Drag reduction and mechanical degradation in polymer solutions in flow

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A list of conclusions from experimental studies of drag reduction (*DR*) and mechanucal degradation in flow (*MDF*) is made. A statistical-mechanical model of chain conformations developed by the author[9] is used, and its consequences for *DR* and *MDF* established. Experimental findings are explained in terms of the model, including those considered to be puzzling and contrary to expectations. A relation between the extent of mechanical degradation and flow time is derived. The equation obtained for relative drag reduction in function of time reproduces perfectly the experimental data for polystyrene+toluene solutions reported by Hunston and Zakin[12]. Some predictions from the present model have yet to be tested experimentally.

Keywords Polymer solutions; macromolecular conformations; chain scission; drag reduction; mechanical degradation; turbulent liquid flow

INTRODUCTION

The presence of small amounts of certain polymers can produce spectacular reduction in the frictional losses of fluids in turbulent flow through conduits[1]. The drag reduction has an immense field of applications, both current and potential. Increasing pipeline capacities is one example. The Alaska pipeline comes to mind immediately, and important research on this is being conducted by Burger and collaborators[2,3]. Another example is improving capacities of storm sewers[4]. In fire fighting, we have a similar problem of increasing capacities of fire hoses. A way to increase the speed of a ship consists of the injection of a polymer solution at the bow. Further, there is the case of inhibition of fuel misting in aircrafts; appropriate additives, such as used by Hoyt, Taylor and Altman[5], reduce the fire danger in case of accident or crash. The phenomenon in question takes place in man-made capillaries, as studied by Kozicki and Wu[6]. Drag reduction also takes place in blood flow; therefore, less energy is needed to assure blood circulation. Consequences of this simple fact form the point of view of the amount of *food needed for the population of the globe* are of staggering dimensions.

This list of advantageous situations could be made still longer, but a big snag exists: drag reduction decreases with flow time. This is due to mechanical degradation of added polymer[7,8].

Both drag reduction (*DR*) and mechanical degradation in flow (*MDF*) are necessarily related to macromolecular conformations in solution. Therefore, we shall discuss these phenomena in terms of a model[9] in which each chain is assumed to consist of compact (relatively rigid) and extended (flexible) bundles. Given the importance of both *DR* and *MDF*, a considerable body of experimental data has been accumulated. Therefore, we shall enumerate the main conclusions derived from the best and most reliable experiments[10-12]. Then we shall relate the approach developed in[9] and computations pertaining to it[13] to *DR* and *MDF*; present some calculations of drag reduction and mechanical degradation in flow based on the derived equations; from the previous section; and finally confront conclusions derived from the present model with the experimental findings, including all those listed in the following section. Our approach enables explanation of experimental observations, even quite puzzling ones, as well as allowing quantitative predictions to be made.

EXPERIMENTAL EVIDENCE

There exists a fairly large amount of experimental information on *DR* and on *MDF*. However, much of the data had been obtained in non-uniform and non-defined shear fields, leading to mutually contradictory conclusions. More recently, some results in uniform and well-defined shear fields have been obtained, notably by Zakin, Hunston and their colleagues[10-12]. Let us now enumerate principal conclusions from these investigations:

(a) Drag reduction is directly proportional to the relative molecular mass (molecular weight) M of polymer, regardless of solvent type;

(b) The concentrations required for equal drag reduction Λ are several times greater in a poor solvent;

(c) The loss of drag reduction through mechanical degradation during time t can be, to a first approximation, described by:

$$\frac{\Lambda}{\Lambda_0}=e^{-Rt} \tag{1}$$

where R is a parameter, not a true rate constant;

(d) More mechanical degradation was observed in a poor solvent under fixed flow conditions than in a good solvent under the same flow conditions. If a limiting molecular weight M_∞ is defined by:

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$$M_\infty = \lim_{t\to\infty} M, \qquad (2)$$

tthenfor a given polymer, values of M_∞ are lower in the poor than in the good solvents. This conclusion was characterized as contrary to expectations;

(e) Bond cleavage along the macromolecule backbone is neither random, nor does it occur exclusively at the midpoint of each chain;

(f) The extent of mechanical degradation, as characterized by M_∞, is independent of the initial molecular weight M_0. Degradation of polydisperse samples narrows the distribution principally through the breaking of large molecules;

(g) Shear degradation at a given shear stress is independent of the viscosity of the solvent;

(h) Entanglements do not play a dominant role in the degradation mechanism;

(i) The degradation rate increases or remains the same as the concentration is decreased;

(j) The parameters M, M_0 and M_∞ can be interrelated by:

$$\frac{M-M_\infty}{M_0-M_\infty}=e^{-R't} \qquad (3)$$

The relation is an approximate one, however, and R' is not a true rate constant.

DEVELOPMENT OF THE MODEL

We shall now return to the model of conformations mentioned before[9] and pursued by numerical calculations reported in[13]. We want to extract from the model the implications it has for the phenomena of drag reduction and mechanical degradation in flow. The route between these phenomena and any theoretical approach is not exactly an obvious one. Reviewers of *DR* have declared[7,8] that the mechanism of the phenomenon is unknown.

In ref 9 it has been assumed that a polymeric chain consists of compact and extended bundles. Consequences of this assumption for segmental densities, for interacting surface areas, and so on, have been already pointed out. In the present context, it has to be noted that the existence of the two kinds of bundles affects rigidity of the chain and of its parts. We are not dealing here with rigidity inherent to the chain itself, particularly since the situation can be changed by changing the solvent. A compact bundle exhibits properties intermediate between a freely-jointed chain and a rigid chain in the usual sense; we shall call this phenomenon *quasirigidity*. It should be noted that, except for the name, our bundles have nothing to do with the bundles of Pechhold[14].

We are now ready to tackle the phenomena or *DR* and *MDF*, qualitatively at first. Let us start with one extreme case. A completely freely-jointed chain, essentially one extended bundle, will hardly contribute to drag reduction. Peter Debye has explained to us many years ago[15] that a freely-jointed polymeric molecule suspended in a flowing liquid will rotate as a whole. Berman in his review[8] discusses experimental evidence to the effect that randomly coiled molecules in spherical shape produce little or no *DR*. It is worth noting that Berman consequently stresses the role of molecular interactions and calls[8,16] for an explanation of the phenomena involved at the molecular level—precisely the line of approach taken in this work.

Among various explanations of the drag reduction phenomenon, a convincing one suggests that drag reducers contribute to laminarity of the flow. Therefore, it is important that in our picture quasirigid compact bundles are intercalated with less rigid (including the case of freely-jointed) extended bundles. To see this better, let us take the extreme case of a completely rigid molecule. Such a molecule would, after a while, align its longest axis with the direction of the flow. The contribution of a rigid macromolecule to drag reduction would be relatively small. For the same reason, a compact bundle will tend to align itself with the flow too, although perhaps not as fast and not as perfectly as a rigid rod. Consider now a pair of compact bundles connected to each other via an extended bundle. We can picture the compact bundles as aligned parallel to each other with the extended bundle providing a somewhat skewed (rather than a completely perpendicular) connection. The domain of solvent molecules between the compact bundles will approximately form a straightlinear channel. We know that in turbulent flow the dissipation of energy takes place by the exchange of momentum between fluid domains or eddies[17]. In fact, turbulence is sometimes characterized as 'eddies within eddies within eddies'. Clearly, the behaviour we have just pictured for a pair of compact bundles pertains to any number of such bundles. The resulting *channelling* should produce at least two effects contributing to the laminarity of the flow: decrease in the number of domains and decrease in the momentum exchange between the domains.

Let us now extend the same picture, to see what it tells us about mechanical degradation. Again, since we have two kinds of bundles, we have two kinds of behaviour: approximating the liquid flow to a wind, *oak-like* and *willow-like*. Energy furnished to a segment in an extended bundle will move along relatively easily, until a 'slug' – a compact bundle – will be encountered. Thus, in extended bundles we essentially have a chain relaxation process (outwardly complicated by flow patterns). By contrast, compact chains, because of the quasirigidity, are more prone to degradation. Just as in necking in solid bodies under tension (see a textbood of meterials science, for instance p 307 in ref 18), fracture takes place at the weakest point. Only here weak points at the first sight appear to be strong ones; they are destroyed since attacks by shearing forces occur repetitively. Hence the comparison to oaks and willows.

We thus conclude that the energy furnished to a polymeric chain in solution goes into at least two processes: degradation and relaxation. There is an analogy here with the behaviour of the chains in solid phases when undergoing fracture. As noted by Andrews[19], the energy furnished during fracture is much higher than the bond fracture energy proper; the excess energy is dissipated in plastic and viscoelastic deformations. Taking into account such energy separation enables a quantitative treatment of the impact transition temperature of solid polymers[20].

We already have a certain overall qualitative picture of drag reduction and mechanical degradation. Let us now make it more detailed, and quantitative at the same time. One way to define the drag reduction, is in terms of the frictional coefficient f, namely[8]:

$$\Lambda = 100\left(1-\frac{f}{f_1}\right) \qquad (4)$$

the quantity without an index refers to solution while that with subscript 1 to pure solvent. Frictional coefficients (friction factors, drag coefficients) for pure liquids and for solutions are discussed by Rodriguez[17], and also in various textbooks of transport phenomena; the coefficients pertaining to forces acting between a polymer molecule and the surrounding solvent have been discussed in particular by Flory[21] and also by Morawetz[22]. Drag reduction clearly depends on a number of factors, including shear stress τ, the molecular mass of polymer M, polymer concentration c (here in g cm^{-3}), nature of solvent and polymer, and temperature T. Because of *MDF*, both Λ and M depend on time t: $\Lambda=\Lambda(t)$ and $M=M(t)$. Throughout this paper we shall take M to be the number average value. Consider a system which is initially monodisperse for simplicity, and introduce parameters characterizing the start of the flow: $\Lambda_0=\Lambda(0)$ and $M_0=M(0)$. At any time thereafter we have lower values of both Λ and M. Since other conditions remain the same, we assume:

$$\frac{\Lambda}{\Lambda_0}=\frac{M}{M_0} \tag{5}$$

We note that equation (5) is not compatible with empirical relations (1) and (3). Apparently researchers who have devised (1) and (3) have considered the time dependence of *DR* and *MDF* separately. However, Hunston and Zakin[12] say that 'At low concentrations the changes in molecular weight can only be followed by measuring changes in drag reduction'. The calculation of M from Λ is based on calibration curves of Λ vs. concentration c for each M. Such curves are given by Zakin and Hunston[23], and will be analysed in some detail in a later paper[24]. A conclusion from this analysis is that equation (5) represents a good approximation.

Above we listed some cases of the advantageous use of the phenomenon of *DR*. It is evident that, in each case, the key question which appears is: how much *DR* will be preserved after a certain time t? Equation (2) tells us that the answer can be formulated in terms of the mass M. We shall, therefore, concentrate now on the evaluation of $M(t)$.

We note that at $t=0$ the number of molecules per unit volume is

$$\frac{N_2}{V}=\frac{cN_A}{M_0} \tag{6}$$

where N_A is the Avogadro number, N_2 the total number of polymer molecules in solution and V is the solution volume. Analogously, at $t=\infty$ we have

$$\frac{N_{2\infty}}{V}=\frac{cN_A}{M_\infty} \tag{7}$$

where M_∞ was defined by equation (2).

On the basis of (6) and (7) we can calculate a_∞, the number of bonds per unit volume broken at $t=\infty$:

$$a_\infty=cN_A\left(\frac{1}{M_\infty}-\frac{1}{M_0}\right) \tag{8}$$

Clearly, at $t=0$ we have a_∞ bonds available for breaking.

For $t\neq\infty$, the number of bonds $a(t)$ broken per unit volume is given by a generalization of (8):

$$a=cN_A\left(\frac{1}{M}-\frac{1}{M_0}\right) \tag{9}$$

At any time t, denote by U_d the energy 'invested' in the flow process into chains in the unit volume which has resulted in degradation. We then have:

$$a=\frac{U_d}{\varepsilon} \tag{10}$$

where ε represents the energy necessary to break one bond (either all such energies are equal or ε represents an average value); thus, $U_d=U_d(t)$. From (9) and (10) we have:

$$M=\frac{M_0}{1+\frac{M_0}{cN_A}\cdot\frac{U_d}{\varepsilon}} \tag{11}$$

Consider now the number of vulnerability points W in a molecule, at which bond breaking will take place if sufficient energy is provided. In terms of the quantities introduced above (cf. equation (6)), we can write:

$$W=\frac{M_0}{cN_A}\cdot\frac{U_\infty}{\varepsilon} \tag{12}$$

where $U_\infty=U_d(\infty)$. As a special case of equation (11) we now have:

$$M_\infty=\frac{M_0}{1+W} \tag{13}$$

Given equations (11)–(13), the problem reduces to constructing the function $U_d(t)$. We note that a part of the energy furnished to polymer chains in one unit volume in flow is *not* used for degradation, but instead goes into relaxation. Of course, stress relaxation of chains is a well-known phenomenon in solid state physics. Further, U_∞ is a time-independent constant for a given system. If we denote the yet unspent part of U_∞ by $U(t)$, we have $U(0)=U_\infty$ while $U(\infty)=0$; at any time:

$$U=U_\infty-U_d \tag{14}$$

Since the amount of energy per unit volume which goes into one of these processes depends on the amount of polymeric material present, we can introduce specific quantities (superscript sp) per 1 g of polymer such as U_∞^{sp}.

It is only reasonable to assume that both degradation and relaxation are first order processes with respect to the energy received. Each of these will have its respective proportionality constant, h or h_r. In the model which we are using[9] the total number of bundles b is the sum of the numbers of bundles of the two kinds:

$$b=b_c+b_e \tag{15}$$

We note that in a more favourable solvent b_e/b is higher[13]. Clearly, compact bundles are the main receivers of the degradational energy U_d, while extended bundles are the main receivers of the relaxational energy U_r. The problem of separation of the input energy into U_d and U_r will be the subject of further work.

There exist factors which we have not yet taken into consideration. Both b_c and b_e change with concentration, but this is a relatively weak dependence. The nature of the solvent determines from the start the b_c/b ratios. Vollmert[25] stresses in his textbook that a given polymer at a given temperature can have hydrodynamic volumes of the chain v_2 differing by a factor of 30, depending on the solvent. Thus, intra- as well as intermolecular interactions play a role. Moreover, a higher value of v_2 results in a larger surface of the chain exposed to degradation, and necessarily we have faster *MDF*. The shear stress τ clearly intervenes too, since the input energy U^{sp} depends on τ as well as on v_2. It is interesting here to refer to polymer degradation by light, as discussed by Rånby and Rabek[26] on the basis of results of their research teams and of their earlier review of the entire field[27]. Rånby and Rabek[26] stress that the energy transfer in photodegradation can be intermolecular as well as intramolecular.

As for entanglements, there seems to be an established opinion that they contribute to degradation. While we do not deny this, a simple analysis of possible angles between two chains at a point of entanglement suggests that energy transfer effect can take place too. Thus, we assume that entanglements contribute *simultaneously* to chain degradation *and* relaxation in flow. Which effect is dominant depends on whether a given chain is more oak-like or willow-like, that is on the fraction of compact bundles b_c/b.

To see better why statement of the kind 'degradation is produced by entanglements' are one-sided at best, consider a case of behaviour of solid polymers: stress–strain characteristics in gaseous environments at low temperatures. One is inclined to expect that, along with concomitant occurrence of crazing, the materials will be weakened by the environment. In a number of cases, however, an *increase* in the tensile strength has been reported by Brown and his school[28–31]. The phenomenon has been explained by Brown[29] in terms of blunting the points of stress concentration by gases from the environment. We have here a good example of caveats involved in polymer behaviour, and of the necessity of multi-facet approaches to explain it.

On the basis of the above discussion, we write:

$$\frac{\mathrm{d}U}{\mathrm{d}t} = -hU \qquad (16)$$

By integrating (16) we obtain:

$$U = U_{\infty} e^{-ht} \qquad (17)$$

By a simple substitution of (17) into (16) we get:

$$\frac{\mathrm{d}U}{\mathrm{d}t} = -hU_{\infty} e^{-ht} \qquad (18)$$

On the other hand, by differentiating (14) we have:

$$\frac{\mathrm{d}U}{\mathrm{d}t} = \frac{-\mathrm{d}U_d}{\mathrm{d}t} \qquad (19)$$

Comparing (18) and (19) and performing integrations we arrive at:

$$U_d = U_{\infty}(1 - e^{-ht}) \qquad (20)$$

By using (12) and (20), equation (11) becomes:

$$M = \frac{M_0}{1 + W(1 - e^{-ht})} \qquad (21)$$

Equation (21) represents the desired relation between the extent of mechanical degradation and flow time.

The result (21) can be substituted into (5):

$$\frac{\Lambda}{\Lambda_0} = [1 + W(1 - e^{-ht})]^{-1} \qquad (22)$$

Let us discuss the relations just derived. Equation (22) expresses the change of *DR* with time in terms of *MDF*. One should distinguish here between two aspects of degradation: its final result expressed by the value of M_{∞}; and its velocity as expressed by the degradation rate h. The lack of this distinction (talking about 'stronger degradation') has led to some apparent contradictions in the literature on *MDF*.

To predict the M_{∞} behaviour, consider the specific input energy U^{sp}_{∞}. Polymer concentration has a role here, since it affects the b_c/b ratio. The dependence is not very pronounced, however, and in fact quite weak in good solvents[13]. Thus, the value of U^{sp}_{∞} depends mainly on the shearing stress τ. As noted elsewhere[9], the assumption that all bundles are of equal length is another idealization; in reality we have a distribution of the number of segments in a bundle around an average value r_b. Now let us take a compact bundle with r'_b segments which under a given stress τ is still small and willow-like enough to avoid degradation, while a bundle containing $r'_b + 1$ segments degrades. In other words, U^{sp}_{∞} goes symbatically with τ. Equations (12) and (22) then tell us that an increase of τ leads to a lower nondegradable molecular weight M_{∞}.

Consider now the parameter h, which plays the role of a rate constant in equations (21) and (22). Since more exposure of a chain surface produces faster degradation, h goes symbatically with the volume v_2 pervaded by each chain. We have[9,13]:

$$v_2 = bv_c\left[\gamma - (\gamma - 1)\frac{b_c}{b}\right] \qquad (23)$$

Here v_c is the volume of a compact bundle; with the volume of an extended bundle denoted by v_e we have $\gamma = v_e/v_c$. An increase of the polymer concentration produces an increase of b_c/b.[13] Then, according to equation (23) the pervaded volume decreases. The rate parameter h decreases also, and we have slower degradation in more concentrated solutions. There is an opposite contribution of more oak-like segments (more degradation prone, higher b_c/b), but apparently in most cases the first of the effects just described is the dominant one.

NUMERICAL CALCULATIONS

Experimental data on *DR* and *MDF* obtained by Hunston, Zakin and their colleagues stand out by their quality. We have applied the equations to Λ/Λ_0 data for polystyrene in toluene obtained by Hunston and Zakin[12]. Their initial molecular weights $\bar{M}_w \cdot 10^{-6}$ were 7.1, 4.1 and 2.4. Of course, the original *DR* as well as the extent of *MDF* were highest for the highest value of M. Therefore, we have used their data for initial $\bar{M}_w = 7.1 \cdot 10^6$ and for two different concentrations, 1000 ppm and 100 ppm.

Höcker and Flory[32] have calculated the value of the energy exchange parameter X_{12} for ethylbenzene + polystyrene mixtures from experimental enthalpy of dilution data. They have obtained $X_{12} = 8.8\ \mathrm{J\,cm^{-3}}$, and this value is probably not far from that for toluene + polystyrene mixtures. Thus, an assessment of X_{12} for the latter system is possible. Substitution of X_{12} into equations in ref 9, plus evaluation of the remaining parameters, would then lead to a value of b_c/b. Since the result would be only approximate, we have not followed this route. The value of M_∞ in experiments of Hunston and Zakin[12] is $1\cdot10^6$. From equation (13) we thus obtain the number of vulnerability points $W = 6$; we note that W is an integer by definition.

So as to use equation (22), we need a relation between the rate constant h and polymer concentration c. h is proportional to the volume v_2 pervaded by one polymeric chain. For simplicity we assume:

$$h = h'v_2 \tag{24}$$

where h' is a proportionality constant and v_2 is given by equation (23). As found in ref 13, the dependence of b_c/b on concentration depends on interactions in solution and the interchange energy parameter X_{12}, but a good approximation of v_2 is obtained from the Rudin[33,34] relation. The latter reads:

$$\alpha^3 = \frac{\varepsilon_0}{1 + \dfrac{\varepsilon_0 - 1}{c_\theta}\cdot c} \tag{25}$$

where α is the Flory expansion factor[21], ε_0 a constant and c_θ the polymer concentration at the θ point (Rudin's ε_0 has of course nothing to do with our ε). Denoting the unswollen volume of a polymer molecule by v_0, we can write:

$$v_2 = v_0\alpha^3 \tag{26}$$

Then from (24) we obtain:

$$h = \frac{1}{h_0 + h_1 c} \tag{27}$$

where clearly $h_0 = (v_0\varepsilon_0 h')^{-1}$ and $h_1 = (\varepsilon_0 - 1)/(v_0\varepsilon_0 c_\theta h')$.

We remember that (26) in conjunction with (25) represents only an approximation to (23), and (24) is an independent assumption. Thus, more extensive testing by experimentalists of (27) for various polymer + solvent systems appears worthwhile.

To perform the computations, we have simply substituted (27) into (22):

$$\frac{\Lambda}{\Lambda_0} = [1 + W(1 - e^{-t/h_0 + h_1 c})] \tag{28}$$

Equation (28) embraces the assumptions made earlier. We note that with two parameters we have dependence on both time and concentration of the *DR* decay, and the same applies also (see equation (21)) to the extent of *MDF*.

We have used the experimental Λ/Λ_0 values of Hunston and Zakin and solved an overdetermined system of equations (28) in two unknowns, h_0 and h_1. Since the concentrations differ by a factor of 10, we have simply assumed in one series of calculations $c = 10$ and in the other $c = 1$. With sime in s, this leads to the values of $h_0 = 119.35$ and $h_1 = 34.59$, with the residual variance $2.8\cdot10^{-8}$. Since the experimental data have been provided with three significant figures only (that is within $1\cdot10^{-3}$) the agreement between calculated and experimental values is perfect. The results are shown in *Figure 1*. The broken horizontal line represents Λ/Λ_0 corresponding to M_∞.

It should be noted that the existence of a common value of M_∞ independent of concentration represents another approximation. It is reasonable in favourable solvents, in which the dependence of b_c/b on c is a weak one[13]. For poor solvents we predict measurable changes of M_∞ with polymer concentration.

DISCUSSION

We now return to the list of experimental findings to review them in terms of our model. The conclusion (a) hardly requires further discussion: the longer the polymeric chain, the more drag reduction it produces. The finding (b) is easily understandable too: in a poor solvent the volume pervaded by the polymeric chain is relatively small, and this directly affects the drag reduction capability.

As for the finding (c), the reason why the parameter R is not a true rate constant can be seen by comparing equations (1) and (22). Of course, until the appearance of relations developed in the present work, equation (1) did represent a reasonable estimate.

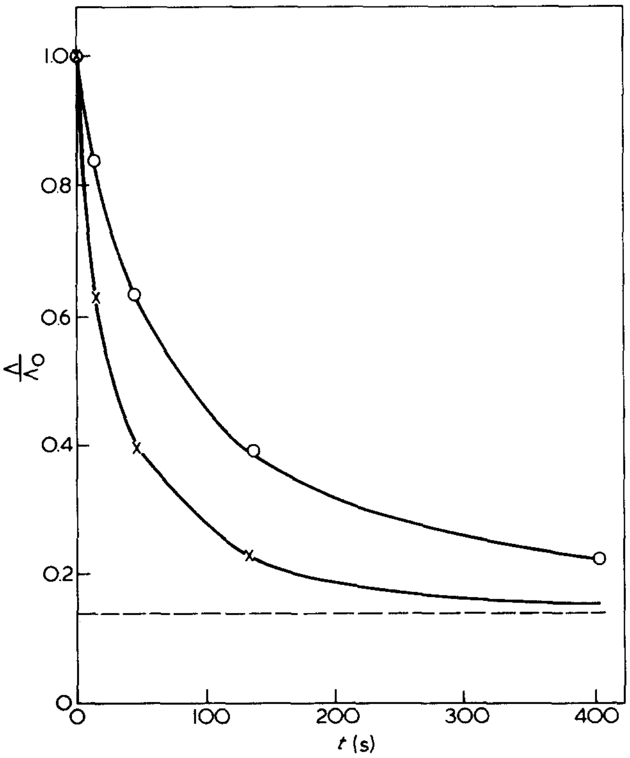

Figure 1 Relative drag reduction Λ/Λ_0 in function of time t for polystyrene + toluene solutions with initial molecular weight $\bar{M}_w = 7.1\cdot10^6$. Circles represent experimental values of Hunston and Zakin[12] for polymer concentration of 1000 ppm and crosses their data for 100 ppm. Continuous lines represent values calculated with equation (28). The horizontal broken line represents M_∞ for both concentrations

Consider now the conclusion (d). Calculations reported in ref 13 show that in a less favourable solvent the b_c/b ratio is higher. This means we have relatively more oak-like or degradation prone segments, as compared with willow-like segments which are more resistant to *MDF*. Other conditions being equal, if the interchange energy parameter X_{12} is higher then more degradation will take place. Ballauff and Wolf[35] have reported that the degradation of polystyrene at what they call moderate shear rates takes only place in a theta solvent (*trans*-decalin), while no chain scission has been detected in toluene under the same conditions. Since toluene is highly favourable and a very good solvent, the results of Ballauff and Wolf contribute one more element to our consistent picture.

More oak-like bundles (that is, a higher value of b_c/b) lead to a higher value of W-Equation (13) then tells us that this produces a lower value of M_∞. Also, from equations (12) and (13) follows another route for decreasing M_∞: increasing U^{sp}_∞ (that is U_∞) by increasing the shear stress τ. Incidentally, commenting on what we have labelled as conclusion (d), Hunston and Zakin[12] have said that 'This ... is somewhat surprising since a hydrodynamic force argument would suggest that the reverse should be true'. A similar comment has been made by Harrington and Zimm[36], but these authors have said also: 'It is possible that the chemical nature of the solvent is important here'. We have already noted the opinion of Berman[8,16] on the role of molecular interactions. Precisely, quantitative seizure of the interactions and of the solvent role has been our leitmotif.

Analyse now the conclusion (e). Kotliar[37] has applied the Monte Carlo approach to chain scission in a polydisperse system. He has found the most probable value $M_w/M_n = 2$ for random scission. Since the respective experimental value[11] is approximately 1.5, the process is definitely not random. Bueche[38] starting from the assumption of a freely-jointed chain has arrived at the conclusion that the midpoint breaking is strongly preferred. Yu, Zakin and Patterson[11] have found that Bueche's predictions are not, in general, confirmed by experiment. Bueche predicts[38] that $M_0/M_\infty = 2^n$ where n is an integer; in calculation reported in the preceding section we have obtained perfect fit with $M_0/M_\infty = 7$. A certain preference for scission in the middle part of the chain (not exactly at the midpoint) has been found experimentally[11]. Moreover, Ballauff and Wolf[39] have developed a formal general solution of the degradation rate equations, and it turns out[40] that experimental results can be described by assuming that the probability of a chain scission is Gaussian about the midpoint of the chain. The problem merits further study, particularly since Webman, Lebowitz and Kalos[41] have found by computer simulation of a polymer chain that the response to a strong external stretching force is nonlinear, consistent with a non-Gaussian nature of the end-to-end vector. The preference for scission in the middle part of the chain can be explained in terms of sequences of compact and extended bundles in a polymeric chain, such as, in obvious notation, the sequence (8) in[13]:

$$\text{eeeceeecceccccecccceecceeceee} \tag{29}$$

We see in the above sequence that the input energy can be better dissipated in a relaxational way if we are closer to chain ends. Another possibility compatible with the model developed in refs 9 and 13 is the sequence (7) in ref 13:

$$\text{eecceeecceeccceeccceeecceecce} \tag{30}$$

In either case, in experiment as well as in our model, indeed the bond cleavage neither occurs at random nor does it take place only at the midpoint of the chain. The cleavage depends on the number and distribution of compact bundles in the chain.

The experimental finding (f) is an interesting one. To see the dependence (or otherwise) of M_∞ on M_0, consider a numerical example. Assume $W = 9$. From equation (13), displaying four significant digits, we then have $M_\infty = 0.1000\ M_0$. From equation (12), with $U^{sp}_\infty = U_\infty/c$, we obtain $U^{sp}_\infty/(\mathrm{N_A}\varepsilon) = 9/M_0$. Now take longer chains of the same polymer with, say, $M'_0 = 3M_0$. We preserve the same concentration c in g cm^{-3}. Since we have the same kind of polymer in the same solvent, the parameter $U^{sp}_\infty/(N_A\varepsilon)$ remains constant in going from M_0 to M'_0. The new value of W, call it for consequence W', computed from equation (12) is 27. We have concluded[13] that an increase of M produces a proportional increase of b, b_c, b_e and all $N_{yy'}$, so that b_c/b remains the same. As a consequence of this, there is also a simple proportionality between M_0 and W. Substituting W' into equation (13) we obtain $M'_\infty = 0.1071\ M_0 \neq 0.1000\ M_0$. We thus conclude that, for a given kind of polymeric material in a given solvent, the value of M_∞ *does* depend on M_0. The dependence is weak, however, and apparently not even noticeable unless experiments are made with a precision higher than that presently prevailing.

The conclusion (g) is easily explicable in terms of our approach. Thermodynamics of intermolecular interactions and not viscosity is decisive for the degradation.

As for the conclusion (h), our point of view is different from that of the earlier authors, who consider entanglements only as a hindrance to flow and a factor contributing to degradation. For instance, Bueche[38] says that '... it is necessary that the molecules disentangle from each other in order for flow to occur'. Thus, Bueche has disregarded the possibility of two (or several) entangled molecules flowing together. Our point of view on this has been stated previously: in addition to the roles of entanglements treated by earlier authors, the role of energy transfer via entanglements has to be taken into account.

Given the dual role of entanglements, the immediate question is: which of the two effects is larger? Let us assume temporarily that the earlier authors who have observed only the destructive role of entanglements are right in the sense that this role is predominant. Then the degradation rate h should increase when the polymer concentration c increases. The experiments, however, tell us that the inverse is true; see equation (27). Therefore, the entantlements do *not* play a dominant role in the degradation mechanism – an important fact pointed out by Hunston and Zakin[12], listed here as (h) in the second section. A related point has been raised by Müller and Klein[42] – see below. We conclude that earlier authors had largely exaggerated the role of entanglements in the behaviour of polymer solutions in flow. It is very interesting to refer here to the molecular theory of elasticity of polymer networks developed by Flory[43,44]. This theory has now been amply confirmed by experiments[45,46]. With respect to entanglements, the conclusion from the Flory theory is that in earlier approaches the contribution of entanglements to measurable quantities had been grossly exaggerated. In networks this contribution is considerable only at low extension ratios[43,44]. As for the flow situation, experiments indicate that the extension ratios are high.

The conclusion (i) can be related to equation (24) in conjunction with (23). Still simpler, (i) can be related to the approximate formula (27). The fact that in some cases the degradation rate appears independent of polymer concentration can also be explained we have a competition between the two effects discussed in the third section.

As for the conclusion (j), to see why the parameter R' is not a true rate constant we can compare equation (3) with (21) and (13). Again, before the advent of a more fundamental approach relation (3) was certainly a plausible one.

Our list of conclusions (a)–(j) has been extracted from the work of Zakin, Hunston, Patterson *et al.*[10–12] This has provided a certain consistency in our analysis of the body of experimental findings. Other experimentalists, however, have also obtained highly useful results. In 1959 Rodriguez and Winding[47] established that *MDF* decreases with increasing *T*. The same conclusion has been reached by Porter and collaborators[48,49]. This fits perfectly the present approach. As noted in ref 13, a temperature increase produces a decrease of the interchange energy parameter X_{12}. Thus, we have a more favourable solvent, smaller b_c/b, and less mechanical degradation in flow.

After the main lines of the work described in this paper had been developed, Müller and Klein[42,50–52] reported detailed investigations of *MDF* of poly(decylmethacrylate) in tetrahydrofuran. They describe the degradation kinetics in terms of concentrations rather than molecular masses; the relation between the two approaches has yet to be studied. In other aspects, the results of Müller and Klein provide remarkable experimental confirmation of the ideas developed in the present paper. Throughout this paper and the related studies of conformations[9,13] we have been stressing the role of the solvent and of the intermolecular interactions. Discussing *MDF*, Müller, Klein and Rottloff[52] declare that '... spielt die thermodynamische Güte des Lösungmittels bezüglich des Polymeren eine wesentliche Rolle'. Further, in contrast to earlier ideas of midpoint or random breakage, we have the notion of the number of vulnerability points *W*. Müller and Klein[51] concluded from their experiments that the poly(decylmethacrylate) molecules break into four pieces; that is, in their case $W = 3$.

As an extension of the work just mentioned, Müller and Klein[41] have studied *MDF* of polyisobutylene, polystyrene, poly(vinyl chloride), poly(methyl methacrylate), poly(methyl acrylate) and 1,4-polybutadiene in tetrahydrofuran. They have found that the degradation rate constants increase with decreasing solvating power of the solvent. Discussing this, the authors say: 'Explanations from literature ... are based on the concept of entanglements. Use of these explanations here seems to be doubtful, since the concentrations are far below the critical concentrations for entanglements'. Müller and Klein provide another explanation which they admit is speculative[42]; Müller now says[53] that the explanation provided in the present work is much more convincing. Another conclusion of the same authors from their experiments[42] is that at the moment of chain rupture the polymer molecule is *not* totally extended. This fits perfectly with our model of coexisting compact and extended parts of the chain.

One more important contribution of Klein and his collaborators[50–52] is the study of dependence of their rate constant on the hydrodynamic volume, our v_2. They have used the same ideas of Rudin[33,34] which we have already studied elsewhere[13], as well as reconsidered in this paper. Müller and Klein have demonstrated experimentally the connection between v_2 and the degradation kinetics. This confirms another element in our picture of the behaviour of polymer-containing liquid phases.

Throughout this paper, we have tacitly assumed that the polymer solutions are above their respective θ temperatures. This has been done mainly for convenience, to simplify our considerations. To have a complete picture, however, let us now deal with solutions below the θ point.

The entire polymeric chain now acquires the compact configuration[9,13], except for the complications produced by entanglements. As discussed above, for situations at $T > \theta$ the entanglements play a minor role in degradation, if any. Now there is a difference: an increase in polymer concentration c at a $T < \theta$ *cannot* make the chain any more compact, and therefore any smaller. In general entanglements can contribute to both degradation and relaxation of the chains. At $(b_c/b) = 1$, however, all polymer chains are oak-like, and entanglements become purely destructional, contributing to degradation only. An *increase* in polymer concentration produces more entanglements. Therefore, higher c produces now an increase of the degradation rate. This conclusion from our model already has a confirmation in experimental facts: precisely this has been reported by Breitenbach, Rigler and Wolf[54] for *MDF* of polystyrene in cyclohexane solutions below the θ temperature.

A leitmotif of this work and of papers quoted above[9,13] is the existence of differences in rigidity (or flexibility) between parts of the same polymeric chain. An interesting experimental study of such partial rigidity had been conducted by Doddi, Forsman and Price[55] for poly (tert-butylethylene oxide) in solutions of xylene and *o*-dichlorobenzene. They have found by osmometry, viscometry and light scattering the existence of rigid helical block conformations, with the structure the same as found by Price and Fukutani[56] by n.m.r. and X-ray diffractometry in the solid state. The rigid blocks in solution are intercalated[57] with less rigid parts of the same chains.

SOME CONCLUDING REMARKS

Apparently, earlier approaches provide explanations for some of the aspects of *DR* and *MDF*, but then lead to predictions contrary to experimental facts for some other aspects. By contrast, our model seems to be capable of dealing with the totality of the phenomena involved.

By applying the approach developed in ref 9, we have explained a number of experimental findings, including those labelled as puzzling and contrary to expectations. We have also made predictions that have yet to be tested experimentally – see for instance point (f) in the preceding Section. At the same time there is, for example, more to the quantity *h* than we have discussed in this paper. Thus, more work has to be done, both theoretically and experimentally. The pursuit of further ramifications of the present approach depends in part on the availability of sufficiently extensive and accurate experimental data.

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