JOURNAL OF MATERIALS SCIENCE 24 (1989) 1612–1616

Brittle fracture of low molecular weight polymers

ANTONIOS G. MIKOS, NIKOLAOS A. PEPPAS
School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907, USA

A new model is presented to predict the fracture energy of polymers with molecular weights smaller than the threshold value for the formation of chain entanglements. A fracture mechanism is assumed that calls for the sliding of the polymer chains in a microscopic craze at the crack tip. The plastic work is related to the chain interpenetration distance, which has been derived from the solution of the Fokker–Planck equation. The predictions of the model agree with experimental data of the fracture energy of polystyrene.

1. Introduction

The fracture energy of brittle polymers increases with the polymer molecular weight, M, up to the critical value, $2M_e$, corresponding to the onset of chain entanglements [1]. (The parameter M_e is the molecular weight between entanglements.) The fracture energy at this threshold molecular weight is an order of magnitude larger than the thermodynamic work of cohesion. For values of M larger than $2M_e$ the fracture energy increases abruptly with M and eventually reaches a plateau value [2, 3].

In a previous publication [4] we proposed a theory to predict the molecular weight dependence of the fracture energy and strength for polymers with $M > 2M_e$ using the structural and entanglement characteristics of the chain molecules. A chain scission criterion was invoked for the chain segments being entangled about the fracture plane and the theoretical predictions agreed with experimental measurements for polystyrene and poly(methyl methacrylate). The theory was also used [5] to investigate the effect of chain entanglements on the autohesion of linear polymers and predict the time dependence of the refracture energy of poly(methyl methacrylate) interfaces.

Polymers with molecular weights smaller than $2M_e$ are characterized by virtual lack of chain entanglements. The fracture mechanism of such low molecular weight polymers has been proposed by Haward *et al.* [6] and Kramer [7]. These investigators postulated that a craze exists at the crack tip as shown in Fig. 1. The craze is a cavitation zone with bundles of extended polymer chains bridging the confining glassy regions. Polymer chains anchored in both glassy regions about the craze can support any applied stresses. The microscopic mechanisms for the craze growth have been studied by Lauterwasser and Kramer [8]. The craze becomes unstable and the crack propagates when chain macromolecules fail to span the craze.

When chain entanglements are present, polymer chains do not have to connect the glassy regions themselves because they can form stable polymer fibrils. Kramer [7] developed a model to calculate the fracture energy of low molecular weight polymers from the craze fibril extension ratio and the craze surface drawing stress observed in high molecular weight polymers. The predictions of the model were in good agreement with experimental results.

The polymer chains in the craze are mobile, contrary to those in the glass, and can slide on each other to create two new surfaces. Kammer [9] suggested that the stored elastic energy is dissipated to heat resulting in the formation of a plastic zone. The local temperature rise in the crack vicinity increases the mobility of the polymer chains and, therefore, triggers off the craze formation and crack propagation.

A new theory is proposed here to predict the fracture energy of low molecular weight polymers from their thermal and structural properties. The fracture energy is related to the thermal energy required to form an unstable craze, the thickness of which is calculated using a stochastic model. The predictions of the theory are compared with the experimental data of the fracture energy of polystyrene.

2. Stochastic modelling of chain interpenetration

We define the interpenetration distance of a polymer chain in an arbitrary direction as the projection of the chain to an axis parallel to that direction. The interpenetration distance δ_x is generally equal to or larger than the projection r_x of the end-to-end distance of the chain to the x axis. (Here the x axis is defined normal to the fracture plane.) The parameter δ_x is a stochastic variable and its average value, $\bar{\delta}_x$, is calculated as

$$\bar{\delta}_x = \int_0^\infty \delta_x P(\delta_x)\, d\delta_x \qquad (1)$$

were $P(\delta_x)\, d\delta_x$ is the probability that a polymer chain has interpenetration distance in the range from δ_x to $\delta_x + d\delta_x$. The polymer chain can span a craze only if its interpenetration distance is larger than the primordial craze thickness, i.e., the craze thickness prior to deformation (see Fig. 2).

The probability density function $P(\delta_x)$ has been

0022-2461/89 $03.00 + .12

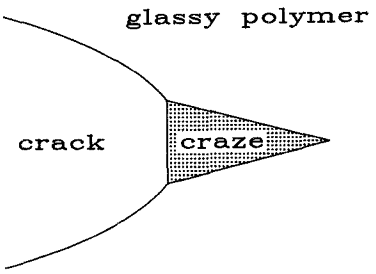

Figure 1 Schematic presentation of a craze formed at the crack tip in brittle polymer fracture.

calculated by Weidmann *et al.* [10]. An alternative method is proposed here to derive the function $P(\delta_x)$ from the solution of first passage problems [11]. The mathematical approach is similar to that we employed [5] to describe the tube disengagement and chain relaxation of high molecular weight polymers in polymer autohesion.

In the stochastic modelling of chain interpenetration the equivalent Gaussian chain of the actual macromolecule is considered. The degree of polymerization N and the statistical link length b are defined for polycarbon chains [4] as

$$N = 2N_0/3C_\infty \qquad (2)$$

$$b = (3/2)^{1/2}C_\infty l \qquad (3)$$

where N_0 is the degree of polymerization of the real chain, C_∞ is the characteristic ratio, and l is the bond length. The polymer chain is assumed long enough (i.e., $N_0 \gtrsim 50$) that the characteristic ratio is independent of the chain length.

A Gaussian chain is a Markov chain, because the orientation of any link is independent of that of any previous one. Therefore, the chain configuration can be visualized as the result of the random flight of a Brownian particle with jump length equal to the link length b. The probability, $p(0, 0; x, N)\,\mathrm{d}x$, that the end of the Nth link of a polymer chain starting from $x = 0$ be found between x and $x + \mathrm{d}x$ is equal to that of a Brownian particle starting from $x = 0$ and located in the range from x to $x + \mathrm{d}x$ after N jumps. The density function $p(0, 0; x, N)$ is the solution of the Fokker–Planck equation [11]

$$\frac{\partial}{\partial N}p(0, 0; x, N) = \frac{b^2}{6}\frac{\partial^2}{\partial x^2}p(0, 0; x, N) \qquad (4)$$

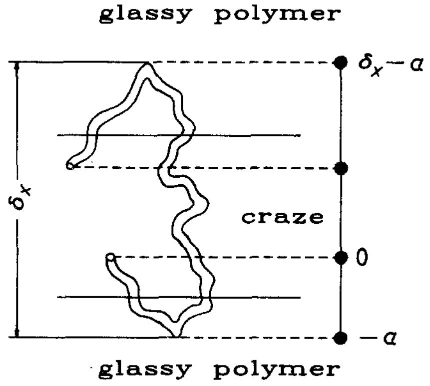

Figure 2 Schematic presentation of a polymer chain with interpenetration distance δ_x spanning a primordial craze. The x axis is normal to the fracture plane and its origin is located at one chain end. The chain configuration constitutes the trajectory of the random flight of a Brownian particle.

If we consider the one-dimensional diffusion of a Brownian particle along the x-axis, the interpenetration distance, δ_x, of a polymer chain of degree of polymerization N is equal to the maximum separation of two positions, namely $x = -a$ and $x = \delta_x - a$, of the particle about its starting point, $x = 0$, after N jumps (see Fig. 2). The density function $P(\delta_x)$ is obtained by solving a first-passage problem twice.

$$\begin{aligned} P(\delta_x) = &-2\left(\frac{b^2}{6}\right)^2 \int_0^N \mathrm{d}N_1 \\ &\times \int_0^{\delta_x} \mathrm{d}a \frac{\partial}{\partial x} p(x, N_1, a, \delta_x)|_{x=-a} \\ &\times \int_0^{N-N_1} \mathrm{d}N_2 \frac{\partial}{\partial x}\left(\frac{\partial}{\partial a} p(x, N_2, a, \delta_x)|_{a=0}\right)\Bigg|_{x=\delta_x} \\ &\times \int_0^{\delta_x} \mathrm{d}x \frac{\partial}{\partial a} p(x, N - N_1 - N_2, a, \delta_x)|_{a=0} \end{aligned} \qquad (5)$$

The function $p(x, N, a, \delta_x)$ is the solution of Equation 4 subject to absorbing boundary conditions at $x = -a$ and $x = \delta_x - a$.

$$\begin{aligned} p(x, N, a, \delta_x) = &\frac{2}{\delta_x}\sum_{i=1}^{\infty} \sin\left(\frac{i\pi a}{\delta_x}\right)\sin\left(\frac{i\pi(x+a)}{\delta_x}\right) \\ &\times \exp\left(-\frac{i^2\pi^2 b^2 N}{6\delta_x^2}\right) \end{aligned} \qquad (6)$$

The term $(b^2/6)(\partial/\partial x)p(x, N, a, \delta_x)|_{x=-a}$ in Equation 5 is equal to the probability that a particle initially located at $x = 0$ reaches the point $x = -a$ for the first time after a number of jumps between N and $N + \mathrm{d}N$ without ever crossing the point $x = \delta_x - a$. Also, the term $(\partial/\partial a)p(x, N, a, \delta_x)\,\mathrm{d}a$ is equal to the probability that a particle starting from $x = -a$ is found between x and $x + \mathrm{d}x$ after N jumps without moving further than $x = -a - \mathrm{d}a$ to the left and $x = \delta_x - a$ to the right. The probability that a particle reaches the point $x = -a$ for the first time before it moves to $x = \delta_x - a$ is described by the right-hand side of Equation 5. The coefficient two accounts for the symmetric case that the particle advances to its extreme position to the right before that to the left.

The function $P(\delta_x)$ can also be expressed as

$$P(\delta_x) = P(\delta_0)/(\overline{r_x^2})^{1/2} \qquad (7)$$

where $P(\delta_0)$ is the probability density function of the normalized interpenetration distance, δ_0, defined as

$$\delta_0 = \delta_x/(\overline{r_x^2})^{1/2} \qquad (8)$$

The mean square projection of the end-to-end distance, $\overline{r_x^2}$, is related to N and b as follows

$$\overline{r_x^2} = Nb^2/3 \qquad (9)$$

3. Fracture energy

The fracture energy, G_F, of a brittle polymer is defined as the energy required to separate one unit interfacial area [12]. It consists of two components: (i) the plastic work, W_p; and (ii) the thermodynamic work of cohesion, W_c.

$$G_\mathrm{F} = W_\mathrm{p} + W_\mathrm{c} \qquad (10)$$

The work of cohesion is reversible, whereas the plastic work is irreversibly dissipated to heat. The value of W_c represents the limiting fracture energy of an ideal brittle material. For most polymers the energy dissipated to other processes, such as static electrification and light and acoustic emissions, is much smaller than W_p and can be neglected.

The value of W_p is postulated equal to the thermal energy required to form an unstable craze per unit area. The craze thickness ranges from zero to its maximum value at the crack tip. The craze thickness before deformation at the crack tip is invoked equal to average chain interpenetration distance. It is apparent from Fig. 2 that the value of $\bar{\delta}_x$ characterizes a stable craze and not that of $\overline{(r_x^2)}^{1/2}$. Consequently, the plastic work is obtained as

$$W_p = \bar{\delta}_x \varrho c(T_g - T) \qquad (11)$$

where ϱ is the polymer density, c is the specific heat and T is the experiment temperature. A craze is obtained when the local temperature becomes equal to the glass transition temperature, T_g, which is a function of the chain length for low molecular weight polymers [13]. Equation 11 should be regarded in a scaling context, because a polymer chain has a finite probability to exhibit any interpenetration distance up to its fully extended length.

The work required to pull apart an unstable craze per unit area is equal to the thermodynamic work of cohesion

$$W_c = 2\gamma \qquad (12)$$

where the polymer surface tension, γ, is evaluated at the craze temperature, T_g. The value of γ varies with the temperature and is dependent on the molecular weight only in the oligomeric range [12].

4. Results and discussion

The variation of the probability density function $P(\delta_0)$ with the normalized interpenetration distance, δ_0, is computed numerically from Equations 5 and 7 and is shown in Fig. 3. The probability that the value of δ_x is smaller than $0.6\overline{(r_x^2)}^{1/2}$ and larger than $4\overline{(r_x^2)}^{1/2}$ is approximately equal to zero. The average chain interpenetration distance, $\bar{\delta}_x$, is calculated from Equation 1 as

$$\bar{\delta}_x = 1.59\overline{(r_x^2)}^{1/2} \qquad (13)$$

The same results were also obtained by Weidmann *et al.* [10], who derived an analytical expression for $P(\delta_x)$. Nevertheless, the proposed analysis is more general, because it includes the calculation of the chain length probability associated with the extreme location and, therefore, can be used to solve problems involving segmented chain structures, e.g., block copolymers.

Recognizing that the degree of polymerization, N_0, of the real chain is related to the molecular weight, M_0, and the number of backbone bonds, j, of the monomer repeating unit as

$$N_0 = \frac{jM}{M_0} \qquad (14)$$

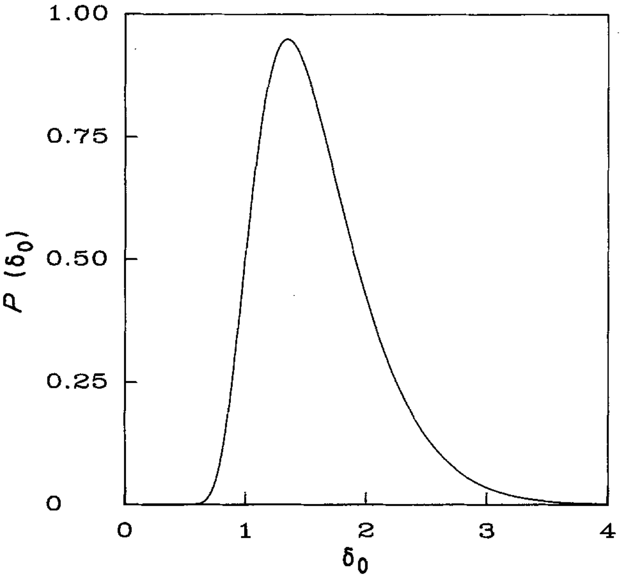

Figure 3 Variation of the probability density function, $P(\delta_0)$, with the normalized chain interpenetration distance, δ_0.

the fracture energy, $G_F(M)$, is derived from Equation 10 as

$$G_F(M) = 0.92\left(\frac{C_\infty jM}{M_0}\right)^{1/2} l\varrho c(T_g - T) + 2\gamma \qquad (15)$$

The important feature of the model is that the fracture energy is only related to polymer material properties. The scaling law $G_F \sim M^{1/2}$ is not valid because of the molecular weight dependence of T_g.

Experimental data [1] of the fracture energy of monodisperse polystyrene (PS) samples of different molecular weight, which were obtained by a cleavage technique at $T = 293$ K, are compared with theoretical predictions from Equation 15 in Table I. The glass transition temperature of PS satisfies Equation 16 over the entire molecular weight range [13]

$$\frac{1}{T_g} = \frac{1}{T_g(\infty)} + \frac{1.2 \times 10^5}{T_g^2(\infty)}\frac{1}{M} \qquad (16)$$

with $T_g(\infty) = 373$ K. The surface tension (in $\mathrm{J\,m^{-2}}$) of PS is expressed as a function of temperature [14] as

$$\gamma = 6.18 \times 10^{-2} - 7.2 \times 10^{-5}\,T \qquad (17)$$

The other physical properties of PS used in the calculations include: $C_\infty = 10$, $j = 2$, $M_0 = 104$, $l = 1.54 \times 10^{-10}$ m [15]; and $\varrho = 1050\,\mathrm{kg\,m^{-3}}$, $c = 1300\,\mathrm{J\,kg^{-1}\,K^{-1}}$ [16].

The predictions of the model agree well with the experimental results for the first four samples. The

TABLE I Fracture energy components of various monodisperse polystyrene samples

M	T_g (K)	W_p ($\mathrm{J\,m^{-2}}$)	W_c ($\mathrm{J\,m^{-2}}$)	$G_{F_{calc}}$ ($\mathrm{J\,m^{-2}}$)	$G_{F_{exptl}}$* ($\mathrm{J\,m^{-2}}$)
3550	342.0	0.247	0.074	0.321	0.34
10300	361.7	0.590	0.072	0.662	0.60
20500	367.2	0.899	0.071	0.970	0.94
34500	369.6	1.203	0.070	1.273	1.64
111000	371.9	2.225	0.070	2.295	96.7

*Reference [1].

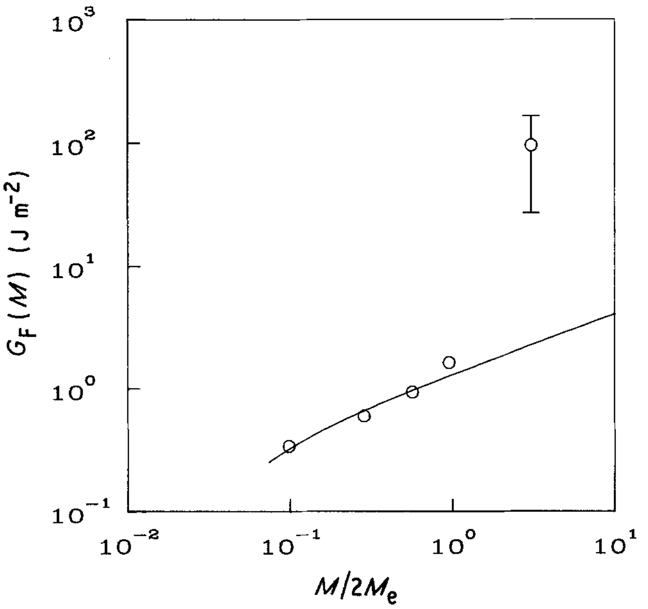

Figure 4 Comparison of theoretical predictions with experimental results [1] of the variation of the fracture energy, $G_F(M)$, of monodisperse polystyrene samples with the normalized molecular weight, $M/2M_e$.

measured value of G_F for $M = 111\,000$ is two orders of magnitude larger than the calculated one. This discrepancy is expected, as the employed fracture mechanism is valid only for values of M smaller than $2M_e$. The primordial craze thickness is not limited to the chain interpenetration distance when the polymer chains can be entangled. For PS the molecular weight between entanglements is 18 100 [17].

The plastic work dominates over the work of cohesion as the molecular weight increases. The plastic work diminishes for test temperatures close to the glass transition temperature. Also, the fracture energy is equal to the thermodynamic work of cohesion for oligomers having T_g lower than the experiment temperature. Here the change of γ with M [12] must be included in the calculations. From Equation 16 it is implied that PS samples with $M < 1180$ exhibit glass transition temperatures smaller than 293 K.

The variation of the fracture energy, $G_F(M)$, with the normalized molecular weight, $M/2M_e$, is also shown in Fig. 4. The agreement between theory and experiment for $M < 2M_e$ supports the proposed fracture mechanism. The other possible fracture mechanism [8] involves the scission of all chain links crossing the fracture plane. In that case the fracture energy would scale to the total number of chain crossings per unit area, which was found [4] independent of the molecular weight. Therefore, from the use of a chain scission fracture criterion one infers that the fracture energy does not change with the molecular weight, contrary to experimental findings. Thus, chain scission only occurs in the fracture of high molecular weight polymers [4].

The fracture energy of low molecular weight polymers can also be estimated from a micromechanical model developed by Kramer [7]

$$G_F = S_c(\lambda - 1)N^{1/2}b \qquad (18)$$

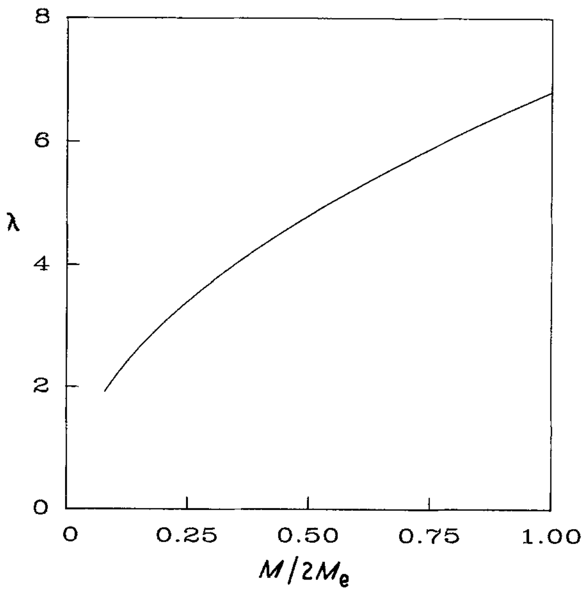

Figure 5 Variation of the maximum extension ratio, λ, of a polystyrene chain with the normalized molecular weight, $M/2M_e$.

Here S_c is the craze surface drawing stress equal to 30×10^6 N m^{-2} for PS. The extension ratio, λ, of the polymer chains at the crack tip was assumed independent of the chain length and equal to the corresponding value for high molecular weight polymers. We showed [4] that for $M > 2M_e$ the maximum extension ratio of the polymer segments before they break is equal to $N_e^{1/2}$, where N_e is the degree of polymerization between two consecutive entanglements. For $M < 2M_e$ a polymer chain cannot be entangled and its maximum extension ratio, λ, is given by

$$\lambda = \frac{Nb}{N^{1/2}b} = N^{1/2} \qquad (19)$$

The variation of λ of a PS chain with the normalized molecular weight, $M/2M_e$, is presented in Fig. 5. The highest value of λ is 6.8 and characterizes a chain with molecular weight $M = 36\,200$.

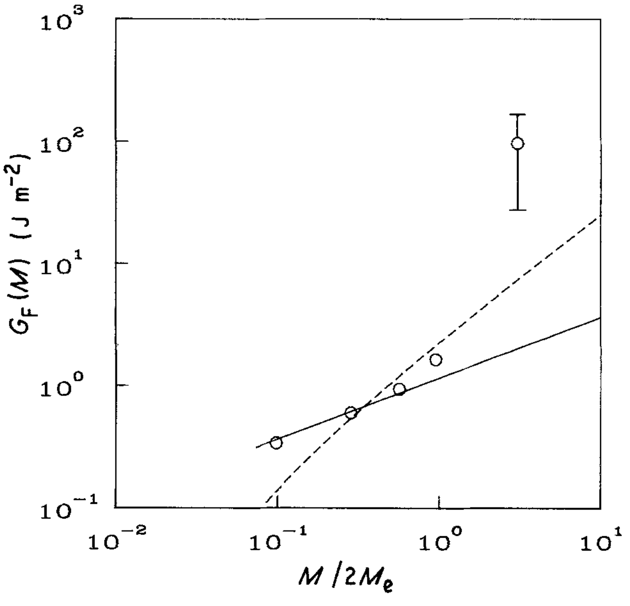

Figure 6 Comparison of theoretical predictions of Kramer's model for $\lambda = 4$ [7] (solid line) and $\lambda = N^{1/2}$ (broken curve) with experimental results [1] of the variation of the fracture energy, $G_F(M)$, of monodisperse polystyrene samples with the normalized molecular weight, $M/2M_e$.

The calculated PS fracture energies from Equation 18 are in better agreement with the measured ones (see Fig. 6) if an average value $\lambda = 4$ [7] is invoked rather than using those from Equation 19. However, polymer chains can only exhibit an extension ratio of 4 for $M > 12\,480$. Shorter chains have a maximum extension ratio always smaller than 4, provided that there is no bond length and bond angle distortion due to the chain deformation. Thus, the lack of experimental data for the craze extension ratio of low molecular weight polymers renders λ in Equation 18 an empirical parameter.

5. Conclusions

Stochastic modelling was used to calculate the average interpenetration distance, $\bar{\delta}_x$, of a polymer chain. The plastic work of fracture was assumed equal to thermal energy needed to heat a zone of thickness $\bar{\delta}_x$ from a reference temperature to the glass transition temperature. A simple model that includes no adjustable parameters was developed to calculate the fracture energy, G_F, of a polymeric material. Theoretical predictions of the fracture energy of polystyrene were in good agreement with experimental measurements for molecular weights, M, smaller than $2M_e$. From the variation of G_F with M we deduced that the polymer chains slide on each other rather than being ruptured in brittle fracture of low molecular weight polymers.

Acknowledgements

This work was supported by a National Science Foundation grant (No CBT-86-17719) and by a David Ross Fellowship to A.G.M. It was presented in a preliminary form at the Materials Research Society Spring Meeting, Reno, Nevada, April 5, 1988.

References

1. R. E. ROBERTSON, in "Toughness and Brittleness of Plastics", edited by R. D. Deanin and A. M. Crugnola, Advances in Chemistry Series (American Chemical Society, Washington, D.C., 1976), Vol. 154, Chap. 7, pp. 89–96.
2. J. P. BERRY, *J. Polym. Sci. A* **2** (1964) 4069.
3. R. P. KUSY and M. J. KATZ, *J. Mater. Sci.* **11** (1976) 1475.
4. A. G. MIKOS and N. A. PEPPAS, *J. Chem. Phys.* **88** (1988) 1337.
5. *Idem, Polymer*, in press.
6. R. N. HAWARD, H. E. DANIELS and L. R. G. TRELOAR, *J. Polym. Sci., Polym. Phys. Edn* **16** (1978) 1169.
7. E. J. KRAMER, *J. Mater. Sci.* **14** (1978) 1381.
8. B. D. LAUTERWASSER and E. J. KRAMER, *Phil. Mag. A* **39** (1979) 469.
9. H. W. KAMMER, *Acta Polym.* **34** (1983) 112.
10. J. J. WEIDMANN, H. KUHN and W. KUHN, *J. Chim. Phys.* **50** (1953) 226.
11. C. W. GARDINER, "Handbook of Stochastic Methods for Physics, Chemistry and the Natural Sciences", 2nd edn (Springer, New York, 1985).
12. S. WU, "Polymer Interface and Adhesion" (Dekker, New York, 1982).
13. T. G. FOX and S. LOSHAEK, *J. Polym. Sci.* **15** (1955) 371.
14. S. WU, *J. Phys. Chem.* **74** (1970) 632.
15. P. J. FLORY, "Statistical Mechanics of Chain Molecules" (Interscience, New York, 1969).
16. "Polymer Handbook", 2nd edn, edited by J. Brandrup and E. H. Immergut (Wiley, New York, 1975).
17. J. D. FERRY, "Viscoelastic Properties of Polymers", 3rd edn (Wiley, New York, 1980).

Received 9 May
and accepted 12 September 1988