Chain extension and degradation in convergent flow*

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Rheology and birefringence measurements showed conclusively that quasi-full chain extension could be achieved in stagnant extensional flow above some critical strain rate of the order of the reciprocal of the chain characteristic time. Degradation in this highly expanded state could be rationalized with a model of chain scission through frictional loading in which the fracture event is controlled by the force balance between polymer solvent viscous friction and the breaking strength of the bond under consideration. In contrast to the process of chain extension, which could be observed only under rather restrictive conditions of flow, polymer degradation is ubiquitous and is readily detected in situations as diverse as convergent flow, ultrasonic irradiation, solution crystallization, turbulence and flow across porous media. Although some extensional flow component was always present in these types of degradation, the residence time in the high strain-rate region is so short that only a limited degree of coil expansion could be expected. Degradation in transient elongational flow indicated a behaviour definitely distinct from the degradation of fully extended chains under stagnant conditions. In particular, the following experimental facts cannot be explained by the model of fully extended frictionally loaded chains: $\dot{\varepsilon}_f \cong M^{-1}$ (where $\dot{\varepsilon}$ is the critical strain rate for chain fracture); $\dot{\varepsilon}_f \cong \eta_s{}^{-0.25}$ (where η_s is the solvent viscosity); degradation yield is a fairly unique function of average fluid velocity or entrance pressure drop and is almost independent of differences in elongational strain rate introduced by nozzle geometry. These facts lead us to the conclusion that the fundamental parameter which governs the rate of degradation of partly deformed coils is not the magnitude of the local stress, but rather the deformation energy accumulated by the coil up to the moment of rupture.

(Keywords: degradation; kinetics; chain extension; elongational flow; polystyrene)

INTRODUCTION

Chemical degradation by the action of stress is a classical field of research dating back to the work of Staudinger in his efforts to prove the existence of macromolecules[1]. The fact that macroscopic mechanical energy could influence molecular reactivity is intriguing and has attracted scientific interest since the beginning of quantum chemistry. In 1936, de Boer formulated his theory of a stressed bond, which, despite all the advances made in computational chemistry, still constitutes the basis for most models of chemical reactivity under stress[2]. In order to fracture a bond that is not undergoing any vibration, approximated by the Morse potential (*Figure 1*), an energy D must be supplied:

$$V(l) = D\{1 - \exp[-a(l - l_e)]\}^2 \qquad (1)$$

where l is the length of the bond, l_e is the equilibrium separation distance of the atoms, D is the bond dissociation energy, $a = (k/2D)^{1/2}$ is a parameter that defines the width of the minimum and k is the force constant of the bond in the neighbourhood of the equilibrium separation.

The principle of action and reaction imposes the condition that the acting external force must be balanced by the internal molecular forces. For an isolated diatomic molecule, this internal force (also called the binding force) is given by the derivative of the Morse potential (*Figure 2*):

$$\begin{aligned} f(l) &= -\mathrm{d}V(l)/\mathrm{d}l \\ &= -2Da\{\exp[-2a(l - l_e)] - \exp[-a(l - l_e)]\} \end{aligned} \qquad (2)$$

This function has a maximum at:

$$l_b = l_e + \ln 2/a \qquad (3)$$

which corresponds to the critical elongation at break, and the force to produce this elongation is known as the breaking strength for the bond under consideration:

$$f_b \equiv f(l_b) = \tfrac{1}{2}Da \qquad (4)$$

If, however, the bond is under tension due to a constant force f_{ext} pulling on either end, the bond rupture activation energy will be decreased by an amount equivalent to the work performed by the mechanical force over the stretching distance from the equilibrium position. The bond potential energy in the presence of stress is given by:

$$V'(l) = V(l) - f_{ext}(l - l_e) \qquad (5)$$

and has a minimum at $l'_e > l_e$ in accord with the intuitive expectation that the bond separation distance should increase in the presence of a tensile stress (*Figure 1*). The new activation energy (D') required to break the stressed bond at a distance l_b could be calculated from the principle of virtual work performed on the bond in going

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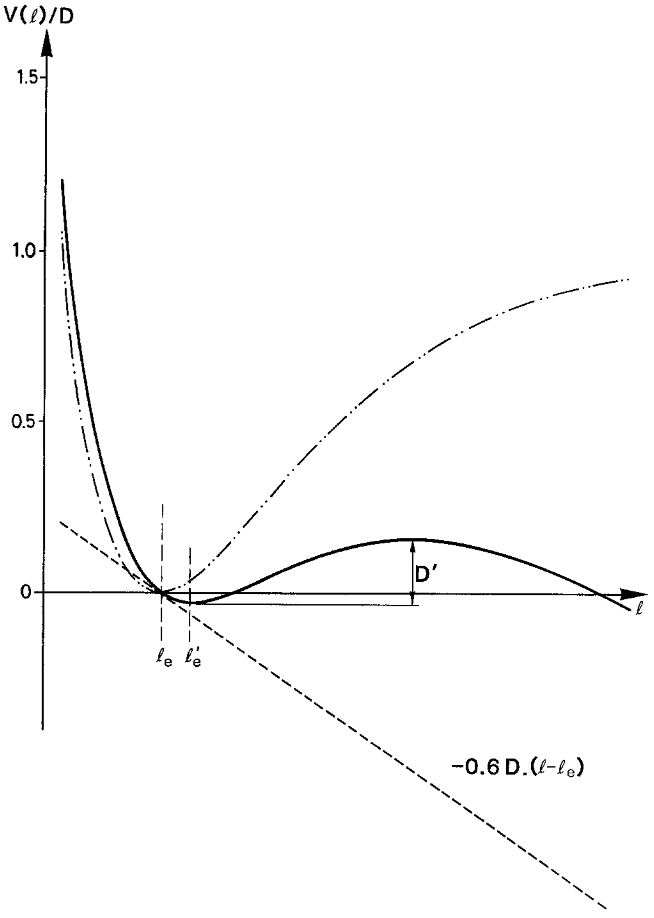

Figure 1 The Morse potential energy of a bond at equilibrium (–··–) and in the presence of an applied stress (——)

from l_e' to l_b (*Figure 2*):

$$D' = \int_{l_e'}^{l_f} \mathrm{d}V'(l)/\mathrm{d}l = \int_{l_e'}^{l_f} [f(l) - f_{\mathrm{ext}}]\mathrm{d}l \qquad (6)$$

The ratio D/D' can be calculated from equations (2) and (6):

$$D'/D = x\ln\{[1 - x - (1 - 2x)^{1/2}]/x\} + (1 - 2x)^{1/2} \qquad (7)$$

and is plotted in *Figure 3* as a function of $x = f/Da$. On the same figure are reported the times to failure as a function of applied axial stress according to the results of Crist *et al.*[3] using an *ab initio* method. To break a chain within some reasonable time interval (for example, 10^{-3} s) requires, however, the same level of stress ($\approx 0.7 f_b$) as found from the simpler de Boer model.

In 1945, Kuhn and Kuhn[4] predicted that flexible long polymer chains could be oriented in flow and, by doing so, suffer large axial stress, which may lead ultimately to fracture of the macromolecule. At almost the same time, Kauzman and Eyring[5], Frenkel[6] and Morris and Schnurmann[7] developed the first theories of mechanochemical degradation in flow. All of these treatments related the process of chain scission with the axial stress acting on the backbone bonds, in a similar fashion as the de Boer model. From a chemical viewpoint, bond scission under stress is a particular case of a unimolecular dissociation reaction whose rate is enhanced by mechanical force. As such, it could be treated with Eyring's transition-state theory, which permits the treatment of rate processes to be brought within the scope of thermodynamic arguments. By combining the de Boer formulation and the transition-state theory, Tobolsky and Eyring developed the rate theory for thermally activated fracture of polymeric threads[8]. According to this theory, the activation energy for bond rupture U_0 ($= D - RT$) is lowered by a quantity $f(\psi)$ in the presence of an axial chain stress (ψ). When put into an Arrhenius-like form, the following expression was obtained for the scission rate constant:

$$k_c = A\exp\{-[U_0 - F(\psi)]/RT\} \qquad (8)$$

In a general way, $f(\psi)$ is identified as the elastic deformation energy, which correlates the applied tension to the work performed by the force $f(l)$ on the covalent bond during stretching by δl from the equilibrium position:

$$f(\psi) \approx f(l)\delta l = -f_{\mathrm{ext}}\delta l \qquad (9)$$

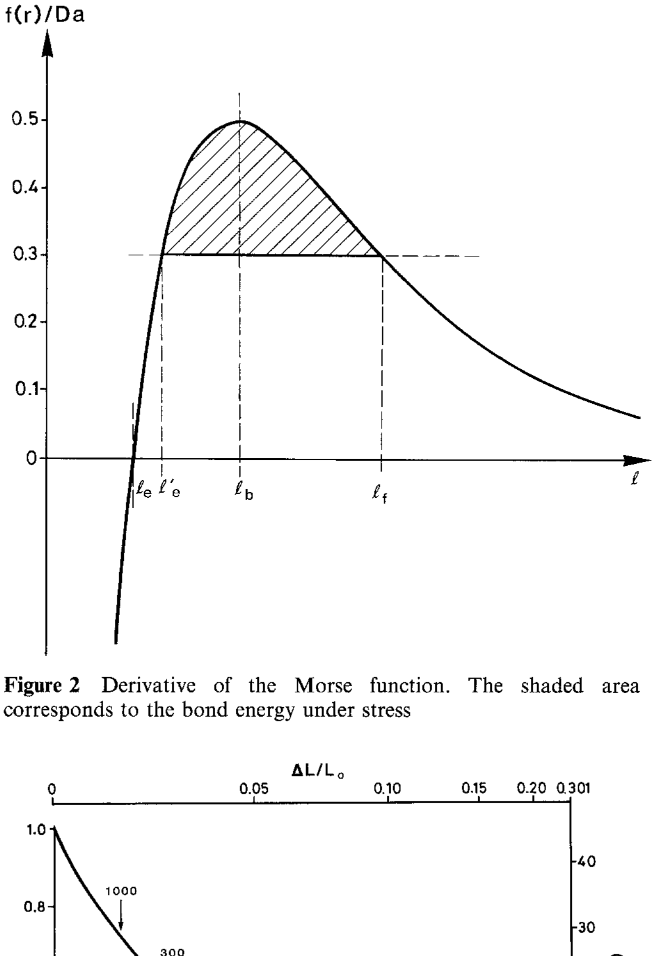

Figure 2 Derivative of the Morse function. The shaded area corresponds to the bond energy under stress

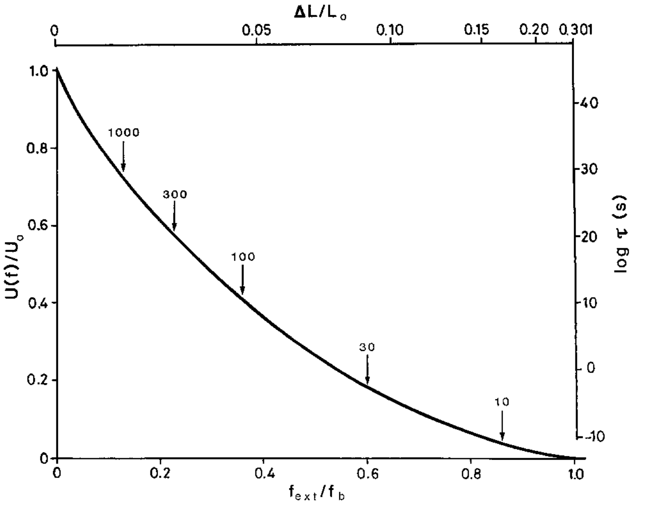

Figure 3 Bond scission activation energy ($U = D - \frac{1}{2}RT$) and lifetime (τ) plotted as a function of applied force. The full curve is derived from equation (6); the other data are taken from ref. 3. The upper abscissa gives the overall elastic strain before failure. The numbers indicate the minimum chain lengths that fail at a particular force

From equation (8) and the shape of the curve in *Figure 3*, it could be verified that the rate of chain scission is appreciable only if the external force is of the order of f_b or ≈ 4–10 nN/chain for a normal covalent bond.

In a recent version of the Tobolsky and Eyring theory, the rate of mechanochemical degradation is considered as a thermally activated barrier to scission (TABS) process and the elastic energy function $f(\psi)$ is explicitly considered in terms of the frictional hydrodynamic force acting over the entire macromolecule[9]. The essence of the derivation, however, is similar to de Boer's formulation of a bond under stress.

The thermodynamic approach to the problem of coil stretching was considered by Treloar[10], who obtained the following expression for the stress–strain relationship of an isolated flexible polymer chain when the two chain ends are kept a distance r apart:

$$f = (kT/l)\mathscr{L}^{-1}(r/L_{\max}) \qquad (10)$$

where $L_{\max}$ is the contour length of the fully extended chain and $\mathscr{L}^{-1}$ is the inverse Langevin function defined by:

$$\mathscr{L}(x) = \coth(x) - 1/x \qquad (11)$$

At the high level of stress necessary to overcome the binding strength, equation (10) shows that bond scission is possible only if $r/L_{\max} > 0.99$ or practically at full chain extension.

Based on the above considerations, it becomes a common conviction that mechanochemical degradation could occur only if a large portion of the chain containing the bond to be fractured is highly stretched. This leads to the pictorial representation of a mechanochemically degraded chain as a highly oriented object, with a breaking strength f_b, frictionally loaded until scission in a similar fashion as a macroscopic string. Recent degradation experiments performed in stagnant elongational flow further reinforce this perception of chain scission by showing that only a small fraction of the polymer molecules that pass close to the stagnation line could be degraded[11]. Chain extension in flow is a rare event, which can only occur under some rather restrictive conditions of flow:

(a) The flow must be elongational, i.e. the extensional component must surpass the rotational component of the velocity gradient.

(b) To overcome the Brownian forces, the fluid strain rate ($\dot{\varepsilon}$) must be larger than the critical value for the coil-to-stretch transition ($\dot{\varepsilon}_{cs}$), defined as:

$$\dot{\varepsilon}_{cs} = A/\tau_Z \qquad (12)$$

In this equation, τ_Z is the Zimm relaxation time for a non-free-draining coil, given by equation (13)[12], and A is a constant varying from 0.5 to 10 depending on the model[13]:

$$\tau_Z = \eta_s[\eta]/(1.18RT) \qquad (13)$$

where η_s is the solvent viscosity, $[\eta]$ the polymer intrinsic viscosity, R the molar gas constant and T the absolute temperature.

(c) The residence time of a fluid element in the high-strain-rate region must be much longer than the chain relaxation time in order for the embedded molecular coil to accumulate sufficient strain for the extension.

Mechanochemical degradation, on the other hand, is ubiquitous in macromolecular systems. There are several examples in the literature which showed that isolated polymer chains in solution can be fractured (sometimes with a surprisingly high efficiency) under situations were large chain extension is not allowed. The most well documented instances are degradation in narrow contraction flow[14] and during ultrasonic irradiation[15]. The first type of flow is classical in the field of rheology; it lends itself to flow modelization and is particularly useful to study chain orientation and degradation in a partially extended state. Starting in 1985, our laboratory has undertaken a series of investigations on the kinetics of chain degradation in transient elongational flow. The results gathered from these experiments strongly point out that the classical model of the frictional loading at break for a polymer chain, which explains consistently the behaviour of fully aligned macromolecules, either in dilute solution, in highly oriented fibres, or in single crystals (of polydiacetylene), is inadequate for chains in a partially uncoiled state. In the first part of this paper, we will present some experimental evidence that brought us to that conclusion. We will then attempt to develop an empirical model which permits us to incorporate these results within the framework of chain unravelling in strong flow.

EXPERIMENTAL

Chemicals

The polystyrene samples used are anionic standards from Polymer Laboratories with $\bar{M}_w/\bar{M}_n \approx 1.04$–$1.05$. They are refractionated on analytical g.p.c. columns to obtain the extremely low polydispersity ($\bar{M}_w/\bar{M}_n \approx 1.01$–$1.02$) required for experiments on the effects of polymer molecular weight and solvent viscosity. All the solvents are of the purest grade available and are distilled prior to utilization. Decalin is a commercial mixture containing 41% *cis*- and 58% *trans*-decahydronaphthalene + 1% tetrahydronaphthalene as determined by gas chromatography.

Degradation apparatus

The degradation equipment represented schematically in *Figure 4* is similar to the one used by Merrill and Leopairat[14]. The most notable modification as compared to the previous design was the use of an interchangeable nozzle. As will be detailed in the 'Results' section under 'Fluid strain rate', changing the nozzle geometry permits one to alter to some extent the degradation flow field. In experiments with high-molecular-weight polymers ($> 3 \times 10^6$) and requiring a much lower range of strain rate, a cell fitted with glass windows was used instead (*Figure 5*). This arrangement corresponds to the opposed jets in which one arm of the outlet was blocked; without the symmetry centre, the stagnation point is destroyed and the flow becomes transient along all streamlines. The introduction of transparent windows is highly versatile since it allows flow visualization and birefringence measurements to be performed on the same flow geometry as the degradation.

Molecular weight determination

Molecular-weight distributions of virgin and degraded polymer solutions are determined by gel permeation chromatography (g.p.c.) on a Waters 150C equipped with a variable-wavelength u.v. detector (Perkin–Elmer 75C) and modified to permit data acquisition and processing on a personal computer (Hewlett Packard

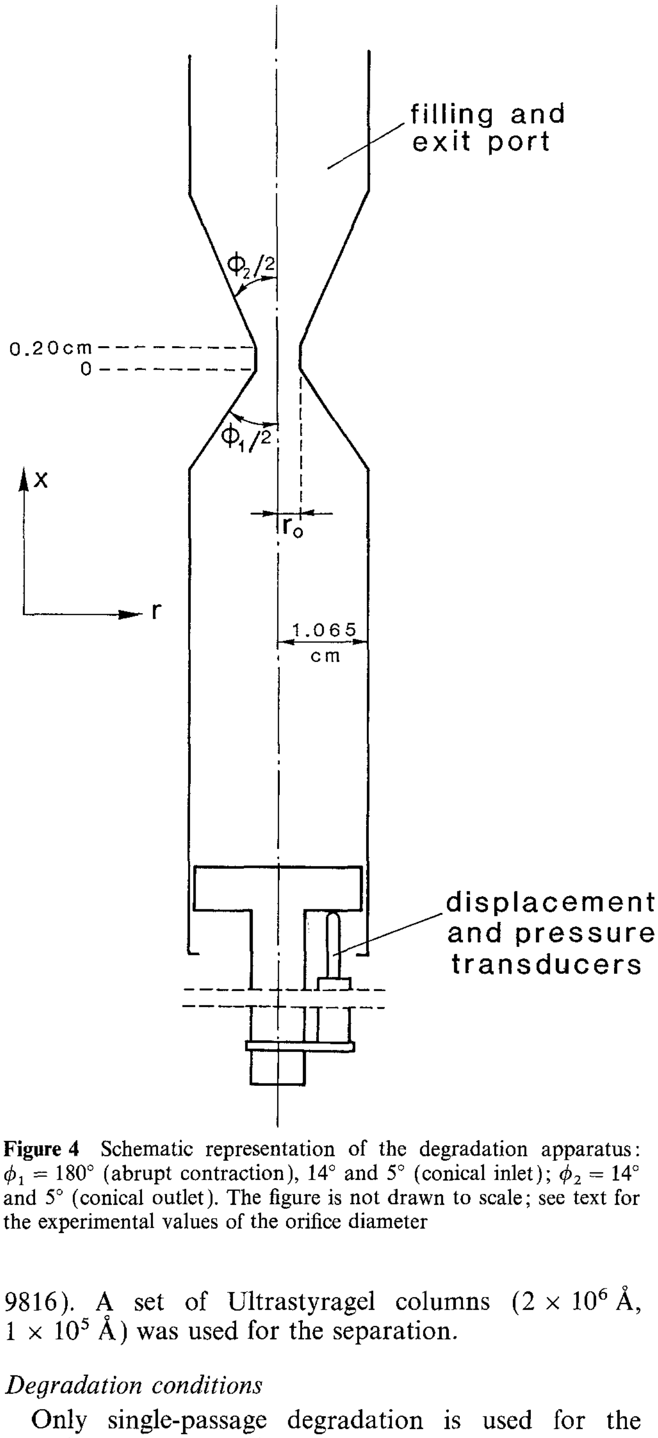

Figure 4 Schematic representation of the degradation apparatus: $\phi_1 = 180°$ (abrupt contraction), 14° and 5° (conical inlet); $\phi_2 = 14°$ and 5° (conical outlet). The figure is not drawn to scale; see text for the experimental values of the orifice diameter

9816). A set of Ultrastyragel columns (2×10^6 Å, 1×10^5 Å) was used for the separation.

Degradation conditions

Only single-passage degradation is used for the experiments. Dissolved oxygen is known to be an efficient radical scavenger; to avoid secondary reactions from macroradicals formed during the degradation, solutions are saturated with air prior to the experiment.

Highly dilute solutions containing 5 ppm of polymer are used for the degradation. The choice of such a low concentration permits one to consider each macromolecule as effectively isolated from all others and to avoid complications from non-Newtonian flow effects.

RESULTS

Initial molecular weight[16]

Polymer molecular weight can affect the rate of flow-induced degradation in at least two respects. First, molecular mobility (characterized by the chain relaxation time) decreases with the chain length, permitting a larger molecular coil to be deformed at a lower fluid strain rate. Secondly, a larger macromolecule, by virtue of its physical size, can accumulate more strain and store more elastic energy. These considerations lead to an increase in bond scission susceptibility with the chain length.

For a chain of length L, fully stretched in the flow direction (x), the stress distribution is readily obtained from the bead–rod model first given by Frenkel[6]:

$$f(x) = f_{\max}[(L/2)^2 - x^2] \qquad (14)$$

The maximum stress at midchain ($f_{\max}$) is given by Stokes' hydrodynamic drag formula:

$$f_{\max} = (3\pi/4)\eta_s\dot{\varepsilon}aL_0(M/M_0)^2 \qquad (15)$$

where a is the hydrodynamic radius of the bead, L_0 the distance between beads, M_0 the molecular weight of a bead and M the molecular weight of the polymer.

From equation (15), the level of strain rate ($\dot{\varepsilon}_f$) necessary to break the polymer chain changes with molecular weight as M^{-2}.

Using the TABS model and the parabolic stress distribution function (equation (14)), Odell *et al.*[9] determined that the probability for bond scission along the chain follows a Gaussian-like distribution function with a maximum at midchain and a standard deviation of $\approx 6\%$ increasing with temperature and chain stiffness. The precise chain halving process, as well as the M^{-2} scaling law, have both been confirmed in opposed-jets flow[17].

In transient elongational flow, on the other hand, chain expansion is limited due to the short residence time[14,18] and it is conceivable that the molecular coil remains essentially non-free-draining up to the point of rupture. This state of partial chain uncoiling should be detected as a deviation from the $\dot{\varepsilon}_f \propto M^{-2}$ law, which is characteristic for perfectly oriented polymers.

Using the device schematized in *Figure 4* with an abrupt contraction nozzle, polystyrene (PS) fractions of different *MW* are degraded under θ-conditions in decalin. To minimize polydispersity effects, only ultra-narrow fractions are utilized for the experiments (*Table 1*). The molecular-weight distribution of the degraded polymer, shown in *Figures 6a* and *6b*, revealed an extremely sharp propensity for midchain scission similar to the results obtained in stagnant elongational flow[17]. The degradation yields as a function of strain rate are presented in *Figure 7*. From these experimental data, the critical strain rates for chain fracture ($\dot{\varepsilon}_f$) are determined and plotted on

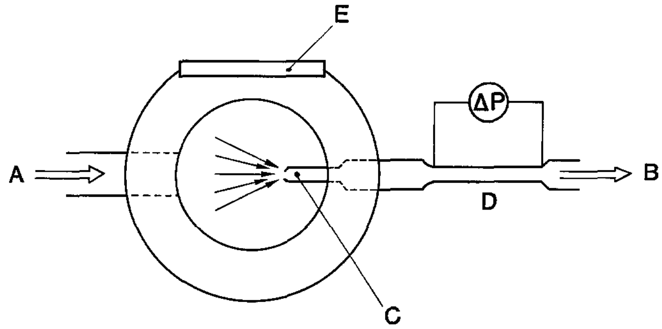

Figure 5 Abrupt contraction cell for flow visualization, birefringence and degradation measurements: A, inlet, from a peristaltic pump of a pressurized reservoir; B, outlet, atmospheric pressure or partial vacuum; C, interchangeable metallic jet; D, capillary flow meter; E, glass window for flow visualization; ΔP, pressure frop (from pressure transducers)

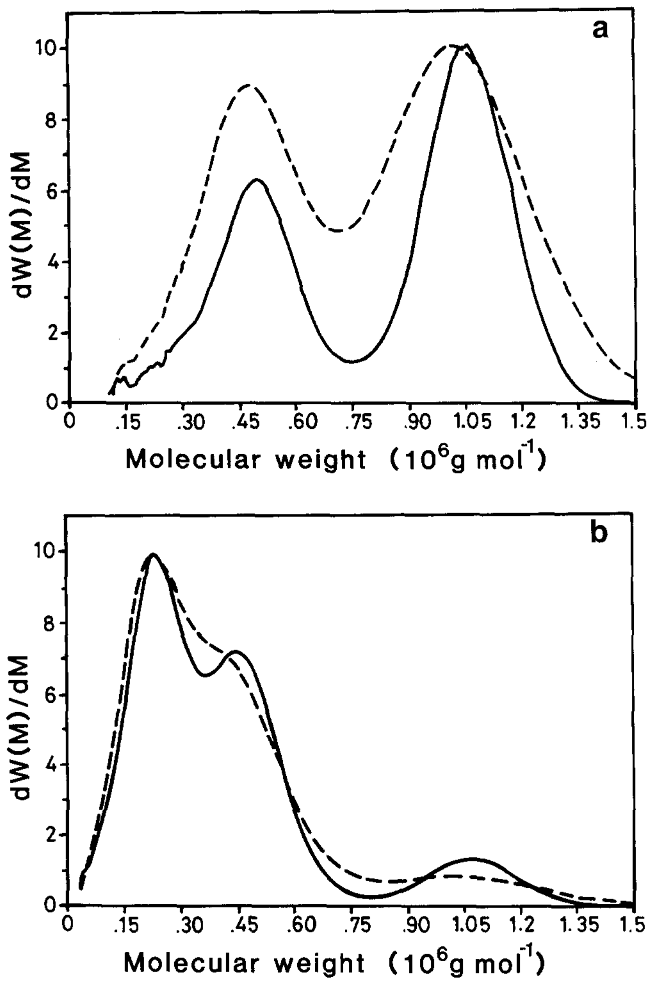

Figure 6 (a) Molecular-weight distribution of a sharp PS function ($\bar{M}_w/\bar{M}_n = 1.017$) degraded at $\dot{\varepsilon}_{max} = 1.7 \times 10^5\ s^{-1}$. (b) Same as in (a), but degraded at $\dot{\varepsilon}_{max} = 3.6 \times 10^5\ s^{-1}$. Curves: (– – –) uncorrected for axial dispersion; (——) corrected for axial dispersion. ($\dot{\varepsilon}_{max}$ is the maximum elongational strain rate along the centreline)

Table 1 Principal characteristics of the polymer fractions used

M_w	M_n	M_w/M_n	τ_Z (μs)	τ_r/τ_Z	σ^a
2.86×10^6	2.80×10^6	1.020	182	0.29	0.12
1.03×10^6	986×10^3	1.017	37.5	0.31	0.070
646×10^3	639×10^3	1.011	18.6	0.34	0.052
426×10^3	421×10^3	1.012	9.8	0.36	0.055

[a] σ is the standard deviation from midchain scission

double-logarithmic scales as a function of molecular weight. A straight line was obtained with a slope of −0.95 (*Figure 8*). This reciprocal dependence of $\dot{\varepsilon}_f$ on M was predicted by Rabin on the basis of slender-body hydrodynamics[19]. The frictional properties of a molecular coil in the unperturbed state are modelled with a solid sphere. For a partly stretched chain, the analogous model would be an impenetrable cylinder with length L and diameter d. In the presence of a steady elongational flow of strain rate $\dot{\varepsilon}$, the increment in hydrodynamic drag force (df^H) on a segment of the cylinder of length dx located a distance x from the centre is given by the results of slender body hydrodynamics:

$$df^H = [2\pi/\ln(L/d)]v\,dx \qquad (16)$$

where $v = \dot{\varepsilon}x$ is the velocity of the solvent relative to the cylinder at position x.

The form factor $2\pi/\ln(L/d)$ changes slowly with aspect ratio (L/d) and could be regarded as constant (C). The total drag on the cylinder is obtained by integration:

$$f^H = C\eta_s \int_{-L/2}^{+L/2} v\,dx = C\eta_s \int_{-L/2}^{+L/2} \dot{\varepsilon}x\,dx = \tfrac{1}{4}C\eta_s\dot{\varepsilon}L^2 \qquad (17)$$

Equation (17) is identical to equation (15) in the limit of large chain extension. It shows that the frictional force is quadratic in the end-to-end distance or equivalently

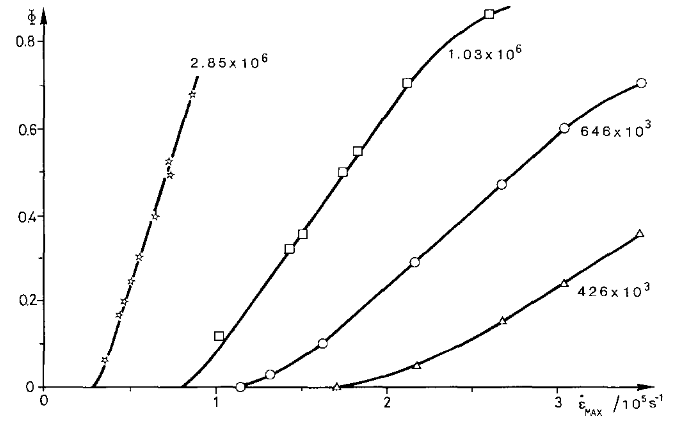

Figure 7 Dependence of scission yield on strain rate and polymer molecular weight

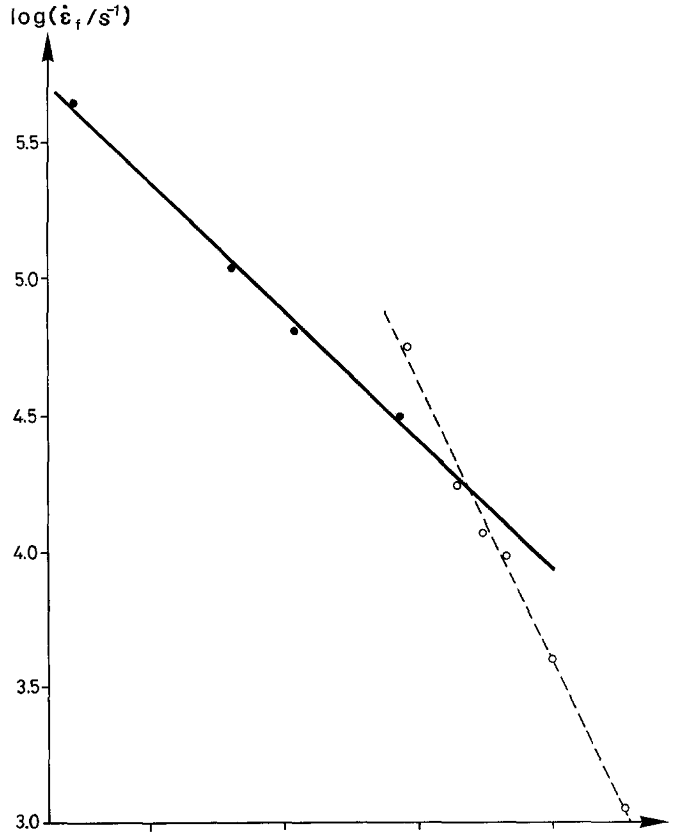

Figure 8 Dependence of the critical strain rate for chain scission ($\dot{\varepsilon}_f$) on polymer molecular weight: (——) transient elongational flow; (– – –) stagnant elongational flow

to R_g^2. From this relation, the following scaling law was derived:

$$\dot{\varepsilon}_f \propto R_g^2 \propto M^{-2\nu} \tag{18}$$

where ν is a parameter equal to $\approx 3/5$ in a good solvent[20], 0.50 in a θ-solvent and 0.33 in the collapsed state[21].

Although the derived scaling law seems to conform to the experimental results under θ-conditions, the slender body hydrodynamics model suffers from one fundamental drawback: Superimposed on *Figure 8* are the values of $\dot{\varepsilon}_f$ measured on the same system (PS–decalin) but under stagnant flow, which show distinctly a slope of -2 predicted from equation (15)[17]. Owing to the stronger dependence of $\dot{\varepsilon}_f$ on chain length, the curve in stagnant flow intersects the transient flow line at $M \approx 4 \times 10^6$. This means that, below this cross-over molecular weight, scission will occur at a lower strain rate in transient flow than under stagnant flow. This conclusion is in complete contradiction with the hydrodynamic screening concept of non-free-draining coils where the gripping action of the flow increases rapidly with the degree of coil expansion regardless of the molecular weight.

Solvent viscosity[22]

In the highly dilute state where each macromolecule is isolated from others, stress is transmitted from the flowing solution to the molecular coil by the viscous friction between solvent molecules and monomeric segments. In most of the current theories of chain dynamics in solution, this frictional contact, known as the 'monomer–solvent friction coefficient' (ζ), is assumed to be directly proportional to the bulk viscosity of the solvent (equation (17)). Solvent viscosity thus plays an active role in channelling part of the kinetic energy of the flow into the chain elastic energy; in this respect, it should stand on the same footing as strain rate and molecular weight as one of the central parameters that control the kinetics of degradation in flow.

In most stress-induced degradation, it was observed that the scission yield decreased with increasing temperature. This finding is universal to the point where negative temperature coefficient was considered as a prime criterion for mechanochemical reaction[23]. The reason for this apparent negative activation energy should be sought in the indirect effect of temperature, which, in addition to increasing the probability of fracture of the stressed bond, promotes at the same time the mobility of the chain and of the surrounding medium characterized by the solvent viscosity, thus lowering the rate of energy input by this combined effect. In transient elongational flow, the direct effect of temperature on the scission rate was shown to be minimal[24]. Even so, it is desirable to look for a system where the solvent viscosity could be studied independently of the other kinetic parameters. Ideally, the solvents used should satisfy the following criteria:

(i) they should cover the broadest range of viscosity at a given temperature;

(ii) they should have similar θ-temperatures (preferably around room temperature) to keep the solvation power constant;

(iii) to recover the polymer for g.p.c. analysis, they should have a sufficiently low boiling point to allow its complete removal by vacuum distillation without thermal degradation of the solute ($T < 120°$C).

The physical properties of some solvents that meet these criteria are listed in *Table 2*. The degradation results in these solvents are reported in *Table 3* and *Figure 9*.

The most outstanding feature revealed by the experimental data is the relative insensitivity of $\dot{\varepsilon}_f$ to a large change in solvent viscosity: increasing η_s by two

Table 2 Physical constants of some selected solvents for PS

Solvent	η_s (mPa s)[a]	ρ (g cm^{-3})[a]	T (°C)[b]	B.p. (°C)[c]
Methyl acetate	0.329	0.902	43.5 (θ)	57
Cyclohexane	0.772	0.765	34.5 (θ)	81
Decalin	2.769	0.890	14.8 (θ)	189–191
1-Methylnaphthalene	2.793	1.014	27.0	241–245
Dimethyl phthalate	32.10	1.200	10.0	283–288
Dioctyl phthalate	65.00	0.985	22.0 (θ)	386
Didecyl phthalate	10.46	0.918	72.5 (θ)	–

[a] η_s and ρ are measured at the temperature given in column 4
[b] The suffix (θ) indicates the θ-temperature
[c] Boiling point at atmospheric pressure, as given in the literature

Table 3 Molecular properties of polystyrene in the different solvents

Solvent	τ_Z (μ_s)	$\dot{\varepsilon}_f^*$ (10^5 s^{-1})	$[\eta]$ (dl g^{-1})	K (dl g^{-1})	a	R_g (nm)	λ (fluid)	σ
Methyl acetate	8	3.48	0.737	72×10^{-5}	0.50	26.1	2.1	0.08
Cyclohexane	23	2.84	0.863	85×10^{-5}	0.50	27.6	5.3	0.07
Decalin	82	2.06	0.812	80×10^{-5}	0.50	27.0	7.1	0.07
1-Methylnaphthalane	240	2.06	2.44	87×10^{-6}	0.74	39.0	15.3	0.04
Dimethyl phthalate	1400	0.92	1.14	67×10^{-7}	0.87	30.2	31.4	0.06
Dimethyl phthalate[a]	9200	0.25	2.77	67×10^{-7}	0.87	40.6	37.7	0.11
Dimethyl phthalate[b]	–	–	1.17	67×10^{-7}	0.87	–	–	–

[a] Polystyrene with $M = 2.86 \times 10^6$, $\bar{M}_w/\bar{M}_n = 1.02$
[b] Measured at $T = 25°$C

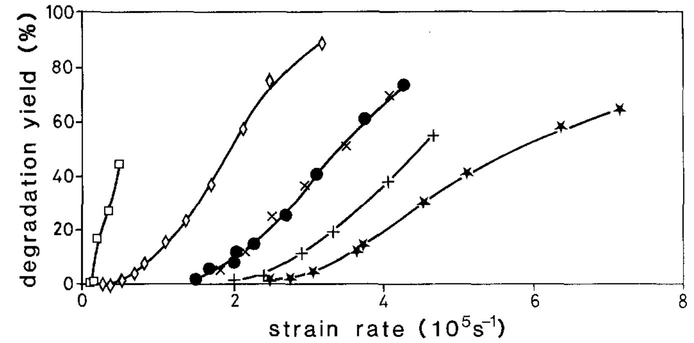

Figure 9 Degradation yield as a function of strain rate $\dot{\varepsilon}_{max}$ and solvent viscosity. Except for the first series, all the data refer to the same PS fraction sample with $\bar{M}_w = 1.03 \times 10^6$, $\bar{M}_w/\bar{M}_n = 1.017$: (□) dimethyl phthalate ($\bar{M}_w = 2.86 \times 10^6$, $\bar{M}_w/\bar{M}_n = 1.02$); (◇) dimethyl phthalate ($\eta_s = 32.1$ mPa s); (●) decalin ($\eta_s = 2.77$ mPa s); (×) 1-methylnaphthalene ($\eta_s = 2.79$ mPa s); (+) cyclohexane ($\eta_s = 0.772$ mPa s); (✱) methyl acetate ($\eta_s = 0.329$ mPa s)

orders of magnitude in going from methyl acetate to dimethyl phthalate merely reduced $\dot{\varepsilon}_f$ by a factor of 3.4, approximately equivalent to $\dot{\varepsilon}_f \propto \eta_s^{-0.25}$ (*Figure 10*). This weak dependence of $\dot{\varepsilon}_f$ on η_s, already noticed in a previous work on the effect of temperature[24], is entirely unexpected from the current model of chain scission through frictional loading, which assumes a proportionality between the molecular stress and solvent viscosity (equation (17)). It is also at variance with the results in stagnant flow where the relation $\dot{\varepsilon}_f \propto \eta_s^{-1}$ was verified[11].

To determine the influence of solvent quality on the degradation kinetics, some comparative experiments were performed in a good solvent (1-methylnaphthalene) and in a θ-solvent (decalin), at temperatures where the two solution viscosities perfectly match each other (*Table 2*). The degradation curves are exactly superimposable (*Figure 9*), suggesting that solvent quality has little influence on the degradation mechanism. A fortuitous coincidence cannot be rejected and it is intended in a future investigation to extend the range of comparison to different polymer molecular weights.

The insensitivity of $\dot{\varepsilon}_f$ to the viscosity of the surrounding medium was rationalized in terms of intramolecular segmental friction, which can activate bond scission during the rapid deformation of the coil. This representation is similar to the large loops 'internal viscosity' model proposed by de Gennes[25]. It fails, however, at present to predict the independence of the scission yields on solvent quality (if this proves to be correct).

Fluid strain rate[26]

As mentioned in the introduction, most of the current theories on mechanochemical degradation consider the force generated on the chain as the dominant parameter that controls the fate of a bond under stress. Whenever this force is comparable to the breaking strength of the bond, scission will occur. By using equation (17), it is possible to relate the breaking strength of a chain with the critical strain rate for degradation ($\dot{\varepsilon}_f$) and solvent viscosity (η_s) through a constant factor (C) pertaining to the coil dimensions.

With highly extended chains in stagnant elongational flow, it has been assessed from these relations that the breaking force to degrade PS and poly(ethylene oxide) (PEO), broadly in the range of 3–13 nN/chain, did indeed correspond to the expected value for the breaking strength of the bonds[17]. The situation is more confusing when chains retained their state of partial uncoiling: during degradation of DNA in capillary flow, Levinthal and Davison claimed that their experimentally determined critical stress of 11 nN/chain is in satisfactory agreement with the theoretical prediction of 8.9 nN for the C–O bond[27]. Using similar devices, Harrington and Zimm found on the contrary that the critical stresses for breaking PS and DNA in simple shear flow are two orders of magnitude smaller than the theoretical estimates based on bond strength[28]. The same conclusion was reached by Merrill and Leopairat in transient elongational flow where the determined breaking stresses were two orders of magnitude below the theoretical estimates[14].

Shear rate is controlled by machine design, whereas the breaking strength is specific to the chemical bond. In order to verify the proportionality between f_b and $\dot{\varepsilon}_f$, the most rational step would be to change the flow geometry and to recalculate f_b for each experimental situation. This procedure is the only means to resolve the discrepancies mentioned previously; unfortunately, it is seldom applied in mechanochemistry.

In one series of experiments, we have kept the basic design of the degradation equipment while changing the orifice diameter and the nozzle angles within sizable limits (*Figure 4*).

At a fixed conical angle and varying orifice diameters, flow-field analysis confirmed that all the strain-rate distribution functions are exactly superimposable onto a single curve when plotted against the dimensionless parameters $\dot{\varepsilon}'_{xx} = \dot{\varepsilon}_{xx}/(\bar{v}_0/r_0)$ and $x' = x/r_0$, where $\bar{v}_0$ is the average fluid velocity at the orifice and r_0 the orifice radius (*Figure 11*).

As compared to the abrupt contraction at an identical flow rate and orifice diameter, the conical entrance provides an increase in spatial distribution of the strain rate by a factor of 3 with the 14° inlet and up to 8 with the angle of 5° (*Figure 10*). This increase in width is accompanied by a decrease of approximately the same

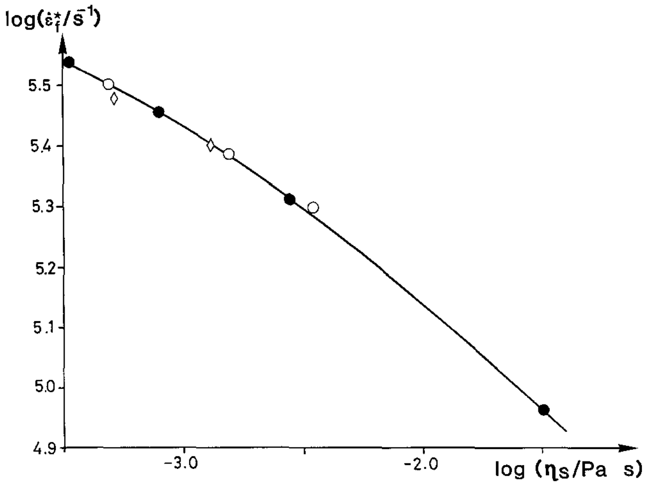

Figure 10 Dependence of the critical strain rate for chain scission ($\dot{\varepsilon}_f$) on solvent viscosity (η_s). Data from this work (●). Previous data from ref. 24, where η_s was changed concomitantly with the solvent temperature: (○) decalin at 7, 22 and 140°C; (◇) dioxane at 22 and 90°C

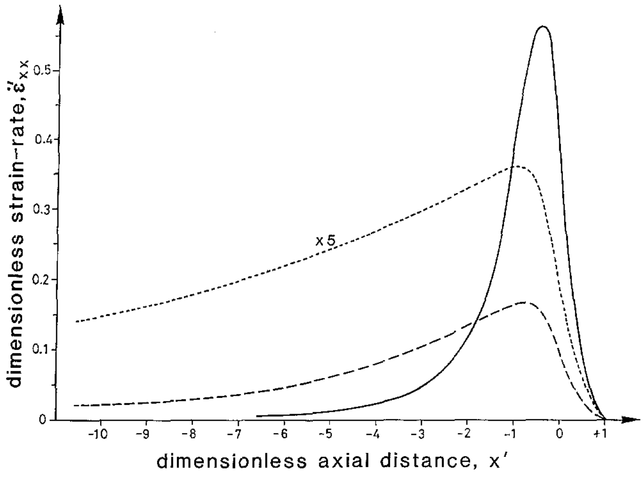

Figure 11 Entrance elongational strain rate ($\dot{\varepsilon}'_{xx}$) calculated along the centreline of the flow tube for the different nozzle geometries (the origin of the abscissa is taken at the orifice entrance): (——) abrupt contraction; (– – –) 14° conical inlet; (······) 5° conical inlet

factor in the amplitude of the fluid strain rate:

abrupt contraction

$$\phi_1 = 90°, \qquad \dot{\varepsilon}_{xx}(\max) = 0.56\bar{v}_0/r_0 \qquad (19)$$

conical inlet

$$\phi_1 = 14°, \qquad \dot{\varepsilon}_{xx}(\max) = 0.17\bar{v}_0/r_0 \qquad (20)$$

$$\phi_1 = 5°, \qquad \dot{\varepsilon}_{xx}(\max) = 0.07\bar{v}_0/r_0 \qquad (21)$$

As with any elongational flow, the velocity field is not homogeneous. Flow is purely elongational along the symmetry axis, with the vorticity component increasing in importance with the distance from the centreline. A semi-empirical kinetics study taking this variation in strain rate into account showed that the result is a broadening in the degradation yield curve as a function of average fluid strain rate[29]. Although experimental results give only a spatially averaged degradation yield, the mentioned calculations showed, nevertheless, that this quantity is sufficient for a comparative description of the degradation process.

In conformity with the previous publications, we have plotted the degradation yields as a function of the maximum strain rate along the centreline for the different nozzle geometries (*Figure 12*). The most apparent feature from the reported data is a lack of any coincidence between the critical strain rate for chain rupture ($\dot{\varepsilon}_f$) and the fluid strain rate ($\dot{\varepsilon}$). This dispersion in the degradation yields suggests that the scission event is not controlled by the frictional stress (proportional to the fluid strain rate) as implied by the model of chain scission through frictional loading. In order to reconcile this with the model of chain scission through frictional loading, the possibility to use a nozzle-dependent coil expansion factor has been explored: since $f_{\max}$ changes as $\dot{\varepsilon}L^2$ (equation (17)), a more expanded coil could also be fractured at a lower strain rate. Such a model is plausible *a priori* from the results of flow-field calculations, which show that the residence time, one of the key parameters to determine the degree of coil expansion, is also changing with the nozzle geometry.

The relaxation time (τ_Z) for the 1.08×10^6 PS sample in decalin, calculated from equation (13), is 88 μs. The corresponding critical strain rate for the coil-to-stretch transition ($\dot{\varepsilon}_{cs}$), based on the most conservative estimate with $A = 0.50$ (equation (12)), would be 5700 s^{-1}.

From the strain-rate distribution curve (*Figure 11*) and by assuming that the coil starts to deform only if $\dot{\varepsilon} > \dot{\varepsilon}_{cs}$, it is possible to calculate the maximum strain ($\lambda_{\max}$) accumulated by the coil in the case of an affine deformation with the fluid element. The values obtained at the onset of degradation actually go in a direction opposite to the expectation. With the abrupt contraction configuration, $\lambda_{\max}$ decreases from 19 with $r_0 = 0.0175$ cm to 8.7 with $r_0 = 0.050$ cm. Values of $\lambda_{\max}$ are even lower with the conical nozzles ($r_0 = 0.025$ cm), varying from 3.3 with the 14° inlet to a mere 1.6 with the 5° inlet.

The results obtained with the 5° conical inlet have important implications, which may stimulate further investigations:

(i) The maximum strain rate at the onset of degradation ($\dot{\varepsilon} = 9800$ s^{-1} at $\bar{v}_0 = 35$ m s^{-1}) is either just sufficient to distort the molecular coil or may be even below the threshold depending on the exact value of $\dot{\varepsilon}_{cs}$ (equation (12)). It is then legitimate to question whether a polymer chain can still be degraded even if the fluid strain rate is lower than the critical value to induce coil deformation. The correctness of this assertion could be verified by using a less viscous solvent or a lower molecular weight (to increase $\dot{\varepsilon}_{cs}$).

(ii) By gradually reducing the angle ϕ_1 of the conical inlet, it is possible to make a smooth transition from an elongational flow to a simple shear flow. If it is correct that isolated molecular coils cannot be degraded in 'weak flow', then at some stage it is predicted that the degradation yields must drop sharply since little chain scission is expected in laminar capillary flow.

Figure 12 reveals an inverse dependence of $\dot{\varepsilon}_f$ on orifice diameter. The existence of a similar relationship with the fluid strain rate (*Figure 10*) suggested that a better correlation could be obtained by reporting the degradation yields as a function of average orifice velocity ($\bar{v}_0$) for the different nozzle geometries. *Figure 13* shows effectively that all the degradation for the abrupt contraction as well as for the conical inlets can be

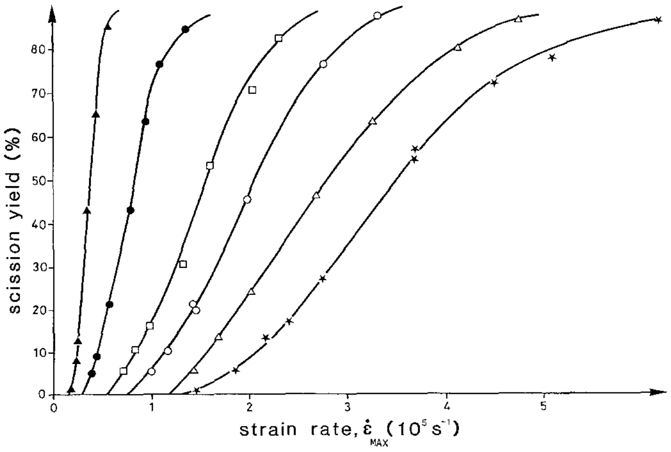

Figure 12 Degradation yield as a function of maximum entrance strain rate ($\dot{\varepsilon}_{\max}$) for different nozzle geometries: (★) abrupt contraction with $r_0 = 0.175$ mm; (△) abrupt contraction with $r_0 = 0.25$ mm; (○) abrupt contraction with $r_0 = 0.34$ mm; (□) abrupt contraction with $r_0 = 0.50$ mm; (●) 14° conical inlet with $r_0 = 0.25$ mm; (▲) 5° conical inlet with $r_0 = 0.25$ mm

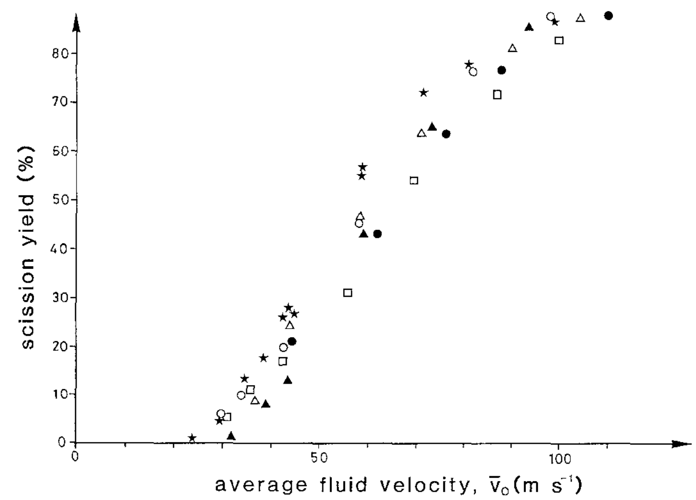

Figure 13 Degradation yield as a function of volumetric average fluid velocity at the orifice ($\bar{v}_0$); the same symbols are used as in *Figure 12*

superimposed onto a single curve. Although some dispersion is still present, it is considerably reduced as compared to the plots of *Figure 12* and, in part, this can be accounted for by the imprecision in the determination of the orifice diameters.

In convergent flows, flow rate and entrance pressure drop are two dependent variables whose relationship is well documented. Instead of reporting the degradation yields as a function of $\bar{v}_0$, the other alternative would be to report the same results as a function of the entrance pressure drop P_{ent} (*Figure 14*): a weak increase in degradation efficiency with decreasing orifice diameter is observed with this type of plot and may have some importance in polymer flow across porous media. The most remarkable feature is certainly the perfect coincidence between the data points obtained with the conical inlets and with the abrupt contraction of identical orifice diameters. Although the velocity fields are quite different in each case, the chains break with identical efficiency at a given pressure drop (or energy input): such a coincidence is certainly not fortuitous and conceals a deeper underlying mechanism that still needs to be sought.

THE CRITICAL ENERGY MODEL

The series of experiments performed in our laboratory and reported in the previous section showed that polymer chains in a partly uncoiled state behave in a quite different and intricate way from chains in a highly extended state. The model of chain scission through frictional loading, which seems to explain correctly the scission kinetics of highly extended chains, is not only in quantitative disagreement but also in qualitative contradiction with the degradation behaviour of partly extended molecular coils:

(a) As already mentioned, most of the reported data in transient elongational flow point to the fact that a partly deformed coil is easier to degrade than a fully extended chain. Apart from the difference in the level of strain rate (see section on 'Initial molecular weight'), a much greater amount of polymer could be degraded in transient elongational flow (90%) than in opposed-jets flow (0.4% per pass)[11].

(b) Using equation (17) and the experimental data for degradation in cyclohexane (*Table 3*), it is possible to evaluate the frictional forces involved during the coil stretching. With $L \approx 690$ nm, $d \approx 130$ nm ($\lambda \approx 5.3$), $\eta_s = 0.772$ mPa s and $\dot{\varepsilon}_f = 1.42 \times 10^5\,s^{-1}$, $f_{max} = 2.5 \times 10^{-11}$ N. This value agrees with the result from Merill and Leopairat[14] but is well below the actual breaking strength of a C–C bond.

The shape of the curves in *Figure 14* satisfies the intuitive expectation that the number of broken bonds should increase with the total energy input into the flowing system; it also suggests the existence of a critical level of energy, corresponding to $P_{ent} \approx 1$ atm or $\bar{v}_0 \approx 35\,m\,s^{-1}$, below which no degradation occurs regardless of the nozzle geometry. From these experimental results, it is tempting to speculate that the principal factor that governs the fate of a stressed macromolecule is not the frictional *force* at break but the amount of elastic *energy* (E_{el}) stored in the deformed molecule. This energy storage, evidently, must originate from the viscous friction betweeen the polymer segments and the flowing solvent molecules during the stretching process.

At modest extension ratio ($\lambda < 4$), the free-energy storage of a freely jointed bead–spring chain is given by the well known theory of rubber elasticity[10]:

$$E_{el} = \tfrac{3}{2}kT\lambda^2 \qquad (22)$$

The value obtained from equation (22) at $\lambda = 4$ is 1×10^{-19} J/molecule; this quantity is much below the dissociation energy U_0 of the C–C bond, which is 5.7×10^{-19} J/bond or 342 kJ mol^{-1} for polystyrene. From the occurrence of chain scission, it must be assessed that the actual value for E_{el} must be significantly larger than that given by equation (22). It is expected, however, that the Gaussian model of a chain is inadequate in transient flow, even for a modest deformation ratio. In convergent sink flow of dilute PEO solution, for instance, it was determined that the elongational stress (σ_e) surpasses the value predicted from the Gaussian dumbbell by two orders of magnitude[30]. This result strongly hints to the fact that a real molecular coil stiffens during a fast deformation and is capable of storing an appreciable amount of elastic energy, much larger than that predicted from equation (22). A few attempts to

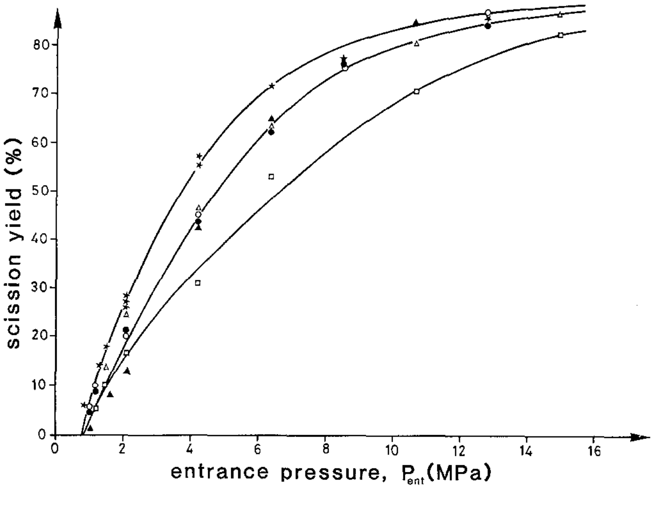

Figure 14 Degradation yield as a function of experimental entrance pressure drop; the same symbols are used as in *Figure 12*. The curves for $r_0 = 0.25$ mm and $r_0 = 0.34$ mm are experimentally indistinguishable

model a real chain with the inclusion of non-equilibrium effects, like 'internal viscosity', non-crossability and self-entanglements, have been reported. Owing to the complexity of the problem, most of the non-steady-state models are only empirical in nature; they are generally designed to fit rather than to predict experimental results and are, therefore, limited in scope. Based on the sink-flow results, Ryskin proposed the 'yo-yo' model of chain unravelling[31]. In this representation, which was first proposed by Kuhn[32] and then by Frenkel[6], the chain starts to uncoil from its most stressed part, i.e. the central portion, which grows in length at the expense of the outer portions. If the flow becomes weaker, the chain will curl back from its ends like a 'yo-yo' toy. The Langevin model for the free-draining ideal chain of Rabin[33] and the recent bead–spring calculations of Magda *et al.*[34] tend to confirm that the centre of the macromolecule is the most stretched part of the chain, even for modest extension ratio. These results are, however, at variance with the FENE bead–spring calculations of Wiest, Bird and Wedgewood, which showed that all the individual links are stretched simultaneously before extensive chain unfolding[35]. In some recent models of chain unravelling, the development of kinks during chain deformation was explicitly taken into account by Larson[36] and by Kausch[37]. With the difference from the former model, kinks in Kausch's model can support some compressive stress depending on the number of defects within the kinked region.

From the standpoint of thermodynamics, the essential quantity that governs the course of a chemical reaction is the chemical potential of the system or, in the case of interest, the free-energy storage within the molecular coil. Owing to the lack of a suitable representation of chain unravelling in non-steady flow, this quantity is difficult to evaluate. A few models of mechanochemical degradation relied on some sort of empirical relationship between the rate of chain scission and an experimental variable that could be directly measured, like the rate of mechanical energy input. The notion of a critical *energy* for bond rupture is not new in itself and has periodically surfaced over the years in the field of mechanochemistry. To rationalize degradation results during capillary extrusion of concentrated polyisobutylene solutions, Bestul[38] derived the following expression for the rate of shear degradation:

$$-\mathrm{d}N/\mathrm{d}t = k_c N = B\exp(-E^*/aJ) \qquad (23)$$

In this equation, B is a constant, N is the number of undegraded polymers at time t, E^* is the mechanical activation energy for bond rupture (approximated as the bond dissociation energy U_0), J is the rate of application of shear energy, which equals the shear rate times the shear stress, and a is a coefficient having the dimension of time and increasing with the polymer molecular weight. The product aJ gives the average amount of applied shear energy that is temporarily stored in bonds.

During ultrasonic irradiation, similar parallels were established between the rate of chain degradation and the ultrasonic intensity[39] or the cavitation energy[40].

More recently, Wolf and coworkers[41] found that moderately concentrated polymer solutions in laminar shear flow do not degrade as long as the quality of the solvent remains high; with decreasing solvent quality, the rate of chain rupture increases steeply in the vicinity of the temperature for phase separation, then decreases again. In order to explain this complex behaviour, Wolf[42] proposed the formation of 'grip points' along the chain: degradation will be observed only if the amount of stored energy per grip point is greater than the activation energy E^* for bond scission. The maximum in the degradation curve as a function of temperature could now be envisioned as a balance between the reduction in coil volume and the increase in stored energy per macromolecule.

Although no intermolecular entanglements could be formed at the low polymer concentration used in the present investigation, the possibility of long-range intramolecular contact points and of local 'kinetic rigidity' implicit in the concept of 'internal viscosity' must be admitted. Under these conditions, stress accumulation becomes possible, leading to bond rupture, in a similar way as through the 'grip points' considered by Wolf.

CONCLUSIONS

Current theories of mechanochemical degradation considered the rate of chain scission as a thermo-mechanically activated process whose rate increases in direct relation to the frictional force generated on the bond. Ultimate mechanical properties of highly oriented polymer chains in dilute solution, fibres or the crystalline state are accurately predicted with this model, leaving little doubt on its ability to explain the physical properties of macromolecules in the fully stretched state.

This model of bond rupture through frictional loading cannot, however, explain the following experimental facts prevalent in the partly uncoiled chains in transient elongational flow:

(i) $\dot{\varepsilon}_f \approx M^{-1}$;

(ii) $\dot{\varepsilon}_f \approx \eta_s^{-0.25}$;

(iii) degradation yield is a fairly unique function of entrance pressure drop and thus of energy introduced into the deformed liquid volume element, and is almost independent of differences in elongational strain rate introduced by nozzle geometry;

(iv) even in a partially uncoiled state, polymers are fractured above $\dot{\varepsilon}_f$ with a sharp propensity for midchain scission.

Interestingly enough, all of these characteristics are also encountered in ultrasonic degradation. In a meticulous series of experiments with ultra-narrow fractions of dextran ($\bar{M}_w/\bar{M}_n < 1.01$), Basedow and Ebert showed conclusively that ultrasonic sonication cut the polymer chains precisely into halves. Furthermore, it was determined that the scission rate constant increases linearly with the polymer molecular weight[15]. These same authors also found that the rate of degradation of dextran was not changed when dissolved in media with quite different viscosities like water, glycerol or ethylene glycol[43]. Finally, as mentioned in the 'Results' section, good correlations were obtained between the rate of ultrasonic and hydrodynamic energy input and the rate of bond scission[39,40].

In order to satisfy one or other of the above facts, three hypotheses have been examined:

(1) The flow is not laminar but turbulent and the flow pattern is not predictable from $\bar{v}$ or an apparent $\dot{\varepsilon}$.

(2) Coil dimensions and local viscosity depend on strain rate and nozzle geometry.

(3) The affinely deforming coil stiffens and is capable of storing an appreciable amount of elastic energy.

In a previous investigation where the degradation yields were systematically measured over a large range of Reynolds number[22], no significant deviation from the observed trend was detected around the critical Reynolds number for turbulence. This implies that the first hypothesis is the least likely explanation. The same is true for the second hypothesis, which necessitates complicated deviations from fundamental behaviour. In light of the experimental results, the most probable hypothesis that can explain the distinctive behaviour of partly uncoiled from highly extended chains is the following. In a rapidly deforming liquid, chain expansion is limited owing to the presence of intramolecular hindrances. The molecular coils are almost statically loaded from the surface of the circumscribed volume element and remain non-free-draining up to the point of rupture: this may explain the observed dependence of $\dot{\varepsilon}_f$ on M^{-1}. Internal relaxation of the chain may relieve some of the axial chain stresses and contribute to a small or moderate elongation. Through intersegmental interactions, stresses are transferred from the surface to the centre of the coil, which can then accumulate enough strain energy for bond rupture.

The problem remains largely unsolved of how the chain knows its centre during the process of loading to explain the precise midchain scission invariably observed. On purely geometrical grounds, it can be appraised that bond rupture should be non-random; since the chain ends are more mobile than the inner parts of the polymer, they should be able to relieve stresses and resist degradation more readily than the middle by reason of symmetry. This argument, however, is not sufficient in itself to explain why the 'centre of the coil' coincides with such precision with the 'centre of the chain', except if the process of chain unravelling can be described by the previously mentioned 'yo-yo' model. It becomes clear that the issue of flow-induced mechanochemical degradation is intimately related to the non-equilibrium conformation of polymer coils, and any attempt to interpret the results beyond the phenomenological stage would be incomplete without a better understanding of chain dynamics. The recent light scattering results from Menasveta and Hoagland[44] constitute an important step in this direction. With the birefringent cell depicted in *Figure 5*, we hope to be able in the near future to clarify some of the features of chain unravelling by determining the state of orientation of the polymer segments in transient elongational flow.

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