be fit to a single exponential, suggests several relaxation processes. Fits to a two-exponential model (eq 4) are

$$d_{33} = Ae^{-t/\tau_1} + Be^{-t/\tau_2} \quad (4)$$

shown in Figure 3. For the annealed sample, approximate half-lives for short-term and long-term decay are 1.5 and 195 days, respectively. We find that the amplitude of the short-term process is more sensitive to the presence of THF and can be greatly diminished by annealing. This argues that the short-term process involves facile chromophore reorientation in THF-rich (high local free volume) microenvironments. Preliminary experiments also indicate that the long-term decay rate of $d_{33}$ is increased by higher chromophore densities and by higher poling fields. That effective poling can be carried out more than 20 °C below $T_g$ underscores the importance of secondary relaxation processes[21] in achieving/dissipating preferential chromophore alignment.

The present results considerably expand what is known about the properties of NLO chromophore-functionalized polystyrenes. Equally important, they suggest future synthetic and processing strategies for materials with even more efficient frequency-doubling properties.

**Acknowledgment.** This research was supported by the NSF-MRL program through the Materials Research Center of Northwestern University (Grant DMR85-20280) and by the Air Force Office of Scientific Research (Contract AFOSR-86-0105).

### References and Notes


(1) (a) Heeger, A. J., Orenstein, J., Ulrich, D. R., Eds. *Nonlinear Optical Properties of Polymers*; Materials Research Society Symposia Proceedings; 1988; Vol. 109. (b) Chemla, D. S., Zyss, J., Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic: New York, 1987; Vol. 1, 2. (c) Willand, C. S.; Williams, D. J. *Ber. Bunsenges. Phys. Chem.* **1987**, *91*, 1304–1310. (d) Khanarian, G., Ed. *Molecular and Polymeric Optoelectronic Materials: Fundamentals and Applications*; SPIE, 1986; Vol. 682. (e) Zyss, J. *J. Mol. Electron.* **1985**, *1*, 25–56. (f) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690–703. (g) Williams, D. J., Ed. *Nonlinear Optical Properties of Organic and Polymeric Materials*; American Chemical Society: Washington, DC, 1983; Vol. 233.

(2) Meredith, G. R.; Van Dusen, J. G.; Williams, D. J. *Macromolecules* **1982**, *15*, 1385–1389.

(3) (a) Singer, K. D.; Sohn, J. E.; Lalama, S. J. *Appl. Phys. Lett.* **1986**, *49*, 248–250. (b) Small, K. D.; Singer, K. D.; Sohn, J. E.; Kuzyk, M. G.; Lalama, S. J. In ref 1d, pp 150–169. (c) Singer, K. D.; Kuzyk, M. G.; Sohn, J. E. *J. Opt. Soc. Am. B* **1987**, *4*, 968–975.

(4) (a) Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. *Macromolecules* **1988**, *21*, 526–528. (b) Katz, H. E.; Dirk, C. W.; Schilling, M. L.; Singer, K. D.; Sohn, J. E. In ref 1a, pp 127–131.

(5) Ye, C.; Marks, T. J.; Yang, Y.; Wong, G. K. *Macromolecules* **1987**, *20*, 2322–2324. Functionalization levels no higher than 12.5% were achieved in early studies with (PS)$CH_2X$ materials.

(6) For examples of chromophore-functionalized liquid crystal polymers (of unknown SHG properties), see: (a) Leslie, T. M.; Demartino, R. N.; Choe, E. W.; Khanarian, G.; Haas, D.; Nelson, G.; Stamatoff, J. B.; Stuetz, D. A.; Teng, C.-C.; Yoon, H.-N. *Mol. Cryst. Liq. Cryst.* **1987**, *153*, 451–477. (b) Griffin, A. C.; Amjad, M.; Howell, G. A. In ref 1a, pp 115–125. (c) LeBarny, P.; Ravaux, G.; Dubois, J. C.; Parneix, J. P.; Njeumo, R.; Legrand, C.; Levelut, A. M. In ref 1d, pp 56–75.

(7) Reported in part at the Fall Meeting of the MRS, Boston, Nov 30–Dec 5, 1987; *Mater. Res. Soc. Symp. Proc.* **1988**, *109*, 263–269.

(8) Panunto, T. W.; Urbanczyk-Lipowska, Z.; Johnson, R.; Etter, M. E. *J. Am. Chem. Soc.* **1987**, *109*, 7786–7797.

(9) (a) Freichet, J. M. J.; Tessier, T. J.; Wilson, C. G.; Ito, H. *Macromolecules* **1985**, *18*, 317–321 and references therein. (b) We thank Dr. D. Keene, Hoechst-Celanese Specialty Operations, for samples.

(10) General phenol etherification methodology: Shirley, D. A.; Ready, W. H. *J. Am. Chem. Soc.* **1951**, *73*, 458–459.

(11) General synthetic methodology: Marvel, C. S.; Sekera, V. C. *Org. Synth.* **1955**, *III*, 366–367. Anal. Calcd for $C_{18}H_{20}N_2O_5S$: C, 57.43; H, 5.36; N, 7.44; S, 8.52. Found: C, 57.17; H, 5.13; N, 7.44; S, 8.59. Mp 95–96 °C; $^1$H NMR ($CDCl_3$) $\delta$ 2.030 (m, 4 H), 2.363 (s, 3 H), 3.180 (m, 1 H), 3.372 (m, 1 H), 3.830 (m, 1 H), 4.010 (m, 2 H), 6.354 (d, 2 H, $J$ = 9.2 Hz), 7.230 (d, 2 H, $J$ = 4 Hz), 7.662 (d, 2 H, $J$ = 7.6 Hz), 7.981 (d, 2 H, $J$ = 9.2 Hz).

(12) Zyss, J.; Nicoud, J. F.; Coquillay, M. *J. Chem. Phys.* **1984**, *81*, 4160–4167.

(13) Functionalization levels determined by solution optical spectrophotometry and elemental analysis were in good agreement. For films, $\lambda_{max}$ = 400 nm (red-shifted ca. 10 nm from THF solution) and is insensitive to functionalization level and annealing. $T_g$ (functionalization level) $\approx$ 108 (15%), 108 (25%), 103 (48%) °C after drying at 100 °C under vacuum.

(14) Unannealed materials exhibit $T_g \approx 50$ °C.

(15) For discussions of the importance of hydrogen-bonding in (PS)OH structure and dynamics, see: (a) Moskala, E. J.; Varnell, D. F.; Coleman, M. M. *Polymer* **1985**, *26*, 228–234. (b) Nakamura, A.; Hatakeyama, T.; Hatakeyama, H. *Polymer* **1981**, *22*, 473–476. (c) Hatakeyama, T.; Nakamura, A.; Hatakeyama, H. *Polymer* **1978**, *19*, 593–594.

(16) Displacements in $\nu_{OH}$ are observed.

(17) (a) Hibma, T.; Pfluger, P.; Zeller, H. R. In *Electronic Properties of Polymers and Related Compounds*; Kuzmany, H., Mehring, M., Roth, S., Eds.; Springer-Verlag: Berlin, 1985; pp 317–326 and references therein. (b) Newman, B. A.; Chen, P.; Pae, K. D.; Scheinbeim, J. I. *J. Appl. Phys.* **1980**, *51*, 5161–5164 and references therein. (c) Blythe, A. R. *Electrical Properties of Polymers*; Cambridge University Press: Cambridge, 1979; Chapter 6. (d) Mathes, K. N. In *Encyclopedia of Polymer Science and Engineering*; Wiley: New York, 1986; Vol. 5, pp 512–593. (e) Block, H. *Adv. Polym. Sci.* **1979**, *33*, 93–167 and references therein.

(18) Jerphagnon, J.; Kurtz, S. K. *J. Appl. Phys.* **1970**, *41*, 1667.

(19) Barzoukas, M.; Josse, D.; Fremaux, P.; Zyss, J.; Nicoud, J. F.; Morely, J. O. *J. Opt. Soc. Am. B* **1987**, *4*, 977–986.

(20) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*, 2nd ed.; Wiley: New York, 1986; pp V-58–59.

(21) Struik, L. C. E. *Physical Aging in Amorphous Polymers and Other Materials*; Elsevier: Amsterdam, 1978; Chapters 1, 2, 9.


**C. Ye, N. Minami, and T. J. Marks***

*Department of Chemistry and the Materials Research Center, Northwestern University Evanston, Illinois 60208*

**J. Yang and G. K. Wong***

*Department of Physics and the Materials Research Center, Northwestern University Evanston, Illinois 60208*

*Received May 18, 1988; Revised Manuscript Received July 14, 1988*

## New Entanglement Model of Condensed Linear Polymers: Localized Gauss Integral Model

Entanglement of polymers is usually discussed in terms of the tube model.[1] This model has succeeded in explaining numerous viscoelastic properties of entangled polymers very well, but its physical foundation has not yet been fully established. A more fundamental approach to this problem is to introduce topological invariants such as the Gauss integral (GI) explicitly into the statistical mechanics of polymers.[2] This approach has been used to calculate the modulus of network polymers and the second virial coefficients of ring polymers in the $\Theta$ state, $A_2^{\Theta}$.[3] Although the two theories have so far been studied inde-

0024-9297/88/2221-2901$01.50/0 

pendently, there must be a close relationship between them. In this work, we propose a new model, a "localized Gauss integral model", which links the two theories. This model shows that $G_N$, the plateau modulus of linear polymers, had a close relationship with $A_2^{\Theta}$. It can also predict the concentration dependence of $G_N$. The GI is defined by $\int\int dr_1\, dr_2\, \nabla(1/r_{12})$, where $r_1$ and $r_2$ are the two curves, and applies to both closed loops and open segments of sufficient length. For example, let us consider a pair of linear or ring polymers, in which the GI has a value $t$, and the relative position of the centers of mass is $w$. To a good approximation, the distribution function of $t$ is given by[4a]

$$P(t|w) = (1 - g/h)\delta(t) + (g/h)(4\pi x^2/h)^{1/2} \exp(-4t^2x^2/h) \quad (1)$$

$$x = (8\bar{\gamma} n^{1/2})^{-1/2} \quad (2)$$

where $g$ and $h$ are single- and double-contact probabilities among the submolecules, $n$ is the number of main-chain bonds per polymer, and $\bar{\gamma}$ is the topological interaction parameter per main-chain bond. In ring polymers, GI takes integral values $T$: $T = 0$, $T = \pm 1$, ..., and its distribution function, $P_t(w)$, is given by the integration of $P(t|w)$ with respect to $t$ over $[T - {}^1/_2, T + {}^1/_2]$. By use of the eq 1 for $P(t|w)$, the topological second virial coefficient is given by

$$A_2^{\Theta} = (N_A/2n_r^2M_0^2) \int (g_r/h_r)(1 - \mathrm{erf}\,(x_r/h^{1/2}))\, dh \quad (3)$$

where $N_A$ is Avogadro's number, $M_0$ is the molecular weight per main-chain bond, and the subscript attached to $x$, $n$, $g$, and $h$ indicates that they are for ring polymers.

Now let us consider linear polymers. Entanglements between linear polymers are time dependent, but if they are observed on a time-scale sufficiently shorter than the disengagement time of the tube model, $\tau_d$, the GI will be almost constant and the distribution functions will be given by eq 1. In concentrated systems, however, there is another difficulty in that the GIs are not good topological invariants for such highly entangled systems, because they represent only the topological states of two polymers, while the polymers in the concentrated systems entangle with other polymers simultaneously and form complicated topological states which cannot be classified by the GI alone. Although higher topological invariants such as Alexander polynomials can be used in principle, it is difficult to introduce them into the statistical mechanics of polymers and it is reasonable to consider the approximation of a "localized Gauss integral (LGI) model". One can argue that the repetition of the GI along any chain certainly gives a tube, and describes the main effect.

Let the system be composed of linear polymers, a, b, ..., each of which is divided into $m$ "local chains", $a_i$ ($i = 1$, ..., $m$) etc., and let $t_{a_ib_j}$ be GI defined for a pair of local chain, ($a_i$, $b_j$). In the LGI model, it is assumed that each $t_{a_ib_j}$ behaves like a topological invariant when it is observed on a time scale $\tau_1$ which is longer than the Rouse relaxation time $\tau_R$, i.e., the time necessary for local configurations of the polymers to randomize, but sufficiently shorter than the disengagement time $\tau_d$, the time required for the entanglement states to change significantly.[1] More precisely, it is assumed that $t_{a_ib_j}$ fluctuates around "quantized" average values, due to the restriction on the chain motion caused by entanglements of its neighboring local chains, $a_{i\pm1}$ and $b_{j\pm1}$. In analogy with ring polymers, $|T_{a_ib_j}| \geq 1$ corresponds to entanglement states and $T_{a_ib_j} = 0$ to a nonentanglement state. The probability of occurrence of the entanglement states, $\epsilon_{a_ib_j}$, is defined by the integration of $P(t|w)$ in regard to $t$ over $|t| \geq 0.5$, i.e.

$$\epsilon_{a_ib_j}(w_{a_ib_j}) = (g_{a_ib_j}/h_{a_ib_j})(1 - \mathrm{erf}\,(x_{a_ib_j}/h_{a_ib_j}{}^{1/2}) \quad (4)$$

where the subscript $a_ib_j$ attached on $w$, $x$, $g$, and $h$ indicates that they are defined in regard to local chain pair ($a_i$,$b_j$). The average number of entanglement partners per local chain, $N$, is given by

$$N(x_l) = (c/n_lM_0)E(x_l) \quad (5)$$

$$E(x_l) = \int \epsilon_{a_ib_j}(w_{a_ib_j})\, dw_{a_ib_j}$$

where $c$ is the concentration (of mass) and $n_l$ the average number of the main chain bonds per local chain. It is assumed that $n_l$ is determined by the condition

$$N(x_l) = 1 \quad (6)$$

Now let us consider the distribution function of the whole system. For simplicity, we assume that there are only two topological states of the local chains, the entanglement $T_{a_ib_j} \neq 0$ and the nonentanglement state $T_{a_ib_j} = 0$. In this approximation, the topological state of the whole system is represented by set $\rho$ of the all local chain pairs, ($a_i$,$b_j$), which are in the entanglement state. Let $P(\rho,\{r\})$ be the distribution function of the whole system in the entanglement state $\rho$, where $\{y\} = (r_{a_i}, r_{b_j}, ...)$ is a set of coordinates of the centers of the local chains, and let it be split into the "phantom" part, $P_{ph}(\{r\})$, and the "topological" part, $P_{top}(\rho,\{r\})$, as follows: $P(\rho,\{r\}) = P_{ph}(\{r\})P_{top}(\rho,\{r\})$. The phantom part is given by the distribution function of the Rouse model. It is assumed that the topological part, $P_{top}(\rho,\{r\})$, is given by a superposition of the entanglement and nonentanglement probability of the local chains as follows:

$$P_{top}(\rho,\{r\}) = \prod_{(a_ib_j)\in\rho} \epsilon_{a_ib_j} \prod_{(c_kd_l)\in\rho} (1 - \epsilon_{ckdl}) \quad (7)$$

The pseudoequilibrium values of $r_{a_i}$ and $n_{a_i}$ in the entanglement state $\rho$, $\tilde{r}_{a_i}(\rho)$ and $\tilde{n}_{a_i}(\rho)$, are determined by the following conditions:

$$\partial P(\rho\{r\})/\partial r_{a_i} = 0 \quad (8)$$

$$\partial P(\rho,\{r\})/\partial n_{a_i} = 0$$

We further introduce the following simplification: Let $l_{a_i}$ and $w_{a_ib_j}$ be vectors $\tilde{r}_{a_{i+1}} - \tilde{r}_{a_i}$ and $\tilde{r}_{a_i} - \tilde{r}_{b_j}$, respectively, and let $|l_{a_i}, \theta_{a_i}, \phi_{a_i}|$ be intramolecular polar coordinates defined by $l_{a_i} = |l_{a_i}|$, $\cos\theta_{a_i} = l_{a_i}l_{a_i-1}/l_{a_i}l_{a_{i-1}}$, and $\phi_{a_i}$ is the internal rotation angle between $l_{a_i}$ and $l_{a_{i-2}}$ about $l_{a_{i-1}}$. For simplicity, we neglect distribution of ($n_{a_i}$, $l_{a_i}$, $\theta_{a_i}$, $w_{a_ib_j}$) among the local chains and assume that they take the same values, ($n_l$, $l$, $\theta$, $w$), in the all local chains; i.e.

$$n_{a_i} = \tilde{n}_l \qquad l_{a_i} = \tilde{l} \qquad \theta_{a_i} = \tilde{\theta} \qquad w_{a_ib_j} = \tilde{w} \quad (9)$$

Although the all $l_{a_i}$ and $\theta_{a_i}$ are fixed to their pseudoequilibrium values, $\tilde{l}$ and $\tilde{\theta}$, the polymers can still take random configurations due to the degrees of freedom in regard to $\phi_{a_i}$. By this simplification, $P(\rho,\{r\})$ becomes a function of $\tilde{n}_l$, $\tilde{l}$, and $\tilde{w}$, and their values are determined by eq 6 and 8. The angle $\tilde{\theta}$ is determined by the condition that the mean-square end-to-end distance of each polymer should be equal to its equilibrium value; i.e., $\tilde{l}^2(1 + \cos\tilde{\theta})/(1$

**Table I**
**$G_N$, $\bar{\gamma}$, and $A_2^{\Theta}$ of Typical Polymers**

| polymer | $G_N$, dyn/cm$^2$ [7] (bulk) | $b_0$, nm | $\bar{\gamma}$ | $A_2^{\theta}$, $10^{-5}$ cm$^3$/g $M_r = 10^4$ | $10^5$ | $10^6$ |
|---|---|---|---|---|---|---|
| polyethylene | $27.0^{7b} \times 10^6$ | 0.41 | 0.0105 | 88.2 | 40.0 | 15.1 |
| polybutadiene | $12.0 \times 10^6$ | 0.33 | 0.0074 | 42.8 | 21.1 | 8.29 |
| polyisobutylene | $3.2 \times 10^6$ | 0.40 | 0.0036 | 10.4 | 8.31 | 4.02 |
| poly(dimethylsiloxane) | $2.4 \times 10^6$ | 0.43 | 0.0046 | 9.24 | 6.79 | 3.20 |
| polystyrene | $2.0 \times 10^6$ | 0.49[8] | 0.0033[8] | 4.76 | 4.82 | 2.64 |

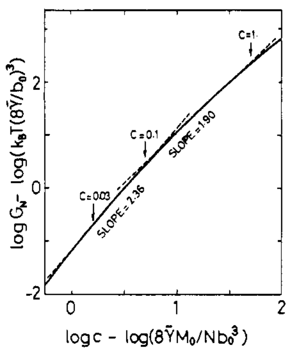


**Figure 1.** Concentration dependence of $G_N$. The arrows represent the positions of $c$ = 1.0, 0.1, and 0.03 for polystyrene; the average slope in $1 \geq c \geq 0.1$ is equal to 1.90 and in $0.1 \geq c \geq 0.03$, 2.36.

$- \cos \tilde{\theta}) = \tilde{n}_1 b_0^2$ where $b_0$ is the Kuhn statistical length per main-chain bond. Since these equations contain an unknown parameter $(x_l, (\tilde{n}_l, \tilde{l}, \tilde{\theta}, \tilde{w})$ are computed numerically as functions of $x_l^6$.

Now the stress tensor of the system is given by

$$\sigma = -\sum_{a_i} \langle r_{a_i} f_{a_i} \rangle / V \tag{10}$$

where $V$ is the volume of the system and $f_{a_i}$ is an average force acting on the center of local chain $a_i$; $f_{a_i} = -k_B T \partial \ln P / \partial r_{a_i}$. When approximation (9) is introduced, eq 10 gives the plateau modulus

$$G_N = (cRT/\tilde{n}_l M_0) G_N(x_l)$$

$$G_N(x_l) = \{\tilde{l}^2 + (\tilde{l}F^l + \tilde{w}F^w/2)/3 - \tilde{l}^2(1 + 4F^{nn}/{}^3\!/_5)^{1/2}/\tilde{n}_0 b_0^2 \tag{11}$$

where $F^x$ and $F^{xx}$ ($x = l, w,$ or $n$) are the first and second derivative of log $P$ with respect to $x$. (Derivation of eq 11 will be given elsewhere.) Since $(\tilde{n}_l, \tilde{l}, \tilde{\theta}, \tilde{w})$ have already been computed numerically as functions of $x_l$, so are $G_N(x_l)$ and $E(x_l)$. Using eq 5, 6, and 11, we find

$$G_N/A = x_l^6 \bar{G}_N(x_l)/E(x_l), \qquad A = k_B T(8\bar{\gamma}/b_0)^3,$$
$$c/B = x_l^2/E(x_l), \qquad B = 8M_0\bar{\gamma}/N_A b_0^3 \tag{12}$$

By computation of $G_N(x_l)$ and $E(x_l)$ numerically for various $x_l$, log $G_N/A$ is plotted against log $(c/B)$ in Figure 1. Since eq 12 contains only one unknown parameter $\bar{\gamma}$, it can be determined from experimental data for $G_N$. For polystyrene (PS), for example, we get $\bar{y} = 0.0033$ from $G_N = 2.0 \times 10^5$ dyn/cm$^2$ (bulk)[7] and $b_0$ = 0.49 nm. It is remarkable that the same $\bar{\gamma}$ is obtained from $A_2^{\Theta}$ data using eq 3.[8] The power, $\alpha$, of the concentration dependence of $G_N$ is given by the slope of the curve in Figure 1; for PS, experimental data are $\alpha$ = 2.0 in the high concentration region $C \geqslant 0./$[10] and $\alpha$ = 2.3 in the low concentration region $0.1 \geq c \geq 0.03$;[11] theoretical values are $\alpha$ = 1.90 and 2.36, respectively, in the same regions (see Figure 1), a very good agreement with the experiments. As shown before,[4b] eq 3 leads to good agreement in the molecular weight dependence of theoretical and experimental $A_2^{\Theta}$. It is important that these results have been obtained by using the same topological distribution function[1] with a single adjustable parameter $\bar{\gamma}$, although $G_N$ and $A_2^{\Theta}$ are seemingly quite different quantities. Although PS is the only polymer for which $A_2^{\Theta}$ has so far been measured, there are numbers of experimental data of bulk polymers for which we can calculate $\bar{\gamma}$ and $A_2^{\Theta}$ using their bulk $G_N$ data. In Table I, $G_N$ and $b_0$ of typical bulk polymers and their $\bar{\gamma}$ and $A_2^{\Theta}$ (for $M = 10^4, 10^5, 10^6$, computed) are summarized. It is interesting that $G_N$ is roughly proportional to $A_2^{\Theta}$ as seen from Table I.

Finally, a comment is given on the relationship between the tube and LGI model. This model is considered to be a kind of transient network, an idea put forward many years ago by Lodge in his book *Elastic Liquids*.[12] In such a model the polymers are temporarily linked together by "entanglement cross-links" (or by pairs of local chains" in the LGI model and motion of the polymers is caused by creation and annihilation (or "renewal") of the entanglement cross-links; this motion is essentially the same as the reptation of the tube model. Although we have not considered the Brownian motion of the polymers explicitly in this work, we have assumed implicitly such a reptative motion. What is new in the model is that it is described in terms of topological theory and that it can predict the absolute value of $G_N$, if $\bar{\gamma}$ is already known from $A_2^{\Theta}$ data. Further discussion will be given in forthcoming work.

**Acknowledgment.** We thank Dr. L. J. Fetters of Exxon Research and Engineering Co. for kindly providing us the $G_N$ data in Table I. This work was supported in part by the Japanese Society for the Promotion of Science, Grant 60470104.

**Registry No.** Polyethylene, 9002-88-4; polybutadiene, 9003-17-2; polyisobutylene, 9003-27-4; polystyrene, 9003-53-6.

## References and Notes

(1) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986.
(2) Edwards, S. F. *Proc. Phys. Soc.* **1967**, *91*, 513. Deam, R. T.; Edwards, S. F. *Philos. Trans. R. Soc. London, A* **1976**, *A.280*, 317.
(3) Iwata, K. *J. Chem. Phys.* **1985**, *83*, 1969.
(4) (a) Iwata, K.; Kimura, T. *J. Chem. Phys.* **1981**, *74*, 2039. Iwata, K.; *Ibid.* **1983**, *78*, 2278. (b) *Macrmolecules* **1985**, *18*, 115.
(5) In the previous papers,[4b] $b_0$ and $\bar{\gamma}$ are defined per monomer. For vinyl polymers, their previous values should be divided by $2^{1/2}$ in this paper.
(6) Iwata, K.; Edwards, S. F., unpublished results.
(7) (a) Graessley, W. W.; Edwards, S. F. *Polymer* **1981**, *22*, 1329. (b) Fetters, L. J., private communication.
(8) In ref 4b, a little larger $b_0$ (0.51 nm) is assumed, which gives a slightly smaller $\bar{\gamma}$ = 0.0029.
(9) Roovers, J.; Toporowski, P. M. *Macromolecules* **1983**, *16*, 843.
(10) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980; Chapter 10.

(11) Osaki, K.; Takaton, E.; Tsunashima, Y.; Kurata, M. *Macromolecules* **1987**, *20*, 525.
(12) Lodge, A. S. *Elastic Liquids*; Academic: New York, 1964.

[†]Present address: Faculty of Engineering, Fukui University, Bunkyo 3-9-1, Fukui 910, Japan.

**Kazuyoshi Iwata[†] and S. F. Edwards***

*Cavendish Laboratory, Cambridge University*
*Madingley Road, Cambridge CB3 OHE, England*

*Received March 8, 1988;*
*Revised Manuscript Received June 21, 1988*