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Scaling Relations for Brittle Fracture of Entangled Polystyrene Melts and Solutions in Elongational Flow

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Abstract

The criterion for brittle fracture of entangled polymer liquids [Journal of Rheology **62**, 221 (2018)] is extended by including the effects of finite chain extensibility and polymer concentration. Crack initiation follows from rupture of primary C-C bonds, when the strain energy of entanglement segments reaches the energy of the covalent bond. Thermal fluctuations will concentrate the strain energy on **one** C-C bond of entanglement segments, leading to bond scission and rupture of polymer chains followed by crack initiation and fast crack growth. In start-up flows, entanglement segments characterized by long relaxation times, i.e., predominantly those in the middle of the polymer chain will be the first to reach the critical strain energy and will fracture. Recent experimental data of Huang [Phys. Fluids **31**, 083105 (2019)] of fracture of a monodisperse polystyrene melt and of several solutions of monodisperse polystyrenes dissolved in oligomeric styrene are in agreement with the scaling relations for critical Weissenberg number as well as Hencky strain and stress at fracture derived from this fracture criterion and the Extended Interchain Pressure model [Journal of Rheology **64**, 95 (2020)].

Keywords: Polymer Melt; Polymer Solution; Fracture; Failure; Chain Scission; Elongation; EIP model; Interchain pressure; Finite Extensibility

1. INTRODUCTION

Failure of polymeric liquids during elongational flow is not only of significant concern for the polymer industry when processes with free surfaces such as blow moulding, fibre spinning, film blowing, and paint spray are involved, but its understanding is also a scientific challenge. Moreover, defects such as melt fracture and sharkskin seen in extrusion processes are directly linked to this phenomenon. Consequently, failure has been the subject of many experimental, theoretical, and computational research endeavours for a long time, while progress in understanding of failure has been limited. A short account of experimental works and theoretical concepts is given in our 2018 publication [1]. Progress was hampered by the fact that failure includes the phenomena of ductile failure (“necking”) and cohesive failure (“rupture” or “brittle fracture”), and until recently, the experimental separation of these two fundamentally different failure modes has been difficult or even impossible. This has changed with the advent of the filament stretching rheometer with locally controlled deformation and deformation rate developed by Hassager and coworkers, which is now commercially available (VADER 1000, Rheo Filament ApS [2]). By measuring the local diameter of the polymer sample during elongation, the true Hencky strain and strain rate can be determined and controlled, while by elongational rheometers prescribing the global deformation of the filament only nominal values of strain and strain rate can be obtained. Using a filament stretching rheometer, Huang et al. [3], and Huang and Hassager [4] showed that when true Hencky strain rate is controlled rather than nominal Hencky rate, the four failure zones of the so-called Malkin plot [5] (purely viscous zone, viscoelastic zone with failure by necking, rubbery zone, glassy zone) are reduced to just two possible states: liquid or solid, and a clear distinction exists between liquid behaviour (unlimited steady-state elongation) and solid behaviour (brittle fracture). For monodisperse polystyrene solutions and a polydisperse polystyrene melt they found that the value of the critical stress at fracture lies between the plateau (G_N) modulus and the glassy (G_g) modulus, and is at least 2 orders of magnitude higher than G_N . They reported that the critical strain remains approximately constant and the critical stress increases only slightly with increasing elongation rate. They also confirmed the high reproducibility of the critical stress/strain values, and demonstrated the simultaneous initiation and propagation of multiple cracks at different spatial positions along the stretched filament.

Considering the origin of crack initiation in polymeric systems, the idea of the largest pre-existing microcrack (i.e. weakest-link), inherited from the Griffith theory [6], is not in

agreement with the critical stress/strain data of Huang and Hassager [3, 4], which show a very high reproducibility. This leaves as possible origins of crack initiation either catastrophic chain disentanglement or rupture of primary C-C bonds of the polymer chain. Main-chain scission in solid polymers, in polymer solutions and polymer melts is well documented. In amorphous and partially crystalline polymers below the glass transition temperature free radicals produced by chain scission can be identified by electron spin resonance (ESR) [49, 50]. The importance of polymer chain entanglements for brittle fracture of solid polymers was shown by Mikos and Peppas [51]. They found their calculated value of $1.0 \cdot 10^{17}$ polystyrene chains per square meter crossing the fracture surface to be in good agreement with experimental evidence of tensile strength, resulting from rupture of primary bonds and not from secondary (van der Waals) forces. Zhurkov and Korsukov [52] documented chain scission under tensile stress in polyethylene and polypropylene at temperatures up to 80°C by infrared spectroscopy, where free radicals can no longer be detected by conventional ESR due to fast recombination. Tabata et al. [53] showed direct evidence for main-chain scission of polymers in semidilute solution caused by high speed stirring using ESR combined with a spin trapping technique. Following earlier works (see e.g. Rehner [54] and references therein), Bestul [55, 56] investigated shear degradation in capillary flow by measuring intrinsic viscosities at successive stages of extrusion of concentrated solutions of polyisobutenes in cetane, and discussed how intra- and intermolecular configurational entropy and potential energy can be concentrated on one “bond-to-be-ruptured”. Ballauf and Wolf [57] studied the degradation of solutions of 4.9-20 wt% of polystyrene in trans-decalin by use of a shear cell at shear rates of $5.0 \cdot 10^3 < \dot{\gamma} < 10^4 \text{ s}^{-1}$. They showed that only a Gaussian breakage probability of C-C bonds with the center of the probability distribution at the midpoint of the chain can reproduce the experimentally observed changes in the molar mass distribution. Mechanical degradation during multiple extrusion cycles in the melt state is well documented for polypropylene [58-61]: The molecular mass and polydispersity reduction as well as the lack of carbonyl groups and gel formation show that chain scission and not oxidation is the dominant degradation reaction. Degradation increases with increasing extrusion rate. Molar mass distribution curves suggest that chain scission occurs close to the middle part of the macromolecule, in agreement with the Bueche theory [62] for mechanical degradation. In controlled rheology experiments, Wang and co-workers [7] reported that beyond a critical strain rate, entangled melts and solutions undergo a yield-to-rupture transition. Birefringence measurements indicate that rupture occurs when the strands between entanglements undergo

non-Gaussian stretching on their path to full extension, and the linear stress-optical rule starts to break down. They concluded that rupture occurs plausibly through chain scission in the limit of finite chain extensibility.

A novel and quantitative criterion of brittle fracture of entangled polymer liquids called the “entropic fracture hypothesis” was presented by the present authors [1]: Crack initiation follows from scission of primary C-C bonds, when the strain energy of an entanglement segment reaches the energy of the covalent bond. Thermal fluctuations lead to short-time concentration of the strain energy on **one** C-C bond of the entanglement segment, and the chain ruptures. In start-up flows, entanglement segments characterized by long relaxation times, i.e., predominantly those in the middle of the polymer chain will be the first to reach the critical strain energy and will fracture. The entropic fracture hypothesis was shown to be in good qualitative agreement with experimental fracture data, but we already noticed that for quantitative agreement finite extensibility effects must be considered.

In a recent paper, Huang [8] investigated systematically the critical strain and stress at fracture for two groups of nearly monodisperse linear polystyrene liquids in controlled elongational flow. The samples in Group A have a similar number Z of entanglements per chain but a different number N_e of Kuhn segments or “monomers” per entanglement strand, while the samples in Group B have different Z but similar N_e . Huang found no obvious dependence of the critical strain at fracture on N_e and Z . By contrast, the critical stress at fracture is clearly independent of the number Z of entanglements per chain, but influenced by the number N_e of Kuhn monomers per entanglement strand.

In the present paper, we analyze the comprehensive data set of Huang [8] by use of the entropic fracture hypothesis, which we extend by taking finite extensibility and polymer fraction of the solutions into account. The paper is organized as follows: We first give a short account of the experimental data and the linear-viscoelastic characterization of the polymer systems considered. Then the Extended Interchain Pressure (EIP) model with finite chain extensibility is presented, followed by the fracture criterion and the resulting scaling relations. A new paradigm of finite extensibility is suggested, followed by comparison of fracture data and model predictions.

2. EXPERIMENTAL DATA AND LVE CHARACTERIZATION

Materials

The molecular characteristics of the polystyrene (PS) melt and solutions are summarised in Table 1 and are taken from Huang [8]. The samples are named in the form of PS-X/4k-Y, where X is the weight average molecular weight of the PS, 4k is the molecular weight of the oligomeric styrene solvent, and Y% is the volume fraction of the PS in the solution. Group A contains three PS samples with different volume fractions (100%, 33%, and 18%), namely, PS-285k, PS-864k/4k-33, and PS-1760k/4k-18. The samples have similar numbers Z of entanglements, but different numbers N_e of Kuhn monomers. Group B contains three PS solutions with similar volume fractions (17%–18%) of polymer, namely, PS-1760k/4k-18, PS-864k/4k-17, and PS-576k/4k-17. These samples have similar values of N_e but different Z.

Mechanical Spectroscopy

The linear viscoelastic properties of the PS samples were obtained from small amplitude oscillatory shear flow measurements using an ARES-G2 rheometer from TA Instruments. An 8 mm plate-plate geometry (with a sample thickness around 0.8 mm) was used for lower frequencies and a 4 mm plate-plate geometry (with a sample thickness around 0.5 mm) was used for higher frequencies in the transition to the glassy regime. The measurements were performed at temperatures 5K (i.e. in the glassy regime) to 80K higher than the corresponding glass transition temperatures of the samples. For each sample, the data were shifted to a single master curve at the reference temperature of 130°C using the time-temperature superposition procedure [8].

Elongational Viscosity Measurements

The stress-strain measurements in elongational flow were performed using a homemade filament stretching rheometer (FSR) [8]. An online control scheme was employed in the FSR to control the mid-filament diameter during stretching, so that the local strain rate was ensured to be constant. It should be noted that necking instabilities in Zones II and III in the Malkin failure master curve [5] can be controlled by the online control scheme in the FSR. Therefore, the four zones in the Malkin master curve are reduced to just two states: steady flow and elastic fracture [3, 4]. All the measurements were performed at 120–130°C, and shifted to the reference temperature of 130°C.

LVE Characterization

From linear-viscoelastic mastercurves of G' and G'' (see Supplementary Material Fig. S1), continuous Baumgärtel-Schausberger-Winter (BSW) relaxation spectra [9] were determined and reported by Huang [8]. The relaxation modulus $G(t)$ is found from the spectrum $H(\tau)$ by

$$G(t) = \int_0^{\infty} \frac{H(\tau)}{\tau} \exp(-t/\tau) d\tau \quad (1)$$

$H(\tau)$ is composed of two part, the entanglement contribution $H_e(\tau)$ and the glassy contribution $H_g(\tau)$,

$$H(\tau) = H_e(\tau) + H_g(\tau) \quad (2)$$

with

$$H_e(\tau) = n_e G_N \left(\frac{\tau}{\tau_t} \right)^{n_e} h(1 - \tau/\tau_t) \quad (3)$$

and

$$H_g(\tau) = n_g G_N \left(\frac{\tau}{\tau_c} \right)^{-n_g} h(1 - \tau/\tau_t) \quad (4)$$

G_N is the plateau modulus, τ_t the longest or “terminal” relaxation time, τ_c the characteristic time constant of the glassy contribution (related to the entanglement segment equilibration time τ_e), and $h(x)$ the Heaviside step function. The values of n_e and n_g are fixed to 0.23 and 0.70, respectively. The physical meaning of the BSW parameters can be found elsewhere [10], and the BSW parameters of the polymer melts considered are given in Huang [8].

The zero-shear viscosity of the samples is related to the BSW parameters by

$$\eta_0 = \int_0^{\infty} G(s) ds = n_e G_N \tau_t \left(\frac{1}{1+n_e} + \frac{1}{1-n_g} \left(\frac{\tau_c}{\tau_t} \right)^{n_g} \right) \cong n_e G_N \tau_t \left(\frac{1}{1+n_e} \right) \quad (5)$$

As $\tau_c \ll \tau_t$, the glassy contribution to η_0 can be neglected. From the plateau modulus G_N of the samples the entanglement molar mass is calculated as [10]

$$M_e = \frac{\rho RT}{G_N} \varphi \quad (6)$$

ρ is the density of polymer melt at the testing temperature (for PS taken as 1000kg/m³), R is the gas constant, and φ is the volume fraction of polymer in the solution with $\varphi = 1$ specifying the melt. With M being the molar mass of the polymer, the number of entanglements per chain, Z , is obtained,

$$Z = \frac{M}{M_e} \quad (7)$$

The relation between the entanglement molar mass of solution, M_e , and melt, M_{em} , is given by

$$M_e = M_{em} \varphi^{-\alpha} \quad (8)$$

The value of the dilution exponent α is model dependent ($1 < \alpha < 4/3$), and a value of $\alpha = 1$ was taken in [10]. The number of Kuhn segments or “monomers” between entanglements is $N_e = M_e / M_0$, where M_0 is the molar mass of the Kuhn monomer. For polystyrene melt, we take $M_{em} = 13300$ g/mol and $M_0 = 610$ g/mol [11].

While the BSW spectrum defined by Eqs. (1) to (4) allows for a reasonable quantification of the plateau modulus G_N , the BSW spectrum does not result in an ideal fit of the G' and G'' mastercurves. We will therefore use parsimonious relaxation spectra here,

$$G(t) = \sum_{i=1} g_i \exp(-t / \tau_i) \quad (9)$$

for characterization of LVE in the experimentally accessible frequency window of all polymers considered. The partial moduli g_i and relaxation times τ_i as determined by the IRIS software [12] result in excellent agreement with the linear-viscoelastic data of G' and G'' (see Supplementary Material).

According to the DE model, the Rouse time τ_R , the disengagement (or reptation) time τ_d and the zero-shear viscosity η_0 are given by [13],

$$\tau_R = Z^2 \tau_e \quad (10)$$

$$\tau_d = 3Z\tau_R \quad (11)$$

$$\eta_0 = \frac{\pi^2}{12} G_N \tau_d \quad (12)$$

We identify here τ_d with the mean quadratic average of the relaxation times of the discrete relaxation spectrum and calculate η_0 from the discrete relaxation spectrum,

$$\tau_d = \frac{\sum_i g_i \tau_i^2}{\sum_i g_i \tau_i} \quad (13)$$

$$\eta_0 = \sum_i g_i \tau_i \quad (14)$$

We note that Huang [8] assumed the equivalence of τ_e and τ_c , i.e. $\tau_e \cong \tau_c$, and calculated the Rouse time in correspondence with Eq. (10) by the relation

$$\tau_R \cong Z^2 \tau_c \quad (15)$$

We prefer to use Osaki's approach [14-17] for quantification of the Rouse time τ_R , which extrapolates the Rouse time of unentangled polymer systems to the Rouse time of entangled polymer melts and solutions, and takes into account the power of 3.4 scaling of the zero-shear viscosity. This leads to the relation,

$$\tau_R = \frac{12 M \eta_0}{\pi^2 \rho RT \phi} \left(\frac{M_{cm}}{M \phi} \right)^{2.4} \quad (16)$$

for the Rouse stretch relaxation time. M_{cm} denotes the critical molar mass in the melt state. For monodisperse polystyrene we take the well-documented value of $M_{cm} = 35 \text{ kg/mol}$ [18], and Eq. (16) has been used successfully for modeling of the transient and steady-state elongational and shear viscosities of PS melts and solutions [19, 20].

Tables 1 shows the molar mass (M), polydispersity index (M/M_n), glass transition temperature (T_g), plateau modulus (G_N), entanglement molar mass (M_e), number of entanglements per chain (Z), number of Kuhn monomers (N_e) per entanglement, zero-shear viscosity (η_0),

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terminal/reorientational/disengagement/reptation time (τ_d), Rouse stretch relaxation time (τ_R) of the monodisperse polymers samples considered in this study. The discrete relaxation spectra of all samples are reported in Table S1 (Supplementary Material).

Table 1. Molecular characterization (M , M/M_n), glass transition temperature (T_g), plateau modulus (G_N), entanglement molar mass (M_e), number of entanglements per chain (Z), number of Kuhn monomers (N_e) per entanglement, and material parameters η_0 , τ_d , and τ_R from linear-viscoelastic data using IRIS [12] spectra.

	PS-285k	PS-864k/4k-33	PS-1760k/4k-18	PS-864k/4k-17	PS-576k/4k-17
<i>Group</i>	A	A	A/B	B	B
M [kg/mol]	285	864	1760	864	576
M/M_n	1.09	<1.15	1.13	<1.15	-
T_g [°C]	107.5	92.0	89.0	89.0	89.0
G_N [Pa]	252040	25 942	6850	6690	6890
M_e [kg/mol]	13.3	40.3	73.9	78.2	78.2
Z [-]	21.4	21.0	22.8	10.2	6.7
N_e	21.8	66.1	121.1	128.2	128.2
η_0 [MPa·s]	531	28.0	19.1	1.25	0.278
τ_d [s]	8643	3695	11399	624	109
τ_R [s]	360	173	252	73.8	29.7

3. THE EXTENDED INTERCHAIN PRESSURE (EIP) MODEL

The Molecular Stress Function (MSF) model is a generalized tube segment model with strain-dependent tube diameter [21-25]. The extra stress tensor $\sigma(t)$ of the MSF model with consideration of finite extensibility effects [26] is given by a history integral of the form

$$\sigma(t) = \int_{-\infty}^t \frac{\partial G(t-t')}{\partial t'} f \lambda \mathbf{S}_{DE}^{IA}(t, t') dt' \quad (17)$$

The strain measure $\mathbf{S}_{DE}^{IA}$ represents the contribution to the extra stress tensor originating from the affine rotation of the tube segments assuming “Independent Alignment (IA)” [27, 28], and is given by

$$\mathbf{S}_{DE}^{IA}(t, t') \equiv 5 \left\langle \frac{\mathbf{u}' \mathbf{u}'}{u'^2} \right\rangle_0 = 5 \mathbf{S}(t, t') \quad (18)$$

with $\mathbf{S}(t, t')$ being the relative second order orientation tensor. $\mathbf{u}' \mathbf{u}'$ is the dyad of a deformed unit vector $\underline{\mathbf{u}'} = \underline{\mathbf{u}'}(t, t')$,

$$\mathbf{u}' = \mathbf{F}_t^{-1} \cdot \mathbf{u} \quad (19)$$

$\mathbf{F}_t^{-1} = \mathbf{F}_t^{-1}(t, t')$ is the relative deformation gradient tensor, and u' is the length of $\mathbf{u}'$. The orientation average is indicated by $\langle \dots \rangle_0$,

$$\langle \dots \rangle_0 \equiv \frac{1}{4\pi} \oint \oint [\dots] \sin \theta_o d\theta_o d\varphi_o \quad (20)$$

i.e. an average over an isotropic distribution of unit vectors $\mathbf{u}$.

$\lambda = \lambda(t, t')$ represents the inverse of the relative tube diameter a/a_0 , and at the same time the relative length of a deformed tube segment,

$$\lambda(t, t') = \frac{a_0}{a(t, t')} = \frac{l(t, t')}{l_0} \quad (21)$$

t' indicates the time when the tube segment was created by reptation processes with equilibrium tube diameter a_0 and equilibrium length l_0 .

In the Gaussian limit, the molecular stress function $f = f(t, t')$ is equal to the tube stretch λ .

However, this is valid only as long as $\lambda < 0.5 \lambda_{max}$ [29], where $\lambda_{max} \cong \sqrt{N_e}$ represents the maximum stretch (i.e. a fully extended entanglement segment), and N_e the number of Kuhn monomers in an entanglement segment. Outside the Gaussian regime, tension in the chain can be described by the inverse Langevin function, or, due to its mathematical complexity, approximations of it, like the so- called Warner [30] or Padé approximations [31]. Since the

latter version seems to be more accurate, nonlinear elasticity caused by finite extensibility (FENE) is implemented in the EIP theory in the following way:

$$f = c(\lambda, \lambda_{\max})\lambda \quad (22)$$

c is a nonlinear spring coefficient, representing a relative Padé inverse Langevin function with [32]

$$c = \frac{\left(3 - \frac{\lambda^2}{\lambda_{\max}^2}\right) \cdot \left(1 - \frac{1}{\lambda_{\max}^2}\right)}{\left(3 - \frac{1}{\lambda_{\max}^2}\right) \cdot \left(1 - \frac{\lambda^2}{\lambda_{\max}^2}\right)} \quad (23)$$

We also tested second- and third-order functions presented recently by Howard [41] which are close to optimum in the sense of minimizing the magnitude of the maximum relative error in the approximation of the inverse Langevin function and found no significant difference to the use of Eq. (23).

We note that stretch $\lambda(t, t')$, tension $f(t, t')$, and orientation $\mathbf{S}(t, t')$ are relative quantities characterizing an entanglement segment created by reptation processes at time t' and still existing at time $t > t'$ when the stress is measured. For simplicity, we drop the dependence on t and t' . While $\mathbf{S}_{DE}^{IA}$ is determined directly by the deformation history according to eq.(18), λ is found as solution of an evolution equation taking into account affine tube segment deformation balanced by Rouse relaxation and the interchain pressure. In [1], we used an evolution equation for solutions, which did not take into account finite extensibility effects, and which characterized solutions by rescaling of the Rouse time due to the shift of the glass transition temperature. Here, we modify the stretch evolution equation of Narimissa et al. [19] by including the effect of finite extensibility into the interchain pressure term in the same way as explained in detail by Rolón-Garrido et al. [26],

$$\frac{\partial \lambda}{\partial t} = \lambda(\kappa : \mathbf{S}) - \frac{\lambda - 1}{\tau_R} \left(1 - \frac{2}{3} \varphi^4\right) - \frac{2\varphi^4}{9\tau_R} \lambda^2 (\lambda f^2 - 1) \quad (24)$$

with initial condition $\lambda(t = t', t') = 1$. In eq.(24), the first term on the right hand sides describes an affine deformation, the second term Rouse relaxation, and the third term represents the interchain pressure contribution with Rouse time τ_R as defined by Eq. (16). Eq. (24) reduces to the evolution equation of the EIP model of Narimissa et al. [19] in the Gaussian limit, i.e when $c=1$ and $f=\lambda$. Eqs. (17) and (24) represent **the EIP model with finite chain extensibility**, and are solved numerically.

From Eq. (24) follows in elongational flow at high Weissenberg numbers $Wi = \dot{\epsilon}\tau_R$ (with strain rate $\dot{\epsilon}$) and large stretch, when full orientation (i.e. $\kappa : \mathbf{S} = \dot{\epsilon}$) and equilibrium stretch (i.e. $\partial\lambda/\partial t = 0$) are reached and the Rouse relaxation term can be neglected, that the product of molecular stress f and stretch λ is proportional to the square root of Wi and inverse proportional to the square of the polymer fraction ϕ ,

$$f\lambda = c\lambda^2 = \frac{3}{2}\phi^{-2}\sqrt{2Wi} \quad (25)$$

and the tensile stress is expected to reach a value of,

$$\sigma = 5G_N f\lambda = \frac{15}{2}G_N\phi^{-2}\sqrt{2Wi} \quad (26)$$

We note that in this asymptotic limit, the product $f\lambda$ does not depend on the finite extensibility function $c = c(\lambda, \lambda_{\max})$, but is a sole function of polymer fraction ϕ and Wi .

From Eq. (26) and considering that $G_N = G_{Nm}\phi^2$, the universal relation for the high Wi tensile stress of melts and solutions of Narimissa et al. [19] is recovered,

$$\sigma = \frac{15}{2}G_{Nm}\sqrt{2Wi} \quad (27)$$

with G_{Nm} being the plateau modulus of the melt.

4. THE STRAIN ENERGY OF A POLYMER CHAIN IN A TUBE

The entropic free energy $w(N_e)$ of a chain segment of a linear entangled chain with a large number of monomers N_e (Kuhn segments or monomers with length b) in a tube with diameter a is given by [33-35],

$$w(N_e) = 3kT \frac{N_e b^2}{a^2} + cst \quad (28)$$

k is Boltzmann's constant, and T the absolute temperature. Taking the melt state (indicated by the index m) as reference state for the strain energy, $N_e = N_{em}$ represents the number of monomers in an entanglement segment of length and diameter a_{0m} at equilibrium with $a_{0m}^2 = N_{em}b^2$. If the entropic free energy of an entanglement segment in the melt is scaled to the equilibrium thermal energy $3kT$ by setting the constant cst to zero, $w(N_{em})$ represents the

“interchain pressure energy” of the entanglement segment when squeezed by the neighbouring polymer chains in a tube with strain-dependent tube diameter $a \leq a_{0m}$,

$$w(N_{em}) = 3kT \frac{a_{0m}^2}{a^2} = 3kT\lambda_m^2 \quad (29)$$

In solutions, the number of monomers in the entanglement segment is increased by $N_e = N_{em}\varphi^{-1}$ and the tube diameter at equilibrium is a_0 with $a_o^2 = N_e b^2 = a_{0m}^2 \varphi^{-1}$. Then the interchain pressure energy $w(N_e)$ is given by Eq. (28) as $w(N_e) = 3kT a_0^2 / a^2 = 3kT\lambda^2$, and from w being proportional to the number of monomers, $w(N_e) \propto a_0^2 \propto N_e$, it follows immediately that

$$w(N_{em}) = 3kT \frac{a_0^2}{a^2} \frac{N_{em}}{N_e} = 3kT\lambda^2 \varphi \quad (30)$$

From the identity $\lambda^2 \varphi = \frac{a_0^2}{a^2} \frac{a_{0m}^2}{a_0^2} = \lambda_m^2$, we see that the strain energy $w(N_{em})$ is independent of the degree of dilution and depends only on the ratio of the equilibrium tube diameter a_{0m} in the melt state to the strain-dependent tube diameter a .

The strain energy increases with the square of chain stretch as long as Gaussian chain statistics applies. At larger deformations, finite extensibility effects cannot be neglected, and the tension increases over-proportionally with the stretch. In agreement with the stress tensor equation (17) we model this effect by use of the nonlinear spring constant c of Eq. (23), resulting in a strain energy function of the form

$$w(N_{em}) = 3kTc\lambda^2 \varphi = 3kTf\lambda \varphi \quad (31)$$

5. THE BOND ENERGY OF CARBON-CARBON BONDS AND THE FRACTURE CRITERION

The bond energy of carbon-carbon bonds in hydrocarbons is reported as 348kJ/mol (see e.g. [36, 37]), i.e. the bond energy of a single C-C bond with Avogadro's number $N_A = 6.02 \cdot 10^{23}$ is:

$$U = \frac{348kJ}{N_A} = 5.78 \cdot 10^{-19} J \quad (33)$$

On the other hand, the thermal energy w_{eq} at a temperature T of $393K$ ($120^\circ C$) is,

$$w_{eq} = 3kT = 1.62 \cdot 10^{-20} J \quad (34)$$

with Boltzmann's constant $k = 1.38 \cdot 10^{-23} J / K$. Thus, the bond energy U is about 36 times larger than the thermal energy w_{eq} at $120^\circ C$, which is why the polymer chain will not rupture due to Brownian motion at equilibrium, while chain scission may be caused by ultraviolet (UV) radiation with more than 3.6 eV [38].

The strain energy $w(N_{em}) = 3kTf\lambda\phi$ of a chain segment with N_{em} monomers is distributed along the segment. We make the hypothesis that when the strain energy of the segment reaches the critical energy

$$w_c = 3kTf_c\lambda_c\phi = U \quad (34)$$

the total strain energy of the chain segment will be concentrated on **one** C-C bond by thermal fluctuations, and this bond will then rupture. Ligoure and Mora [43] report thermal vibration frequencies in the range of $\omega_{th} = 10^{10} - 10^{12} s^{-1}$, which include bond rotation and bond stretching. Using an Arrhenius ansatz, the lifetime of a C-C bond can be estimated as

$$\tau_0 = \frac{1}{\omega_{th}} \exp(U/kT). \text{ According to the Eyring kinetic theory of fracture, the lifetime also}$$

depends on the force F carried by a link of length δ , whose stored energy can supply a portion of the activation energy [43, 52]. If we identify this link having a stored energy $F\delta$ with a chain segment carrying a strain energy w , the resulting bond lifetime reduces to

$$\tau = \frac{1}{\omega_{th}} \exp\left(\frac{U - w}{kT}\right) = \tau_0 \exp(-w/kT). \text{ Thus, when the strain energy } w \text{ reaches the bond}$$

energy U , the bond will rupture within a very short time. We note that while our fracture hypothesis is based on activation energy considerations, Wang et al. [44] presented a conceptual framework of force-coupled bond dissociation in the case of rubber failure recently. They consider the distortion of the covalent bond potential due to the effect of an external force, which reduces the energy barrier that the breaking bond needs to overcome by thermal fluctuations.

We recall that stretch and tension are relative quantities, and therefore the strain energy $w = w(t, t')$ is also a relative quantity. In start-up flows segments with long relaxation times, i.e. those preferably in the middle of the chain, will be the first to reach the critical energy w_c and will fracture. Chain segments closer to the ends of the chain, which due to reptation processes have shorter relaxation times and see less stretch and tension within the time interval of t' (creation) and t (observation), will not reach w_c and are less likely to fracture. This is in agreement with experimental evidence [57-61] presented in the Introduction. When a bond ruptures, the newly created ends of the chain segment will recoil within a segmental Rouse time, thereby dissipating the strain energy, which may then be transmitted to primary C-C bonds of adjacent chains leading to further chain scissions. We assume that as soon as the strain energy $w = w(t, t' = 0)$ accumulated between the start-up of deformation at time $t' = 0$ and time $t = t_c$ reaches the critical energy $w_c = w(t = t_c, t' = 0)$, a sufficient concentration of locally ruptured chains is reached, i.e. the damage probability as e.g. defined by Verneray et al. [45] for rubber networks becomes equal to one and crack initiation will occur. Crack initiation is followed by crack growth, which leads within a very short time (about 200ms according to Huang et al. [3]) to brittle fracture of the polymer liquid. At time $t = t_c$, the critical Hencky strain at fracture, $\varepsilon_c = \dot{\varepsilon} t_c$, is reached and the critical tensile stress at fracture, $\sigma_c = \sigma(t_c)$, is given by the stress equation (17). Crack initiation can take place at several locations simultaneously along the polymer sample under tension, and high-speed images revealed indeed that multiple cracks propagate [3, 4], one of which leading to rupture of the sample, while the others close up elastically. Crack profiles and energy dissipation during crack propagation were investigated in detail by Huang et al. [3] and are not considered here.

From the fracture hypothesis defined by Eq. (34), the maximum achievable product of critical molecular stress f_c and critical stretch λ_c is obtained,

$$f_c \lambda_c \varphi = c \lambda_c^2 \varphi = \frac{U}{3kT} \cong 36 \quad (35)$$

Eqs. (29) and (35) define a critical tube diameter a_c in terms of the equilibrium tube diameter a_{0m} of the melt,

$$a_c \cong \frac{1}{6} \sqrt{c} a_{0m} \quad (36)$$

at which the critical interchain pressure energy is reached and rupture of primary C-C bonds and thus brittle fracture is expected to occur. We called this fracture mode “entropic fracture” [1], as explained above it is caused by thermal fluctuations, and entanglement segments are not fully stretched when fracture occurs. This is in contrast to the “enthalpic” fracture hypothesis of Lake and Thomas [36] as modified by Mazich and Samus [39]. These authors assumed that all bonds are fully stretched at fracture and when a chain with N C-C bonds between two entanglement points ruptures, the strain energy $w_c = NU$ corresponding to the bond energy of **all** N C-C bonds in the entangled chain segment is dissipated. Instead of using this energy argument, one might also consider a corresponding force argument: Assuming a generally accepted bond fracture strength of $4 nN$, the critical stress needed to rupture the chains (again assuming fully stretched and oriented chain segments) would be more than an order of magnitude larger than the stress at rupture observed experimentally as shown in [1, 42].

Combining the fracture criterion of Eq. (35) with the asymptotic tensile stress at high Wi and high stretch according to Eq. (26), we expect at sufficiently fast and large elongations a critical tensile stress

$$\sigma_c = 5G_N f_c \lambda_c = \frac{15}{2} G_N \varphi^{-2} \sqrt{2Wi_c} \cong 5G_N \frac{U}{3kT} \varphi^{-1} \quad (37)$$

From the first and last term of this identity, we expect the following scaling relation for the normalized critical stress $\sigma_c \varphi / G_N$ at fracture,

$$\frac{\sigma_c \varphi}{G_N} \cong 5 \frac{U}{3kT} \cong 180 \quad (38)$$

The reduced critical Weissenberg number Wi_c / φ^2 for the onset of fracture,

$$\frac{Wi_c}{\varphi^2} \cong \frac{2}{9} \left(\frac{U}{3kT} \right)^2 \cong 288 \quad (39)$$

is obtained from the two last terms of Eq. (37). Wi_c is the minimum Weissenberg number for fracture to occur, i.e. fracture is expected only for $Wi \geq Wi_c$. The characteristic numbers “180” and “288” in the scaling relations result from the combination of the fracture criterion with the EIP model.

6. A NEW PARADIGM OF FINITE EXTENSIBILITY

Finite extensibility is defined as

$$\lambda_{\max}^2 = N_e = N_{em} \varphi^{-1} \quad (40)$$

and is considered to be a constant material property. However, the fracture data of Huang [8] reveal (as demonstrated below in Figs. 2a,b and 4) that finite extensibility is actually a dynamic property: At fast deformations with large Wi , there is not sufficient time to reach equilibrium within the entanglement segment. The relevant Wi is therefore not $Wi = Wi_R = \dot{\epsilon} \tau_R = \dot{\epsilon} \tau_e Z^2$, which characterizes the full chain, but rather

$$Wi_e = \dot{\epsilon} \tau_e = Wi / Z^2 \quad (41)$$

τ_e is the equilibration time of an entanglement segment and increases with dilution in OS at iso- T_g temperature according to $\tau_e = \tau_{em} \varphi^{-2}$ [40]. Thus, while for $Wi_e < 1$ equilibrium in the entanglement segment of the solution is reached and $\lambda_{\max}^2 = N_e = N_{em} \varphi^{-1}$, the time scale at $Wi_e \geq 1/\varphi^2$ corresponding to $Wi_{em} = \dot{\epsilon} \tau_{em} \geq 1$ is set by τ_{em} , and $\lambda_{\max}^2$ reduces to $\lambda_{\max}^2 = N_{em}$. To account for the reduction of $\lambda_{\max}^2$ with increasing Wi_e , we use the empirical relation

$$\lambda_{\max}^2 = N_{em} \frac{1/\varphi + a Wi_e}{1 + a Wi_e} = N_{em} \frac{Z^2/\varphi + a Wi}{Z^2 + a Wi} \quad (42)$$

a is a numerical parameter, the only free parameter of the model.

7. COMPARISON OF THE FRACTURE HYPOTHESIS TO EXPERIMENTAL EVIDENCE

In the following we compare predictions of our entropic fracture model for the origin of brittle fracture of entangled polymer liquids to the experimental data of Huang [8]. We consider first melt PS-285k and solutions PS-864k/4k-33 and PS-1760k/4k-18, which feature a similar number of entanglements Z , but widely differing numbers of Kuhn monomers N_e per entanglement (Group A). This is followed by discussion of Group B comprising the three solutions PS-1760k/4k-18, PS-864k/4k-17, and PS-576k/4k-17, which have different numbers of entanglements, but similar numbers of Kuhn monomers.

7.1 Polymer systems of Group A (PS-285k, PS-864k/4k-33 and PS-1760k/4k-18)

Fig.1 shows the comparison between experimental data and model predictions of Hencky strain at break ε_c , reduced tensile stress σ/G_N as well chain stretch λ , molecular tension f and strain energy w as a function of Weissenberg number $Wi = \dot{\varepsilon}\tau_R$ for melt PS-285k. Fractured samples are indicated by full symbols and full lines, steady-state stress by open symbols and dotted lines for experimental data and model prediction, respectively. At higher Wi in the range of 60–300, it is not clear whether PS-285k failed due to elastic fracture or due to failure of the online control scheme leading to fast necking [8]. Such points are presented as asterisks. For PS-285k, the number of entanglements is $Z=21.4$, and the number of Kuhn monomers N_{em} per entanglement is 21.8 and therefore $\lambda_{\max}^2 = N_{em} = 21.8$. As demonstrated in Fig.1a, using this value of $\lambda_{\max}^2$ in equation (23) for the nonlinearity function $c = c(\lambda^2, \lambda_{\max}^2)$ leads to excellent agreement of data and model for the Hencky strain at break ε_c . The prediction of the onset of the reduced critical tensile stress at fracture σ_c/G_N (Fig.1b) is in quantitative agreement with the data, while at higher Wi the predicted fracture stress increases (Fig.1b) when approaching the regime of the glassy modes with storage and loss modulus larger than G_N . As seen in Fig.1c, the entanglement stretch at fracture is limited to $\lambda = 3.9$, which means that entanglements which fracture are not fully stretched, but reach 83% of maximal stretch $\lambda_{\max} = \sqrt{N_{em}} = \sqrt{21.8} = 4.7$. This is in agreement with earlier findings of Wang et al. [7] that chain scission occurs on the way to full chain extension. The tension in the entanglements reaches a maximum value of $f = 9.3$, and the fracture criterion

of maximum reduced free energy $w_s = w/3kT = f_c \lambda_c \cong 36$ is confirmed by comparison with the experimental data in Figs. 1a and b.

Also shown in Fig. 1 are predictions for the Gaussian limit, i.e. for $\lambda_{\max}^2 = N_{em} \rightarrow \infty$, which we had considered earlier [1]. The Hencky strain at break ε_c turns out to be larger (dash-dotted line in Fig. 1a) and is clearly not in quantitative agreement with the experimental data. However, because the product $f\lambda$, the tensile stress σ , and the strain energy w do not depend on the finite extensibility function $c = c(\lambda, \lambda_{\max})$ at larger deformations (see Eqs. (25) and (26)), there is no significant change in the prediction of the reduced critical tensile stress at fracture σ_c / G_N . In the Gaussian limit, $\lambda = f = \lambda_G$ reaches a limiting value of $\lambda_G = \lambda_c = \sqrt{\frac{U}{3kT}} = 6$ according to Eq. (35) with $c=1$, which is larger than the maximum stretch $\lambda_{\max} = 4.7$ of the entanglement segment (Fig. 1c). This shows the importance of taking into account finite extensibility in the evolution equation (24) of the stretch.

(a)

Fig.1: Comparison of data (symbols) and predictions (lines) as a function of Weissenberg number $Wi = \dot{\varepsilon}\tau_R$ for melt PS-285k. Samples which failed by fast necking are presented as asterisks.

(a) Critical Hencky strain at break ε_c . Solid line is prediction for $\lambda_{\max}^2 = N_{em} = 21.8$, dash-dotted line is prediction for the Gaussian limit ($\lambda_{\max}^2 = N_{em} \rightarrow \infty$).

(b) Reduced tensile stress σ/G_N . Fractured samples are indicated by full symbols and full lines, steady-state stress by open symbols and dotted lines.

(c) Normalized free energy $w_s = w/3kT$, tension f , stretch λ of entanglement segment. Dash-dotted line is prediction of stretch λ_G for the Gaussian limit ($\lambda_{\max}^2 = N_{em} \rightarrow \infty$).

The solutions PS-864k/4k-33 and PS-1760k/4k-18 have similar numbers of entanglements as melt PS-285k with $Z=21$ (PS-864k/4k-33) and $Z=22.8$ (PS-1760k/4k-18), but the number of Kuhn segments per entanglement is much larger with $N_e = N_{em} \phi^{-1} = 66.1$ for PS-864k/4k-33 and $N_e = 121.1$ for PS-1760k/4k-18. As seen in Figs.2 a and b, using these values of $\lambda_{\max}^2 = N_e$ in equation (23) for the nonlinearity function $c = c(\lambda^2, \lambda_{\max}^2)$ leads to the correct prediction of the onset of fracture at a critical Weissenberg number of $Wi_c \approx 30$ and $Wi_c \approx 12$, respectively, but at higher Wi , the predictions of the Hencky strain at break ε_c are constant and significantly higher than the values of ε_c observed experimentally, which decrease with increasing Wi . Replacing $\lambda_{\max}^2$ in Eq. (23) by $\lambda_{\max}^2 = N_{em} = 21.8$ does not affect the onset of fracture, but reduces the Hencky strain at break ε_c to a level which is reached experimentally at high Wi . It is evident that $\lambda_{\max}^2$ decreases with increasing Wi , and using the relation (42) with parameter $a=20$ for PS-864k/4k-33 and $a=2$ for PS-1760k/4k-18 leads to nearly quantitative agreement of data and prediction. As seen in Figs.2 c and d, the chain stretch at fracture reaches a maximum of $\lambda = 5.6$ for PS-864k/4k-33, which corresponds to 69% of maximal stretch $\lambda_{\max} = 8.1$. For PS-1760k/4k-18, the maximal value is $\lambda = 9.0$, which corresponds to 82% of maximal stretch $\lambda_{\max} = 11.0$. Due to the decreasing $\lambda_{\max}^2$ with increasing Wi according to relation (42), the critical stretch λ_c at break then decreases, while the molecular tension f_c continues to increase. The net effect is a constant $w_s = f_c \lambda_c \phi \cong 36$. In the Gaussian limit with $\lambda_{\max}^2 = N_e \rightarrow \infty$ and $c = c(\lambda, \lambda_{\max}) = 1$, λ_G reaches a limiting value of $\lambda_G = \lambda_c = \sqrt{\frac{U/\phi}{3kT}} = 6\phi^{-1/2}$ according to Eq. (35), corresponding to $\lambda_c = 10.4$ and $\lambda_c = 14.1$ for PS-864k/4k-33 and PS-1760k/4k-18, respectively, which is again larger than the maximum stretches (Fig.2 c and d).

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Figs.2 (a) and (b): Comparison of data (symbols) and predictions (lines) of critical Hencky strain at break ε_c as a function of Weissenberg number $Wi = \dot{\varepsilon}\tau_R$ for solutions PS-864k/4k-33 and PS-1760k/4k-18. Short and long dotted line predictions for $\lambda_{\max}^2 = N_e \phi^{-1}$ and $\lambda_{\max}^2 = N_{em} = 21.8$, respectively. Full line prediction by Eq. (42) with parameter $a=20$ for PS-864k/4k-33 and $a=2$ for PS-1760k/4k-18. (c) and (d): Normalized free energy $w_s = w/3kT$, tension f , stretch λ of entanglement segment of solutions PS-864k/4k-33 and PS-1760k/4k-18. Dash-dotted line is prediction of stretch λ_G for the Gaussian limit ($\lambda_{\max}^2 = N_{em} \rightarrow \infty$).

Fig.3 compares experimental data and model predictions of Hencky strain at break ε_c and reduced tensile stress σ/G_N for melt PS-285k and solutions PS-864k/4k-33 and PS-1760k/4k-18. Fractured samples are indicated by full symbols, steady-state stress by open symbols. Fig.3a demonstrates that with increasing N_e and decreasing polymer fraction ϕ the critical Weissenberg number Wi_c at break decreases, while the critical stress at fracture increases (Fig.3b).

(a)

(b)

Fig.3: Comparison of data (symbols) and predictions (lines) as a function of Weissenberg number $Wi = \dot{\epsilon}\tau_R$ for melt PS-285k and solutions PS-864k/4k-33 and PS-1760k/4k-18. Samples which failed by fast necking are presented as asterisks.

(a) Critical Hencky strain at break ϵ_c ,

(b) Reduced tensile stress σ/G_N . Fractured samples are indicated by full symbols and full lines, steady-state stress by open symbols and dotted lines.

7.2 Solutions PS-864k/4k-17, PS-545k/4k-17, and PS-1760k/4k-18 (Group B)

The three solutions of Group B have different numbers Z of entanglements (Table I), but similar numbers of Kuhn monomers $N_e = N_{em}\varphi^{-1}$ and therefore similar maximal stretches $\lambda_{\max}^2$ with $\lambda_{\max}^2 = N_e = 128.2$ for PS-864k/4k-17 and PS-545k/4k-17, and $\lambda_{\max}^2 = N_e = 121.1$ for PS-1670k/4k-18. As in the case of solution PS-1760k/4k-18 and shown in Fig.4, using $\lambda_{\max}^2 = N_e = 128.2$ in the equation (23) for the nonlinearity function $c = c(\lambda^2, \lambda_{\max}^2)$ leads again to the correct predictions of the onset of fracture at a critical Weissenberg number of approximately $Wi_c \approx 10$ for PS-864k/4k-17 and $Wi_c \approx 12$ for PS-545k/4k-17, in spite of the different Z of these solutions. Replacing $\lambda_{\max}^2$ in Eq. (23) by $\lambda_{\max}^2 = N_{em} = 21.8$ does not affect the onset of fracture, but reduces the Hencky strain at break ϵ_c to a level which is seen experimentally at high Wi . As shown in Fig.4, using relation (42) with the same parameter $a=2$ for all three solutions of Group B leads to reasonable agreement of data and prediction.

Fig.4: Comparison of data (symbols) and predictions (lines) of critical Hencky strain at break ε_c as a function of Weissenberg number $Wi = \dot{\varepsilon}\tau_R$ for solutions (a) PS-864k/4k-17 and (b) PS-576k/4k-17. Short and long dotted line predictions for $\lambda_{\max}^2 = N_e \phi^{-1}$ and $\lambda_{\max}^2 = N_{em} = 21.8$, respectively. Full line prediction by Eq. (42) with parameter $a=2$.

A comparison of the critical strain at break and the reduced tensile stress σ/G_N is presented in Fig.5 for the three solutions of Group B with similar N_e but different Z . As seen in Fig.5a, the critical Weissenberg number for the onset of fracture is approximately the same for all three solutions, largely independent of Z . The predicted reduced critical tensile stress at fracture σ_c/G_N (full lines in Fig.5b) increases with increasing Wi in quantitative agreement with the experimental data (full symbols) and shows an enhanced increase with decreasing Z , which is related to the smaller width of the rubber-like plateau with decreasing Z .

(b)

Fig.5: Comparison of data (symbols) and predictions (lines) as a function of Weissenberg number $Wi = \dot{\epsilon}\tau_R$ for solutions PS-1760k/4k-18, PS-864k/4k-17, and PS-576k/4k-17;

(a) Critical Hencky strain at break ϵ_c ,

(b) Reduced tensile stress σ/G_N . Fractured samples are indicated by full symbols and full lines, steady-state stress by open symbols and dotted lines.

8. UNIVERSAL SCALING RELATIONS FOR FRACTURE OF PS MELTS AND SOLUTIONS IN ELONGATIONAL FLOW

Fig. 6 presents the critical strain at fracture as a function of the reduced Weissenberg number Wi/φ^2 . The reduced critical Weissenberg number Wi_c/φ^2 for the onset of fracture given by Eq. (39), $Wi_c/\varphi^2 = 288$, is indicated in the figure by the vertical dotted line. Fracture occurs only at or to the right of this universal line for the melt and all solutions investigated.

Fig.6: Comparison of data (symbols) and predictions (lines) of critical Hencky strain at break ε_c as a function of reduced Weissenberg number Wi/φ^2 for PS melt and solutions. Samples which failed by fast necking are presented as asterisks. Reduced critical Weissenberg number at the onset of fracture $Wi_c/\varphi^2 = 288$, Eq. (39), is indicated by vertical dotted line.

The scaling of the tensile stress according to relation (38) is presented in Fig. 7 as a function of the Weissenberg number Wi_e based on the equilibration time τ_e of the entanglement segments. The critical reduced stress at fracture of $\sigma_c\varphi/G_N \cong 180$ as expected by the scaling relation (38) is indicated by the horizontal dotted line. The experimental data cluster around this line with a trend to increasing $\sigma_c\varphi/G_N$ with increasing Wi_e . Above $Wi_e = 1$, i.e. above

the second crossover of G' and G'' when approaching the transition to the glassy regime, the cluster of fracture data points narrows and the predictions of $\sigma_c \phi / G_N$ converge to a single line.

Fig.7: Comparison of data (symbols) and predictions (lines) of reduced tensile stress σ/G_N as a function of Weissenberg number $Wi_e = \dot{\epsilon}\tau_R / Z^2$ for PS melt and solutions. Fractured samples are indicated by full symbols and full lines, steady-state stress by open symbols and dotted lines. Samples which failed by fast necking are presented as asterisks. The asymptotic critical reduced stress at fracture of $\sigma_c \phi / G_N \cong 180$, Eq. (38), is indicated by the horizontal dotted line.

A combination of the scaling of Figs. 6 and 7 is presented in Fig.8 by plotting the reduced tensile stress $\sigma\phi/G_N$ as a function of the reduced Weissenberg number Wi/ϕ^2 . No fracture is observed to the left of the vertical dotted line indicating the characteristic number $Wi_c/\phi^2 = 288$, while to the right of this line, the critical reduced fracture stress data $\sigma_c \phi / G_N$ cluster around the horizontal line with characteristic number $\sigma_c \phi / G_N = 180$.

Fig.8: Comparison of data (symbols) and predictions (lines) of reduced tensile stress σ/G_N as a function of reduced Weissenberg number Wi/ϕ^2 for PS melt and solutions. Fractured samples are indicated by full symbols and full lines, steady-state stress by open symbols and dotted lines. Samples which failed by fast necking are presented as asterisks. The asymptotic critical reduced stress at fracture of $\sigma_c\phi/G_N \cong 180$, Eq. (38), is indicated by the horizontal dotted line. Vertical dotted line represents reduced critical Weissenberg number at the onset of fracture $Wi_c/\phi^2 = 288$, Eq. (39).

9. CONCLUSIONS

According to our analysis, brittle fracture of entangled polystyrene melts and solutions in homogeneous elongational flow is determined by three characteristic numbers: 36, 180, and 288. These numbers characterise the scaling relations for brittle fracture of the polymer melt and the polymer solutions presented.

The first number relates the thermal energy $3kT$ to the bond energy U of a carbon-carbon bond with $U/3kT \cong 36$. When the strain energy $w(N_{em}) = 3kTf\lambda\phi$ of an entanglement segment with N_{em} Kuhn monomers reaches the bond energy U of one carbon-carbon bond, the chain fractures and the polymer filament fails by chain scission. In start-up flows, segments with long relaxation times, i.e. those preferably in the middle of the chain, will be the first to reach the critical energy w_c and will fracture. This is in agreement with experimental evidence [57-61] as presented in the Introduction. Chain scission is followed by crack initiation and fast crack growth. The product of critical tension f_c and critical stretch λ_c of the entanglement are related to the C-C bond energy by

$$f_c \lambda_c \phi \cong \frac{U}{3kT} \cong 36$$

Polymer chains at fracture are not fully stretched. This is in contrast to the fracture hypothesis of Lake and Thomas [36] as modified by Mazich and Samus [39] assuming that all N carbon-carbon bonds between two entanglement points are fully stretched at fracture, would require $f_c \lambda_c \phi = \frac{NU}{3kT} \cong 36N$. This is larger by two orders of magnitude than what is observed experimentally for the polystyrene melt and solutions considered.

The second number results from the high Weissenberg number limit of the EIP model: The critical tensile stress at fracture in this limit is $\sigma_c = 5G_N f_c \lambda_c$ or

$$\frac{\sigma_c \phi}{G_N} \cong 5 \frac{U}{3kT} \cong 180$$

The high Weissenberg number limit of the evolution equation (25) of the EIP model determines the critical Weissenberg number Wi_c for the onset of fracture, $f_c \lambda_c = \frac{3}{2} \phi^{-2} \sqrt{2Wi_c}$, or

$$\frac{Wi_c}{\phi^2} \cong \frac{2}{9} \left(\frac{U}{3kT} \right)^2 \cong 288$$

and thereby the third characteristic number. The critical Weissenberg number Wi_c is proportional to the square of the polymer fraction ϕ , i.e. $Wi_c \cong 288\phi^2$, and in agreement with experimental evidence, fracture occurs only for elongational flows with $Wi_c / \phi^2 \geq 288$ for all polystyrene systems considered.

The maximum extensibility $\lambda_{\max} = \sqrt{N_e}$ of the entanglement segment determines the Hencky strain at fracture ε_c at $Wi \geq Wi_c$. However, at flow rates larger than the inverse equilibration time $\tau_e = \tau_R / Z^2$ of the entanglement segment, the effective finite extensibility of polymer solutions was found to be the same as for melts, i.e. $\lambda_{\max} = \sqrt{N_{em}}$. This explains why at high Wi , the Hencky strain at fracture for all samples approaches a value of $\varepsilon_c \cong 2.4$. The relevant Weissenberg number is $Wi_e = \dot{\varepsilon} \tau_e = Wi / Z^2$, and at $Wi_e \cong 1$, the reduced critical stress at fracture $\sigma_c \phi / G_N$ attains a value of approximately 180 for all polystyrene systems considered.

Model predictions and scaling relations are in reasonable agreement with experimental evidence for the polystyrene melt and solutions investigated. With the availability of the filament stretching rheometer with locally controlled elongational strain and strain rate [2], experimental fracture data of other polymers than polystyrene can be expected in the near future, which will allow a critical assessment of the universality of the scaling relations for elongational flow presented. Also, progress in incorporating mechanophoric moieties such as spiropyran in the polymer chain signalling directly molecular forces will even permit a direct determination of the spatial distribution of chain stresses [46-48].

Supplementary Material

See supplementary material for linear-viscoelastic mastercurves of G' and G'' (Fig. S1) as well as parsimonious relaxation spectra (Table S1) for the polystyrene melt and solutions investigated.

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