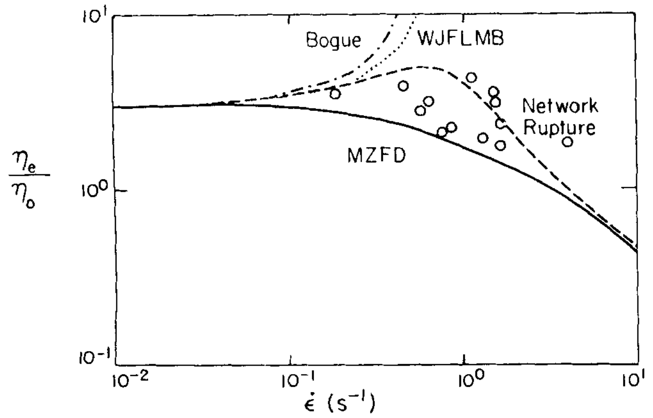

Fig. 3. **$\eta_{e,\text{app}}$ vs. $\dot{\epsilon}$ compared to predictions for η_e of the WJFLMB, Bogue, network rupture, and MZFD models for the HPC solution.**

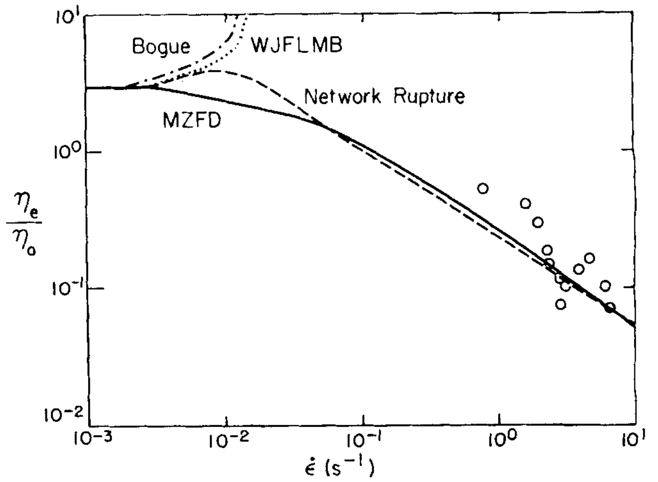

Fig. 4. **$\eta_{e,\text{app}}$ vs. $\dot{\epsilon}$ compared to predictions for η_e of the WJFLMB, Bogue, network rupture, and MZFD models for the PA solution.**

good approximation to η_e may be carried out in the following way:

1. Data on $\Phi(t)$ and $R(t)$ are obtained from a bubble collapse experiment.
2. A constitutive model [such as Equation (10)] is assumed and its parameters determined from suitable viscometric data.
3. $\Phi(t)$ is calculated through solution of Equations (16) and (17) using the observed $R(t)$ data. Comparison with the measured $\Phi(t)$ then gives some indication of the ability of the assumed constitutive equation to describe this elongational flow.
4. From solution of Equation (17), the stress difference $\pi_{\xi\xi} - \pi_{\theta\theta}$ is found. The desired stress difference $(\tau_{rr} - \tau_{\theta\theta})_R$ is found from

$$(\tau_{rr} - \tau_{\theta\theta})_R = (\pi_{\xi\xi} - \pi_{\theta\theta})_{\xi=0} \quad t' \to \infty \qquad (18)$$

5. The stress ratio

$$SR = -\frac{\frac{3}{2}\Phi}{(\pi_{\xi\xi} - \pi_{\theta\theta})_{\xi=0}} \quad t' \to \infty \qquad (19)$$

measures the error in using $\eta_{e,\text{app}}$ in place of η_e.

For viscoelastic fluids, it is necessary to have an initial condition on the stress distribution at the start of collapse. Pearson (1976) shows that the results are relatively insensitive to the assumption made regarding initial stresses. The calculations illustrated here assume the initial distribution to be that which would exist in a Newtonian fluid of viscosity η_o.

Figures 1 and 2 show typical examples of the procedure described above. The relationship of predicted to observed $\Phi(t)$ was discussed more fully in part I. Here we point out the fact that $SR > 1$. More extensive modeling by Pearson (1976) indicates that for any constitutive model which gives a stretch thinning η_e, SR is always greater than unity. For such fluids, then, $\eta_{e,\text{app}}$ is always an overestimate of the true elongational viscosity.

Quantitatively we note that as steady state is approached, the value of 3/2 Φ exceeds the normal stress difference at the bubble wall by a significant amount. However, modeling with a variety of constitutive models suggests that $\eta_{e,\text{app}}$ is at least an order of magnitude estimate of η_e and is probably within a factor of 2 of the true viscosity under the experimental conditions studied so far.

RESULTS AND DISCUSSION

Two polymer solutions were studied: 2% hydroxypropylcellulose in water and 1% polyacrylamide in a 50% solution of glycerine and water. The relevant fluid properties are given in part I, as are the material constants used to fit the modified Zaremba-Fromm-DeWitt model to shear viscometric data.

Data of $\eta_{e,\text{app}}$ as a function of strain rate are shown in Figures 3 and 4 for the two solutions. Also shown are predictions of $\eta_e(\dot{\epsilon})$ for several models, including the modified Zaremba-Fromm-DeWitt model, the Tanner-Simmons network rupture model (Tanner, 1969), the WJFLMB fluid (Spriggs et al., 1966), and the Bogue fluid (Chen and Bogue, 1972). Each model was used with a Spriggs-Rouse relaxtion spectrum (Spriggs, 1965):

$$\lambda_n = \lambda_n - \alpha \qquad (20)$$

$$\eta_n = \eta_o \lambda_n \Big/ \sum_{n=1}^{\infty} \lambda_n \qquad (21)$$

TABLE 1. MATERIAL CONSTANTS FOR VISCOELASTIC MODELS

Model	Constant	HPC	PA
	$\eta_o(p)$	620	2 240
	$\lambda(s)$	1.5	66
MZFD: $\tau^{ij} + \lambda_{ef} \frac{\mathfrak{D}\tau^{ij}}{\mathfrak{D}t} = \eta_{ef}\,\Delta^{ij}$ [see text, Equations (11) to (13)]	a	0.48	0.32
	m	0.76	0.70
Network rupture: $\tau^{ij} = \int_{t-t_R,\ t_R=B/\dot{\gamma}}^{t} \sum_{n=1}^{\infty} \frac{\eta_n}{\lambda_n^2} \exp\left(-\frac{t-t'}{\lambda_n}\right) (C^{-1})^{ij}(t,t')dt'$	b	4.56	2.93
Bogue: $\tau^{ij} = \int_{-\infty}^{t} \sum_{n=1}^{\infty} \frac{\eta_n \lambda_n^{-1}}{\lambda_n^e} \exp\left(-\frac{t-t'}{\lambda_n^e}\right) (C^{-1})^{ij}(t,t')dt'$; $\lambda_n^e = \frac{\lambda_n}{1 + a\lambda_n \left\langle \frac{1}{2} II_\Delta \right\rangle^{1/2}}$; $\left\langle \frac{1}{2} II_\Delta \right\rangle^{1/2} = \frac{1}{s}\int_o^s \left| \frac{1}{2} II_\Delta \right|^{1/2} ds$	a	0.9	0.96
WJFLMB: $\tau^{ij} = \int_{-\infty}^{t} \sum_{n=1}^{\infty} \frac{\eta_n/\lambda_n^2}{1 + \frac{1}{2} II_\Delta (t')\, {}^2\lambda_n^2} \exp\left(-\frac{t-t'}{\lambda_n}\right) (C^{-1})^{ij}(t,t')dt'$	c	0.38	0.56

Material constants are given in Table 1. Both the MZFD and Tanner-Simmons models agree quite well with the data, while those models that predict stretch thickening behavior are clearly inappropriate. In all cases, all material constants were fit to viscometric (shear) data only. Thus, the test of the constitutive equation is severe.

CONCLUSIONS

We believe that the experimental procedures described in this paper and in part I (Pearson and Middleman, 1978) allow calculation of an apparent elongational viscosity which provides a reasonable estimate of the actual elongational viscosity of the fluid. The conclusion follows from the following experimental and theoretical results:

1. Constitutive equations which predict stretch thinning, when used to solve the dynamic equations for bubble collapse, show that the apparent elongational viscosity, as we have defined it, is an overestimate of the actual elongational viscosity and gives a reasonable quantitative estimate of its magnitude.

2. Two viscoelastic constitutive equations which predict stretch thinning, the Tanner-Simmons network rupture model and the modified corotational (Zaremba-Fromm-DeWitt) model, can be used to fit the viscometric shear data of the fluids studied with good precision. When these models are used to predict elongational viscosity as a function of strain rate, the predictions, based completely on parameters established in shear, are in close quantitative agreement with the data for apparent elongational viscosity, as defined and presented here.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation under Grant GK 41899. This support is gratefully acknowledged. We also wish to thank Professor Roger Tanner of the University of Sydney and Professor R. Byron Bird of the University of Wisconsin for their assistance and time in discussing this work.

LITERATURE CITED

Bird, R. B., O. Hassager, and S. J. Abdel-Khalik, "Corotational Rheological Models and the Goddard Expansion," *AIChE J.*, **20**, 1041 (1974).

Chen, J. J., and D. C. Bogue, "Time-Dependent Stress in Polymer Melts and Review of Viscoelastic Theory," *Trans. Soc. Rheol.*, **16**, 59 (1972).

Epstein, P. S., and M. S. Plesset, "On the Stability of Gas Bubbles in Liquid-Gas Solution," *J. Chem. Phys.*, **18**, 1505 (1950).

Middleman, S., *The Flow of High Polymers,* Wiley-Interscience, New York (1968).

Pearson, G. H., Ph.D. dissertation, Univ. Mass., Amherst (1976).

———, and S. Middleman, "Measurement of Elongational Flow Behavior via Bubble Collapse in Viscoelastic Liquids: I., *AIChE J.*, **23**, 000 (1977).

Spriggs, T. W., "A Four-Constant Model for Viscoelastic Fluids," *Chem. Eng. Sci.*, **20**, 931 (1965).

———, J. D. Huppler, and R. B. Bird, "An Experimental Appraisal of Viscoelastic Fluids," *Trans. Soc. Rheol.*, **10**, 191 (1966).

Tanner, R. I., "Network Rupture and the Flow of Concentrated Polymer Solutions," *AIChE J.*, **15**, 177 (1969).

Manuscript received October 8, 1976; revision received July 6, and accepted July 7, 1977.