

Rupture of entangled polymeric liquids in elongational flow^{a),b)}

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Synopsis

Polymer melts and concentrated solutions rupture at high rates of elongation in a manner that is reminiscent of the cohesive failure of solids. We propose a simple molecular picture of rupture of a polymer filament, in which catastrophic failure occurs when the frictional force on an entangled chain can no longer balance the tension in the chain. The model, which is fully predictive and contains no adjustable parameters, captures the rupture characteristics of the available data sets and agrees quantitatively with critical stress–critical strain data and the dependence of critical strain on the Weissenberg number. © 2003 The Society of Rheology. [DOI: 10.1122/1.1530622]

I. INTRODUCTION

Polymer melts and concentrated solutions rupture at high rates of elongation in a manner that is reminiscent of the cohesive failure of solids and is distinct from necking (ductile failure) and surface tension-driven breakup [Petrie and Denn (1976); Petrie (1979)]. This rupture mode appears to be relevant to a number of important issues in the processing of polymeric materials, including melt filament breakage in fiber formation and the onset of surface roughness (sharkskin) in melt extrusion from a die. Rupture of polymer melts has recently been reviewed by Malkin and Petrie (1997), and some data have been correlated with rheological properties and process conditions.

Vinogradov and co-workers (1975) constructed a master curve of elongational strain at rupture for polymer melts with narrow molecular weight distributions as a function of elongation rate, in which they found four regimes. The flow zone occurs at very low elongation rates; here, viscous flow continues until failure is caused by a surface tension-driven instability. Viscoelasticity is important in the transition zone beyond a Weissenberg number (product of polymer relaxation time and the elongation rate) of about 0.5, where both elastic and viscous deformation occurs; the filament ruptures in this regime before reaching a steady-state stress at a constant elongation rate, and the strain at breakage decreases with an increase in the elongation rate. The deformation is almost completely elastic in the subsequent rubbery zone, and there is nearly complete recovery of the strain following rupture; the total strain at rupture increases with the elongational rate in this regime, which is our focus in this work. At very high elongation rates, in the glassy zone, the strain at rupture again decreases with the elongation rate. Malkin and Petrie

^{a)}Dedicated to Professor Giuseppe Marrucci on the occasion of his 65th birthday.

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(1997) claimed that the system ruptures before reaching the steady state if the strain that can be recovered exceeds a value of 0.5. (Elastomers show behavior similar to that of entangled polymeric liquids in the rubbery and glassy regimes, where the elongational strain at rupture first increases and then decreases with an increase in speed or decrease in temperature [Smith (1963)] but the rupture mechanism may not be the same.)

The mechanism by which the rupture of entangled polymeric liquids in the rubbery zone occurs is not understood. Reiner and Freudenthal (1938) proposed a dynamical theory of strength, which assumes that rupture occurs if the stored elastic energy exceeds the tensile strength of the liquid; the tensile strength is itself an unknown parameter. Two consequences of their theory are that the stress at rupture and the time to rupture are independent of the loading history and the rate of strain, both of which are inconsistent with the data of the Vinogradov group. There has been little progress since this work [Malkin and Petrie (1997)]. One notable exception is McKinley and Hassager's (1999) analysis of the Considère condition for failure with the Doi–Edwards constitutive equation, in which they predict an elastic instability at a Hencky strain of 0.86 for an infinite strain rate.

We propose here a parameter-free scaling theory to model the rupture of a polymer filament in the rubbery zone. The theory is based on a simple molecular picture of the entangled melt, in which catastrophic failure occurs when the frictional force on an entangled chain can no longer balance the tension in the chain. The results are in agreement with the experiments of the Vinogradov group.

II. THEORY

We consider a monodispersed polymer melt or concentrated solution with N entanglements per molecule and an average distance a between consecutive entanglements. In the absence of flow, the mean-square end-to-end distance R_0 of a polymer chain is equal to $N^{1/2}a$. We assume the polymer is being stretched in the rubbery regime at a macroscopic rate $\dot{\epsilon}$, and we focus on one test chain, which deforms affinely with the surroundings; this affine deformation is caused by an effective frictional force between the test chain and the surrounding molecules. The tension in the chain is proportional to the mean-square end-to-end distance R . The sliding friction that a chain experiences is $\zeta_e \dot{\epsilon}$ multiplied by the contour length, where ζ_e is a segmental friction coefficient suitably defined for the entangled system. (There is a geometrical factor in the friction equation that accounts for the fact that individual chain segments need not be aligned with the principal stretch direction, but this will be a small effect in the rubbery regime and we neglect it.) We assume that the static friction during affine deformation scales in the same way as sliding friction. Hence, the frictional force can never exceed a value that is proportional to the fully extended segmental chain length, Na , multiplied by $\zeta_e \dot{\epsilon}$. There is no limit, however, to the tension, which increases with the end-to-end distance.

We assume that the forces on the chain become unbalanced if the tension in the molecule exceeds $Na\zeta_e \dot{\epsilon}$, and a catastrophic failure must occur before steady state is reached. (The reasoning here is quasistatic and does not incorporate the chain dynamics after the critical condition has been reached.) The critical end-to-end distance R^* for rupture is therefore given to within scaling constants by

$$\zeta_e \dot{\epsilon} Na = H(R^* - R_0). \quad (1)$$

The effective segmental friction coefficient ζ_e is given by (see the Appendix)

$$\zeta_e = \frac{12\pi^2}{5N_e} \frac{kT}{R^2} \tau_d, \quad (2)$$

and the equivalent entropic spring constant H by [Larson (1999)]

$$H = \frac{3kT}{R_0^2}, \quad (3)$$

where k is the Boltzmann constant, T is the absolute temperature, N_e is the average number of monomers between neighboring entanglements, and τ_d is the disengagement (reptation) time. We have used the end-to-end distance R as the relevant molecular length scale in defining the friction coefficient; this choice is made because, as the chain orients in the direction of flow, it offers comparatively less resistance to flow than in the random configuration. Finite extensibility of the spring can be incorporated into the spring constant H , but this addition has little effect on the results.

Integration of Eqs. (2) and (3) into Eq. (1) leads immediately to a relation for the critical molecular strain at a given rate of elongation:

$$\exp(3\varepsilon_H^*) - \exp(2\varepsilon_H^*) = 4\pi^2 \frac{N^{1/2}}{5N_e} Wi, \quad (4)$$

where $\varepsilon_H = \ln(R/R_0)$ is the Hencky measure of the molecular strain and $Wi = \dot{\varepsilon}\tau_d$ is the Weissenberg number based on the reptation time. The molecular strain is recoverable, so Eq. (4) establishes the macroscopic recoverable strain at failure. The strain is almost completely recoverable in the rubbery zone, so the total strain equals the recoverable strain and Eq. (4) determines the strain–strain rate envelope at rupture.

We assume that the chains are elongated under deformation, and we neglect the small geometrical factor that results from the fact that chain segments are not all aligned with the principal direction of stretch. The number of chains per unit area is a_M^{-2} , where a_M is the monomer length scale. The tensile stress is then given by

$$\sigma_{11} - \sigma_{22} = \frac{H(R^* - R_0)}{a_M^2} = \frac{3kT}{N^{1/2} a a_M^2} [\exp(\varepsilon_H^*) - 1]. \quad (5)$$

This relationship between the critical tensile stress and the molecular strain depends only on the assumed form of the spring constant. The tensile stress at rupture is calculated by incorporating the limiting strain calculated from Eq. (4) into Eq. (5).

III. PREDICTIONS

Equations (4) and (5) are the principal results of the analysis. The model requires four parameters: the molecular weight, the entanglement molecular weight M_e , the length of the monomer unit a_M , and the reptation time τ_d . The number of entanglements per chain N and the average entanglement spacing a can be calculated from these parameters, which can be obtained independently. The data available for comparison with the theory are for a polyisoprene with a molecular weight of 575 000 and a polydispersity of 1.02 [Vinogradov *et al.* (1975); Vinogradov (1975)] and a poly-(1,2 butadiene) with a molecular weight of 135 000 and a polydispersity of 1.75 [Borisenkova *et al.* (1978)]. The parameters used for the polyisoprene are $M_e = 3285$, $a = 4.736$ nm, $a_M = 0.684$ nm, and $G_N^0 = 0.55$ MPa, while the parameters used for the poly-(1,2 butadiene) are $M_e = 2178$, $a = 4.537$ nm, $a_M = 0.617$ nm, and $G_N^0 = 0.81$ MPa. The zero-shear vis-

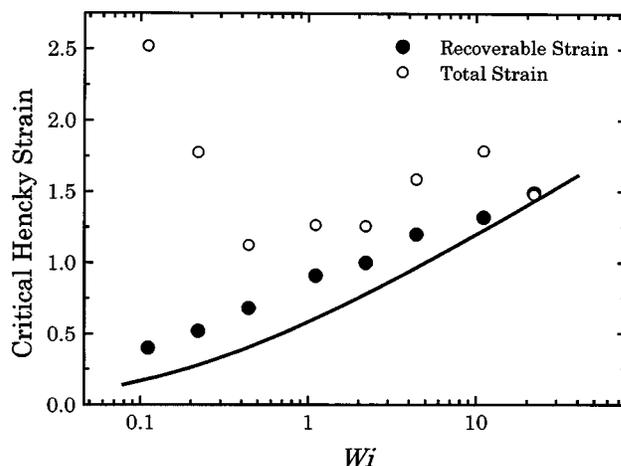


FIG. 1. Hencky strain at rupture as a function of the Weissenberg number for $N = 174$. The data are for a polyisoprene with a molecular weight of 575 000 and a polydispersity of 1.02 [Vinogradov *et al.* (1975)]. The line represents Eq. (4).

cosities η_0 were obtained from the original publications. The values of the plateau modulus G_N^0 , the entanglement molecular weight, and the entanglement spacing were obtained from the review by Fetters *et al.* (1994). The reptation time was estimated from the zero-shear viscosity as [Doi and Edwards (1986)] $\tau_d = 12 \eta_0 / \pi^2 G_N^0$. (There is some ambiguity in the proper choice of the reptation time. We have used this definition throughout.) Bhattacharjee and co-workers (2003a, b) reported values of reptation times that are as much as 5–10 times larger than those given by this definition, although the number of entanglements per chain for their solutions is substantially smaller than for the Vinogradov melts.

Figure 1 shows the recoverable Hencky strain at rupture as a function of the Weissenberg number for the polyisoprene, together with the total strain (strain rate multiplied by time to failure). The data at Weissenberg numbers below 0.5, where the total strain is much larger than the recoverable strain, are in the transition regime. The model predictions are in good agreement with the experimental recoverable strain data in both the rubbery and transition regimes. The prediction of total strain in the transition regime is beyond the scope of the scaling theory, however. The tensile stresses at rupture for polyisoprene and poly-(1,2 butadiene), normalized with respect to the plateau modulus, are shown as functions of the Hencky strain at rupture in Fig. 2. The model is in quantitative agreement for the limiting stress of polyisoprene. The agreement is not as good for the more polydisperse poly-(1,2 butadiene); the elongational behavior is dominated by higher molecular weight fractions in polydisperse systems, and the deviation is in the expected direction. The data and the model predictions are shown on a linear scale in Fig. 3, together with the Malkin–Petrie (1997) empirical correlation $\sigma_{11} - \sigma_{22} = 0.18 + 1.2(\varepsilon_H^* - 0.5)$.

IV. CALCULATION OF TIME TO RUPTURE

Calculation of the time to rupture requires an estimate of the time evolution of the stress, strain, or deformation rate, depending on the mode of the elongational flow. Such a calculation is outside the scope of the scaling theory, but the theory can be combined

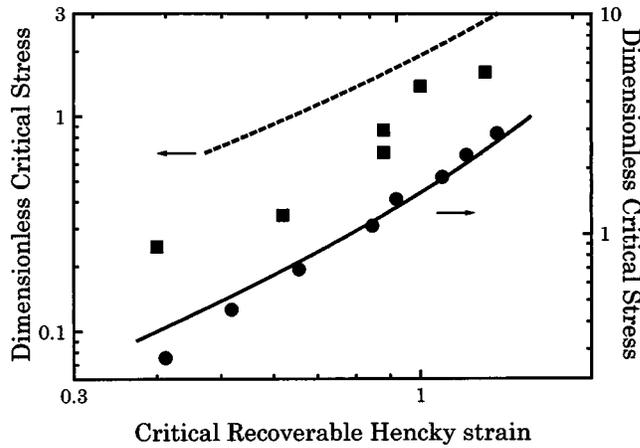


FIG. 2. Dimensionless stress at rupture as a function of recoverable Hencky strain. The data are for a polyisoprene with a molecular weight of 575 000 and a polydispersity of 1.02 (closed circles and line) [Vinogradov *et al.* (1975)] and a poly-(1,2 butadiene) with a molecular weight of 135 000 and a polydispersity of 1.75 (closed squares and dashed line) [Borisenkova *et al.* (1978)]. The lines represent Eq. (5).

with independent calculations that employ a stress constitutive equation for the melt. The time to rupture at a steady elongation rate in the rubbery regime can be estimated by computing the time required to reach the critical stress. We illustrate this approach using the single-mode upper-convected Maxwell model (UCM); the single-mode Maxwell model is unlikely to describe the melt rheology quantitatively, but it suffices for illustrative purposes.

The general equation for the UCM in uniform uniaxial elongational flow is [Petrie (1979)]

$$\tau^2 \ddot{\sigma} + (2 - \tau \dot{\epsilon} - \tau \ddot{\epsilon} / \dot{\epsilon}) \tau \dot{\sigma} + (1 - \tau \dot{\epsilon} - 2\tau^2 \dot{\epsilon}^2 - \tau \ddot{\epsilon} / \dot{\epsilon}) \sigma = 3G\tau \dot{\epsilon}. \quad (6)$$

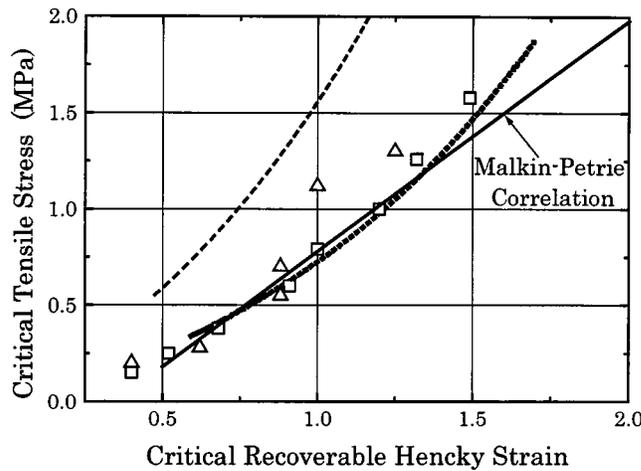


FIG. 3. Limiting tensile stress as a function of recoverable strain at rupture for polyisoprene (the squares are the experimental data and the dotted line is the theory) [Vinogradov *et al.* (1975)] and poly-(1,2 butadiene) (the triangles are the experimental data and the dashed line is the theory) [Borisenkova *et al.* (1978)]. The solid line is the Malkin and Petrie (1997) correlation.

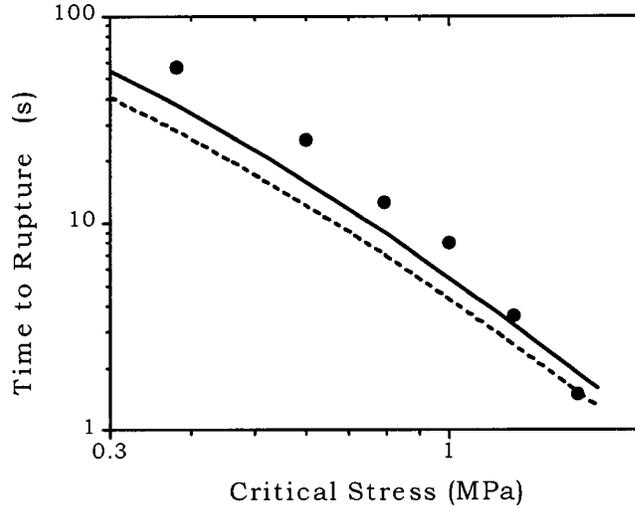


FIG. 4. Time to rupture as a function of tensile stress at rupture for elongation at a constant rate. The points are data in the rubbery regime for a polyisoprene with a molecular weight of 575 000 and a polydispersity of 1.02 [Vinogradov (1975)]. The lines are the prediction using the single-mode upper-convected Maxwell model: broken line, $\tau = 20\tau_d$; solid line, $\tau = 50\tau_d$.

$\sigma = \sigma_{11} - \sigma_{22}$ is the tensile stress, τ is the characteristic relaxation time, and G is the modulus. The product τG must equal the zero-shear viscosity, η_0 . Figure 4 shows the time to rupture at constant elongation rate for the polyisoprene as a function of tensile stress. Only the data for $Wi > 0.5$, which are in the rubbery zone, are included. The proper choice of a mean relaxation time to employ with the UCM is not obvious, except that it should be longer than the average from shear measurements, and predictions are shown for $\tau = 20\tau_d$ and $50\tau_d$. The predictions are in very rough agreement with the experiments—perhaps as good as can be expected with such a crude model—but the shape of the computed time-to-rupture curve is less sensitive to stress than are the data.

When a filament is stretched at constant stress, the rate of elongation is initially at a maximum (it is infinite in the absence of inertia) and then decreases as the steady state is approached. In this case the instantaneous value of the elongation rate fixes the maximum permissible tension in Eq. (1). Rupture occurs when the maximum permissible tension decreases to a value equal to the tension, in which case it follows from Eq. (5) that the critical elongation rate is

$$\dot{\epsilon}_c = \frac{\sigma a_M^2}{\zeta_e N a}. \quad (7)$$

The time to rupture is obtained by solving Eq. (6) for the evolution of the elongation rate at fixed stress until Eq. (7) is satisfied. The time to rupture for the polyisoprene at constant stress is plotted as a function of imposed stress in Fig. 5. The data points for stresses below 0.2 MPa are unlikely to be in the rubbery regime. The quality of the prediction using the UCM is comparable to that for the constant elongation rate, but here the computed time to rupture is more sensitive to the imposed stress than is exhibited by the data.

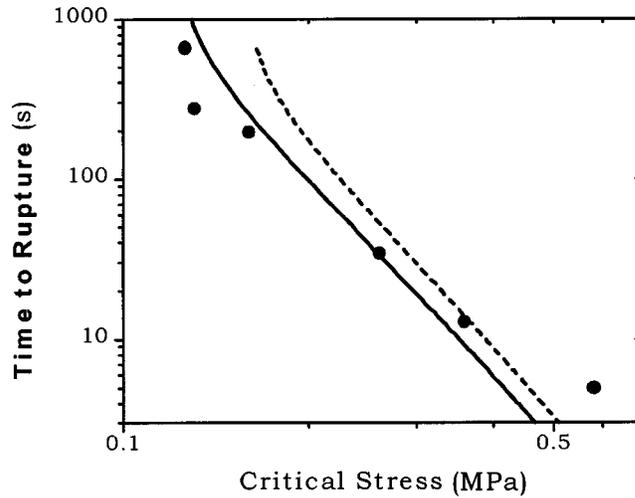


FIG. 5. Time to rupture as a function of tensile stress for elongation at controlled stress. The points are the data for a polyisoprene with a molecular weight of 575 000 and a polydispersity of 1.02 [Vinogradov (1975)], while the lines are the prediction using the single-mode upper-convected Maxwell model: broken line, $\tau = 20\tau_d$; solid line, $\tau = 50\tau_d$.

V. CONCLUSION

The rupture model is fully predictive, with no adjustable parameters, save the ambiguity in the definition of the reptation time. It is clear that the model captures the general rupture characteristics of the available data sets and the empiricisms reported by Malkin and Petrie (1997), and agrees quantitatively with the critical stress–critical strain data and the dependence of critical strain on the Weissenberg number for a monodisperse polymer. Calculation of the time to rupture requires the introduction of a constitutive equation and shows less satisfactory agreement when the single-mode upper-convected Maxwell model is employed. The major limitation to use of the model for predictive purposes is its restriction to the rubbery regime.

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APPENDIX

The zero-shear viscosity of an entangled melt can be written [Ferry (1980)]

$$\eta_0 = \frac{\rho N_a R_0^2 \zeta_0}{36 M_0} Q_e. \quad (\text{A1})$$

Here, ρ is the density, N_a is Avogadro's number, M_0 is the monomer molecular weight, R_0 is the equilibrium mean-square end-to-end distance, and ζ_0 is the segmental friction coefficient. Q_e is a correction for entanglements. We define an effective segmental friction coefficient for the entangled system as

$$\zeta_e = Q_e \zeta_0. \quad (\text{A2})$$

The reptation time is defined as [Ferry (1980)]

$$\tau_d = \frac{15}{\pi^2} \frac{M_e}{\rho RT} \eta_0. \quad (\text{A3})$$

M_e is the entanglement molecular weight. From Eqs. (A1)–(A4) we therefore have

$$\zeta_e = \frac{12\pi^2}{5N_e} \frac{kT}{R_0^2} \tau_d, \quad (\text{A4})$$

where N_e is number of monomers per entanglement (M_e/M_0). The number of entanglements per molecule decreases under flow [Marrucci (1984)], which will tend to decrease the friction between the molecules. The simplest way to introduce this effect in the format employed here is to note that the characteristic length scale for friction is no longer R_0 , but the mean-square end-to-end distance R . Replacing R_0 in Eq. (A4) by R , we obtain

$$\zeta_e = \frac{12\pi^2}{5N_e} \frac{kT}{R^2} \tau_d. \quad (\text{A5})$$

References

- Bhattacharjee P. K., D. A. Nguyen, G. H. McKinley, and T. Sridhar, "Extensional stress growth and stress relaxation in entangled polymer solutions," *J. Rheol.* **47**, 269–290 (2003a).
- Bhattacharjee P. K., J. P. Oberhauser, G. H. McKinley, L. G. Leal, and T. Sridhar, "Extensional rheometry of entangled solutions," *Macromolecules* in press. (2003b).
- Borisenkova, E. K., O. Yu. Sabsai, M. K. Kurbanaliev, V. E. Dreval, and G. V. Vinogradov, "Criterion of ultimate strength of fluid high polymers in uniaxial extension," *Polymer* **19**, 1473 (1978).
- Doi, M., and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986), p. 229.
- Ferry, J. D., *Viscoelastic Properties of Polymers*, 3rd ed. (Wiley, New York, 1980), p. 248.
- Fetters, L. J., D. J. Lohse, D. Richter, T. A. Witten, and A. Zirkel, "Connection between polymer molecular weight, density, chain dimensions, and melt viscoelastic properties," *Macromolecules* **27**, 4639–4647 (1994).
- Larson, R. G., *The Structure and Rheology of Complex Fluids* (Oxford, New York, 1999), p. 114.
- Malkin, A. Ya., and C. J. S. Petrie, "Some conditions for rupture of polymer liquids in extension," *J. Rheol.* **41**, 1–25 (1997).
- Marrucci, G., "Molecular modeling of flows of concentrated polymers," in *Advances in Transport Processes*, edited by A. S. Mujumdar and R. A. Mashelkar (Wiley, New York, 1984), Vol. V, pp. 1–36.
- McKinley, G. H., and O. Hassager, "The Considère condition and rapid stretching of linear and branched polymer melts," *J. Rheol.* **43**, 1195–1212 (1999).
- Petrie, C. J. S., *Elongational Flows* (Pitman, London, 1979).
- Petrie, C. J. S., and M. M. Denn, "Instabilities in polymer processing," *AIChEJ.* **22**, 209–236 (1976).
- Reiner, M. and A. Freudenthal, "Failure of a material showing creep (a dynamical theory of strength)," in *Proceedings of the 5th International Congress on Applied Mechanics*, 1938, pp. 228–233 [reprinted in M. Reiner, *Selected Papers* (Elsevier, Amsterdam, 1975), pp. 141–148].
- Smith, T. L., "Ultimate tensile properties of elastomers. I. Characterization by time and temperature independent failure envelope," *J. Polym. Sci. A* **1**, 3597–3615 (1963).
- Vinogradov, G. V., "Viscoelasticity and fracture phenomenon in uniaxial extension of high-molecular linear polymers," *Rheol. Acta* **14**, 942–954 (1975).
- Vinogradov, G. V., A. Ya. Malkin, V. V. Volosevitch, V. P. Shatalov, and V. P. Yudin, "Flow, high-elastic (recoverable) deformations and rupture of uncured high molecular weight linear polymers in uniaxial extension," *J. Polym. Sci., Polym. Phys. Ed.* **13**, 1721–1735 (1975).