

Rheological Phenomena During the Polymerization of Styrene in a Stirred Tank

YOSHIAKI IDE and JAMES L. WHITE,
*Department of Chemical and Metallurgical Engineering,
The University of Tennessee, Knoxville, Tennessee 37916*

Synopsis

An experimental study of the bulk polymerization of styrene has been carried out. The rate of polymerization, molecular weight, and flow patterns around agitators as a function of conversion have been observed. The rate data are interpreted in terms of free-radical polymerization kinetics. Duerksen and Hamielec's modified termination rate constant and initiator efficiency relations are generally consistent with our data. The flow patterns were interpreted in terms of the mechanics of viscoelastic liquids and observations for nonreacting systems. Specifically, at low conversions for spheres and similar agitators, the flow patterns are dominated by centrifugal forces with fluid drawn in at the poles and expelled at the equator for spherical agitators. At higher conversions, normal stresses interact with the centrifugal forces causing segregated secondary flow regions adjacent to the sphere. At very high concentrations, normal stresses dominate, yielding Weissenberg effects.

INTRODUCTION

The bulk free-radical polymerization of styrene is an important industrial problem and has been considered in both the scientific and patent literatures. The process was known to chemists as far back as the 1840's. However, it remained a laboratory curiosity until the 1930's when commercial production was begun.^{1,2} A summary of work in styrene polymerization through 1951 is given by Boundy and Boyer,² and an updated review has been given by Coulter, Kehde, and Hiscock.³ Styrene may be polymerized by free-radical³ and ionic mechanisms.⁴⁻⁶ Styrene copolymers are indeed commercially manufactured by both free-radical⁷ and anionic⁸ methods, though styrene itself is only polymerized commercially by the free-radical method.

By the nature of addition polymerization, continuous industrial polystyrene reactors must involve the flow at polystyrene solutions through complex geometries and around agitators. Hamielec and his colleagues⁹⁻¹¹ and Nagata and his associates¹² have made studies of styrene polymerization in various reactors, including continuous reactors, emphasizing polymerization rates and molecular weight distributions. As a recent experimental study by Ide and White¹³ has shown, polystyrene-styrene solutions are typical viscoelastic fluids and exhibit non-Newtonian viscosity, normal stresses, and the Weissenberg effect¹⁴ and elastic recoil. Ide and White have observed complex flow patterns around agitators in polystyrene-styrene solutions. It would be expected that bulk polymerizing

polystyrene would exhibit flow behavior typical of viscoelastic fluids within the reactors rather than Newtonian flow characteristics. The existence of complex rheological phenomena in polymerization reactors has been ignored by earlier investigators, and a recent review paper on mixing on polymer reactors does not mention the subject.¹⁵

In this paper, we will report on experimental studies of the bulk polymerization of styrene. Specifically, this investigation covers the variation of flow patterns during the course of the polymerization as well as polymerization rate and molecular weight.

EXPERIMENTAL

Materials

The styrene monomer was a high-purity grade manufactured by Eastman-Kodak. It was distilled to remove inhibitor. The polymerization was initiated by azobisisobutyronitrile (AIBN) obtained from the Fisher Chemical Company.

Procedure

About 2000 ml styrene was polymerized in bulk at 60°C with AIBN initiator present at a concentration of 2.91 g (1.77×10^{-2} mole) per liter. The same series of agitators designed and studied in our earlier work¹³ were used in the bulk polymerizing mixtures. Most agitators were $\frac{3}{4}$ in. in diameter and placed on $\frac{3}{16}$ -in.-diameter shafts. The rotation rate was 120 rpm. The reactor was generally a 3000-ml-capacity 5-in.-diameter Pyrex Resin Reaction Kettle. For the spherical agitator, a 900-ml beaker was used. Samples removed at various times during the reaction were immediately placed into stirred excess methanol. The samples were then dried in a vacuum oven, weighed, and characterized with a gel permeation chromatograph.^{16,17}

Dye was introduced into the bulk polymerizing mixture at various times during the course of the reaction with the different agitators to observe flow patterns. The procedure was generally the same as reported in our earlier paper.¹³ The variation of flow patterns with conversion for the case of the spherical agitator was filmed. A copy of the film is available by writing to one of us (J.L.W.).

RESULTS

Polymerization Process

The conversion and weight-average molecular weight M_w were plotted as a function of time in Figure 1. Despite the depletion in monomer concentration, the polymerization rate is observed to generally increase with time. The molecular weight of the polymer produced remains essentially 160,000 for the first 10 hr of the polymerization (or to about 40% conversion). At higher conversions, the molecular weight rises steeply. The value of M_w/M_n for the early stages of the polymerization is about 2.3. At higher conversions, it rises to about 2.7.

Flow Patterns

The polymerizing system is generally transparent up to about 40% conversion, when it becomes increasingly hazy due to the presence of nitrogen gas bubbles.

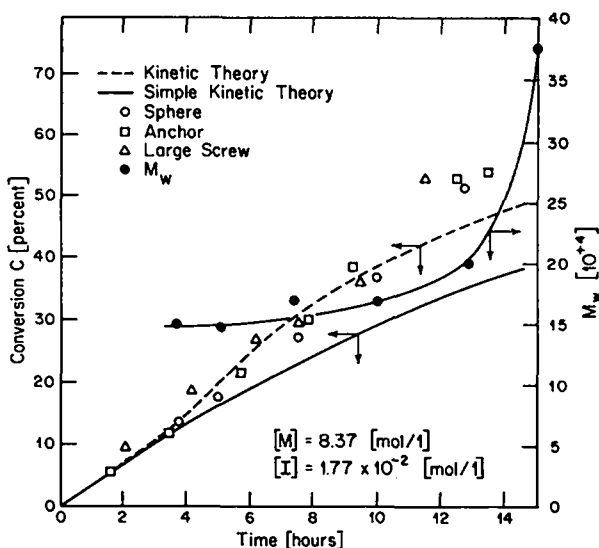


Fig. 1. Conversion and weight-average molecular weight as a function of time during styrene polymerization. Kinetic theory (including Duerksen-Hamaliac correction) and simple kinetic theory (no correction) are compared to date for different agitators.

Eventually, the gas bubble concentration becomes so high that the system becomes translucent and eventually opaque. The agitator cannot be seen at conversions above approximately 45%.

At low conversions, the flow patterns around the sphere and other agitators involve a primary axisymmetric flow and a secondary flow consisting of fluid being drawn in at the poles axially and expelled at the equator. As the conversion increases, the velocities of the secondary flow field around a sphere divides into two regions, one adjacent to the sphere consisting of closed circulating motions and a second at larger distances from the sphere. Similar flow patterns were observed until the gas bubbles obscured the agitator. Figure 2 contains photographs of the flow patterns at several concentrations. At high conversions rates after the agitator had been obscured, the polymerizing system exhibited strong Weissenberg effects.

DISCUSSION

Polymerization Process

The kinetics of styrene polymerization are well established. The rate of reaction in polymerizing styrene initiated by a free radical-producing initiator such as AIBN may be expressed¹⁸ as follows:

$$-\frac{d[M]}{dt} = k_p \sqrt{\frac{fk_t}{k_t}} [I]^{1/2} [M] \quad (1a)$$

where

$$[I] = [I]_0 e^{-k_t t} \quad (1b)$$

is the initiator concentration; $[M]$ is the monomer concentration; k_t , k_p , and k_t are the initiation, propagation, and termination rate constants; and f is the

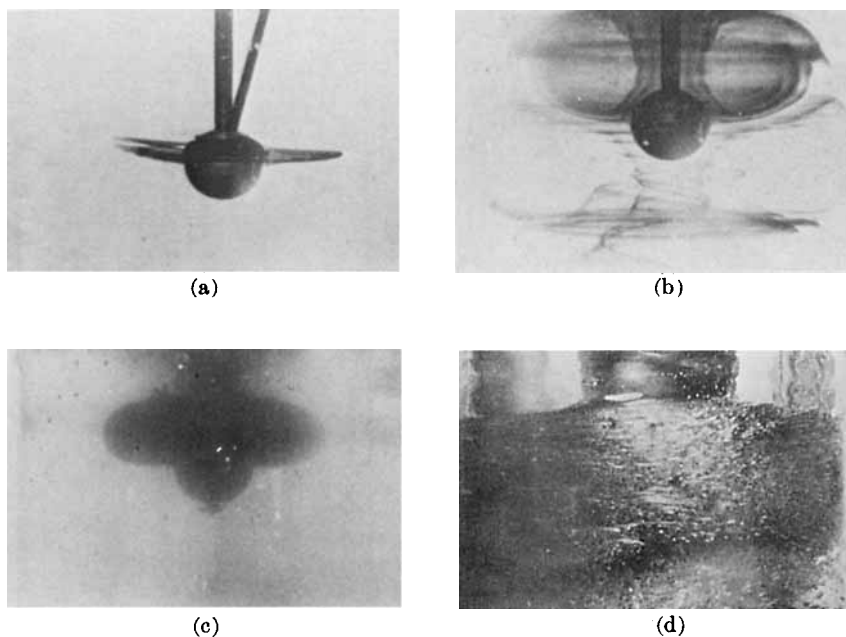


Fig. 2. Flow patterns around spherical agitator in polymerizing styrene at various conversions: (a) 30% conversion; (b) 37% conversion; (c) 45% conversion; (d) high conversion showing Weissenberg effect.

initiator efficiency. The extent of conversion C which is proportional to the polymer concentration may be shown to be

$$C = 1 - \frac{[M]}{[M]_0} = 1 - \exp \left\{ - \frac{2K}{k_t} \left[1 - \exp \left(- \frac{k_i t}{2} \right) \right] \right\} \quad (2a)$$

where

$$K = k_p \sqrt{\frac{f k_i [I]_0}{k_t}} \quad (2b)$$

Experimentally, it has been observed by earlier authors that the rate of polymerization increases at high conversions.^{11,18,19} This is generally attributed to the reduction of the termination rate constant by the high viscosity of the reaction medium. The decrease in k_t results in an increase in free-radical concentration. Quantitative studies of the influence of medium viscosity on the termination rate constant have been carried out by Duerksen and Hamielec.¹¹

We have used eq. (2) to predict the variation of conversion with time. For values k_p , k_t , k_i , and f we have used

$$k_p = 2.41 \times 10^2 \text{ (l./mole-sec)}$$

$$k_t = 9.95 \times 10^7 \text{ (l./mole-sec)}$$

$$k_i = 8.73 \times 10^{-6} \text{ (sec}^{-1}\text{)}$$

$$f = 0.6$$

which have been taken from the literature.^{11, 20-22} The variation of initiator efficiency f and termination rate constant k_t with increasing viscosity during the

reaction was evaluated using the work of Duerksen and Hamielec.¹¹ Figure 1 compares the predicted and observed variation of conversion with time. The Duerksen-Hamielec viscosity dependence correction may be seen to correct for much of the autoacceleration effect.

Flow Patterns

Bulk polymerizing styrene may clearly be considered as a polystyrene-styrene solution and conversion interpreted as concentration. Ide and White¹³ have made a basic study of the character of flow patterns around agitators in polystyrene-styrene solutions. At low concentrations, rotating spheres, discs, and turbines draw in fluid along the axis of the agitator and expel it at the perimeter as is typical of Newtonian fluids.²³⁻²⁵ At high concentrations, the solution is drawn in at its perimeter and expelled along the axis. At intermediate concentrations, the flow field divides into two regions, with differing velocity fields. The different regimes of flow for a sphere (see Fig. 3) are summarized in Figure 4. Similar flow patterns have been observed in polyacrylamide-water-glycerin solutions.²⁶⁻³⁰ The above observations are essentially the same as the flow patterns which were observed during the course of bulk styrene polymerization.

There have been extensive theoretical studies of the character of flow patterns around agitators in Newtonian fluids. About 130 years ago, Stokes³¹ derived the nature of the primary flow pattern about a slowly rotating sphere. This has the form in spherical coordinates (r, θ, ϕ , see Fig. 3) of

$$v_\phi = R\Omega \sin \theta \left(\frac{R}{r}\right)^2 = \frac{R\Omega}{r^2} \sin \theta, \quad v_\theta = v_r = 0 \quad (3)$$

where R is the radius of the sphere and Ω is the angular velocity. Stokes recognized that the rotating sphere would draw in fluid and expel it by centrifugal forces at the equator, but it was not until 1938 that Bickley,³² using a perturbation procedure, was able to place this in analytical form. The predicted flow patterns (see Fig. 4a) near a rotating spheroid or disc in a Newtonian fluid³³⁻³⁵ are similar in character, as is flow in the neighborhood of a rotating turbine.³⁶ The character of the superposed secondary flow patterns around a sphere rotating in a viscoelastic fluid has been considered by Giesekus,²⁶ Thomas and Walters,³⁷

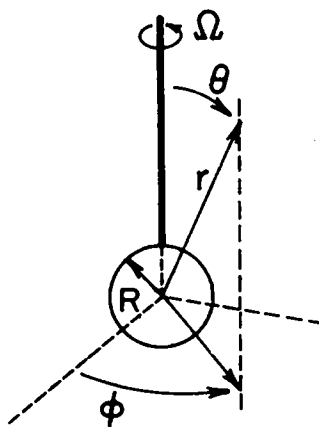


Fig. 3. Rotating sphere in an infinite bath.

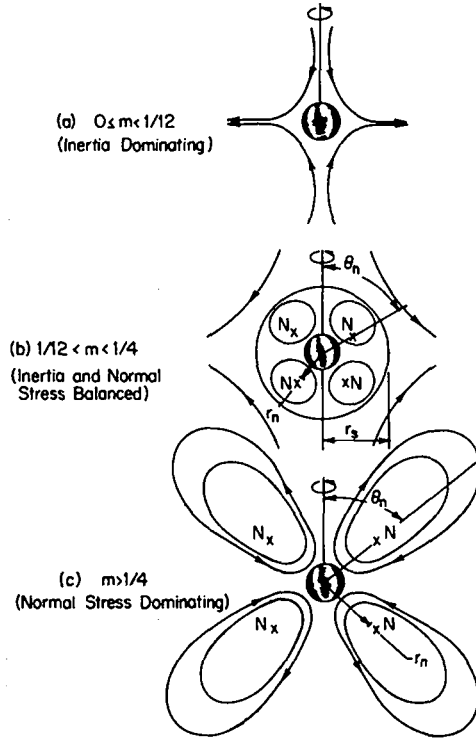


Fig. 4. The secondary flow patterns around a sphere: (a) low levels of viscoelasticity ($0 \leq m \leq 1/12$); (b) intermediate ($1/12 < m < 1/4$); and (c) high levels of viscoelasticity ($m > 1/4$).

Walters and Waters,³⁸ and Ide and White¹³ (see also Langlois³⁹) using perturbation methods similar to those of Bickley but based upon the second-order fluid asymptote of viscoelastic fluid mechanics.⁴⁰⁻⁴³ The velocity field obtained by these authors is of form

$$v_{\theta}' = R\Omega N_{Re} \frac{r^* - 1}{8r^{*5}} (r^* - 12m) \sin 2\theta \quad (4a)$$

$$v_r' = R\Omega N_{Re} \frac{(r^* - 1)^2}{8r^{*5}} [(1 - 4m)r^* - 8m] (3 \sin^2 \theta - 2) \quad (4b)$$

where

$$\begin{aligned} m &= \frac{N_{We}}{N_{Re}} (1 - N_{VR}) = \frac{-\omega_3}{\rho R^2} \left(1 - \frac{\omega_2}{\omega_3} \right) \\ &= \frac{\lambda \eta}{\rho R^2} \left(1 + \frac{\omega_2}{\lambda \eta} \right) \end{aligned} \quad (5)$$

Here, N_{We} is the Weissenberg number and N_{VR} is the viscoelastic ratio number^{41,43}; η is the zero shear viscosity and λ is a characteristic time defined as the ratio of the first to the zeroth moment of the relaxation modulus. The second-order fluid parameters, ω_2 and ω_3 in eq. (5), are derivable from normal stress measurements:

$$\omega_3 = -\lambda\eta = \left(-1/2 \lim_{\Gamma \rightarrow 0}\right) \frac{N_1}{\Gamma^2} \quad \omega_2 = \lim_{\Gamma \rightarrow 0} \frac{N_2}{\Gamma^2} \quad (6)$$

where N_1 and N_2 are the first and second normal stress differences and Γ is the shear rate. The secondary flow patterns of eq. (4) are summarized in Figure 4. For values of m less than $1/12$, centrifugal forces dominate the flow patterns, while for m greater than $1/4$, they are dominated by normal stresses and viscoelasticity. In the range from $1/12$ to $1/4$, the flow field divides into two regions, with segregated vortices near the surface of the sphere.

As we have pointed out, the experiments of Ide and White¹³ show that as concentration increases, the character of the flow patterns about a rotating sphere varies as shown in Figure 4. From eq. (5), it may be seen that this is equivalent to the parameter m increasing with concentration. The m concentration functionality may be determined from normal stress measurements. Few studies of this concentration dependence exist. However, Tanner⁴⁴ has summarized concentration dependence data for polyisobutylene solutions, and Ide and White have made a study for polystyrene-styrene solutions. The latter study shows (at 60°C) that

$$\log \eta = 5.5 \log C + 3.85 \quad (7a)$$

$$\log \lim_{\Gamma \rightarrow 0} \frac{N_1}{\Gamma^2} = 10.5 \log C + 4.85 \quad (7b)$$

The polymer used was a Dow Styron 678 with $M_n = 80,000$ and $M_w = 240,000$. From eqs. (4), (5), and (7), the variation of m and the flow patterns with concentration may be specified if we know the value of ω_2/ω_3 . This is equivalent to the ratio $-2N_2/N_1$. Measurements of N_2 are generally difficult. There have, however, been several studies in the literature on second normal stress differences in polymer solutions⁴⁵⁻⁴⁸ which indicate N_2 to be negative and of order $0.1 N_1$. Ide and White take ω_2/ω_3 to have a value of 0.2. From eqs. (4) and (7b), the transition from regime (a) to regime (b), which occurs at $m = 1/12$, should be at 30%. The transition from regime (b) to regime (c), which occurs at $m = 1/4$, should be at 33%. This is indeed observed by these authors who were also able to predict the positions of the nodes and encapsulating sphere of regime (b).

The polymer produced in the polymerization reaction described earlier in this paper has a lower molecular weight ($M_w = 170,000$) than the polymer used in Ide and White's studies and also possesses a narrower molecular weight distribution. One result of this is that the polymerizing solutions are less viscoelastic and possess lower values of m at equivalent concentrations. The variation from flow regime (a) to regime (b) of Figure 2 is delayed to higher concentrations—from 30% to 37%. The variation to regime (c) is also delayed and to the extent that this transition does not occur until the solution is opaque. The intermediate flow with two secondary flow patterns including a segregated region seems to occur over a wide range of conversions. This may be in part because the auto-acceleration raises the temperature of the reacting mixture which will tend to keep m small despite increasing conversion.

A general point to be reemphasized is that combination of eqs. (2)–(5) and (7) allows the computation of secondary flow patterns as a function of conversion and of residence time in a batch reactor.

A final word about the application to continuous reactors is pertinent. If agitators of such design as to induce the segregated secondary flows of Figures 2b and c were used in a continuous stirred tank reactor, segregation effects would develop, perhaps leading to variation in molecular weight distribution of polymeric products.

References

1. C. Ellis, *Ind. Eng. Chem.*, **25**, 125 (1933).
2. R. H. Boundy, R. F. Boyer, and S. Stroesser, Eds, *Styrene*, ACS Monograph, Reinhold, New York, 1952.
3. K. W. Coulter, H. Kehde, and B. L. Hiscock, in *AICHE Professors' Workshop on Industrial Monomer and Polymer Engineering*, Midland Section AIChE, 1969.
4. M. Morton, E. C. Bostock, and R. Livigni, *Rubber Plast. Age*, **42**, 397 (1961).
5. H. L. Hsieh, *J. Polym. Sci.*, **3**, 153, 173 (1965).
6. D. O. Jordan and A. R. Mathieson, *J. Chem. Soc.*, 611 (1952).
7. J. P. Kennedy and E. G. M. Tornquist, Eds, *Polymer Chemistry of Synthetic Elastomers*, Interscience, New York, 1969.
8. H. L. Hsieh, *Rubber Plast. Age*, **46**, 394 (1965).
9. J. H. Duerksen, A. E. Hamielec, and J. W. Hodgins, *A.I.Ch.E. J.*, **13**, 1081 (1966).
10. A. E. Hamielec, J. W. Hodgins, and K. Tabbens, *A.I.Ch.E. J.*, **13**, 1087 (1966).
11. J. H. Duerksen and A. E. Hamielec, *J. Polym. Sci.*, **C25**, 155 (1968).
12. M. Harada, K. Tanaka, W. Eguchi, and S. Nagata, *J. Chem. Eng. Japan*, **1**, 1 48 (1968).
13. Y. Ide and J. L. White, *J. Appl. Polym. Sci.*, **18**, 2997 (1974).
14. K. Weissenberg, *Nature*, **159**, 310 (1947).
15. E. B. Nauman, *J. Macromol. Sci.-Rev. Macromol. Chem.*, **C10**, 75 (1974).
16. K. H. Altgelt and J. C. Moore, in *Polymer Fractionation*, M. J. R. Cantow, Ed., Academic Press, New York, 1967.
17. J. L. White, D. G. Salladay, D. O. Quisenberry, and D. L. MacLean, *J. Appl. Polym. Sci.*, **16**, 2811 (1972).
18. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, 1953.
19. R. G. W. Norrish and R. R. Smith, *Nature*, **150**, 336 (1942).
20. M. Imoto, M. Kinoshita, and M. Nishigaki, *Makromol. Chem.*, **86**, 217 (1965).
21. J. P. Van Hook and A. V. Tobolsky, *J. Amer. Chem. Soc.*, **80**, 779 (1958).
22. J. C. Bevington, *Trans. Faraday Soc.*, **51**, 1392 (1955).
23. E. J. Lyons, *Chem. Eng. Progr.*, **44**, 341 (1948).
24. J. P. Sachs and J. H. Rushton, *Chem. Eng. Progr.*, **50**, 597 (1954).
25. J. B. Gray, in *Mixing, Theory and Practice*, Vol. 1, V. W. Uhl and J. B. Gray, Eds., Academic Press, New York, 1964, Chap. 4.
26. H. Giesekus, *Proc. 4th Int. Rheol. Congr.*, **1**, 249 (1965).
27. H. Giesekus, *Rheol. Acta*, **4**, 85 (1965).
28. K. Walters and J. G. Savins, *Trans. Soc. Rheol.*, **9**, 207 (1965).
29. D. F. Griffiths, D. T. Jones, and K. Walters, *J. Fluid Mech.*, **36**, 161 (1969).
30. D. F. Griffiths and K. Walters, *J. Fluid Mech.*, **42**, 379 (1970).
31. G. G. Stokes, *Trans. Camb. Phil. Soc.*, **8**, 287 (1845).
32. W. G. Bickley, *Phil. Mag.*, **25**, 746 (1938).
33. S. Goldstein, *Modern Developments in Fluid Dynamics*, Clarendon Press, Oxford, 1938.
34. T. von Karman, *Z.f.A.M.M.*, **1**, 233 (1921).
35. N. D. Waters and M. J. King, *Q. J. Mech. Appl. Math.*, **24**, 331 (1971).
36. A. DeSouza and R. Pike, *Can. J. Chem. Eng.*, **50**, 15 (1972).
37. R. H. Thomas and K. Walters, *Q. J. Mech. Appl. Math.*, **17**, 39 (1964).
38. K. Walters and N. D. Waters, *Brit. J. Appl. Phys.*, **15**, 989 (1964).
39. W. E. Langlois, *Q. Appl. Math.*, **21**, 61 (1963).
40. B. D. Coleman and W. Noll, *Arch. Rat. Mech. Anal.*, **6**, 350 (1960); B. D. Coleman and H. Markovitz, *J. Appl. Phys.*, **35**, 1 (1964).
41. J. L. White, *J. Appl. Polym. Sci.*, **8**, 2339 (1964).
42. A. B. Metzner, J. L. White, and M. M. Denn, *A.I.Ch.E. J.*, **10**, 863 (1966).

43. D. C. Bogue and J. L. White, *Engineering Analysis of Non-Newtonian Fluids*, NATO Agardograph No. 144 (1970).
44. R. I. Tanner, *Trans. Soc. Rheol.*, **17**, 365 (1973).
45. R. F. Ginn and A. B. Metzner, *Trans. Soc. Rheol.*, **13**, 429 (1969).
46. R. I. Tanner, *Trans. Soc. Rheol.*, **14**, 483 (1970).
47. M. J. Miller and E. B. Christiansen, *A.I.Ch.E. J.*, **18**, 600 (1972).
48. O. Olabisi and M. C. Williams, *Trans. Soc. Rheol.*, **16**, 727 (1972).

Received August 16, 1974

Revised September 20, 1974