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Hydrodynamic shielding induced stability of zipping macromolecules in elongational flows

U. S. Agarwal and R. A. Mashelkar^{a)}

National Chemical Laboratory, Pune 411008, India

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Enhanced shear stability of associating polymers during drag reduction observed recently has been attributed to the breakage of reversible associations (e.g., hydrogen bonds) in preference to covalent bonds in the polymer backbone. A simple mechanistic analysis of a perfectly “zipped” assembly of fully extended bead rod chain model of two macromolecules in steady elongational flow is presented. It explains the enhanced stability as a result of (i) distribution (near the vulnerable chain center) of the drag tension into the two parallel “zipped” chains, and (ii) reduction of the drag force due to the enhanced hydrodynamic shielding. Some guidelines for optimum design of shear stable and effective drag reducing macromolecules have been deduced.

I. INTRODUCTION

Long chain polymers find application as flow modifying additives,¹ e.g., for drag reduction during turbulent flows,^{2–4} reducing friction in lubricating oils,⁵ etc. Since the performance of these additives depends on their high molecular weights, their degradation under the intense flow situations encountered may limit their utility. Extensive research has been undertaken in the past to devise shear stable polymeric systems, which will resist such degradation. It has been shown that the shear stability of polymers increases if they are capable of forming interpolymer^{2,3,6–10} or intrapolymer¹¹ associations via secondary interactions. These may be electrostatic, hydrogen bonding, or hydrophobic interactions. The increased shear stability has been attributed to the reversible breakage of secondary bonds in preference to the cleavage of polymer backbone.^{2,3,6,7,10} It is generally believed that these secondary bonds are formed again in regions of lower shear, offering themselves again for sacrifice in the intense flow zones, and are thus responsible for retaining the polymer efficiency. However, we can demonstrate that these arguments are not valid.

Let us consider the interpolymer associations between linear chains.^{6–10} During flow, the reversible bonds between chains are formed in the regions of low deformation rates, at *random* active sites along the chains. As depicted in Fig. 1, the structures so formed would be akin to irregularly branched or graft polymers. Our recent analysis¹² has shown that such branching or grafting can only increase the frictional drag tension at the backbone center and thereby enhance the degradation rate as compared to that in the individual molecules. Such enhanced degradation will be avoided only if the secondary bonds between two given chains would break in preference to the backbone—as has been proposed.⁶ Even then, it is clear that the individual molecules so freed cannot have a higher shear stability as compared to the component polymers. In other words, shear stability of the intermolecular association complex will be limited by the shear stability of the precursor chains. Yet, their experimental observation⁶ is that an associating C-8

ester-acid polymer is more stable than a nonassociating C-8 ester polymer of the same molecular weight. Similarly, Malik and Mashelkar¹⁰ found that a hydrogen bonded interpolymer association complex of a proton donating polymer and a proton accepting polymer is more shear stable than the constituent proton accepting polymer. The contradiction is thus clear.

Let us also analyze the mechanism that was proposed to explain the higher stability of the sodium salt of poly(acrylic acid) (PAA) observed by Ting and Little.¹¹ The intrapolymer association between neighboring COONa groups leads to the formation of a ladder like structure where a “new” $[\cdots\text{O}-\text{C}-\text{O}\cdots\text{Na}\cdots\text{O}-\text{C}-\text{O}\cdots\text{Na}\cdots]$ chain runs parallel with the “original” $[-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-]\cdots$ chain of PAA. Ting and Little¹¹ argued that the enhanced stability was due to preferential breaking and later (in regions of low shear) reformation of the associative bonds (shown as \cdots in the “new” chain structure above). However, again it is clear that once the “new” chain is broken, the entire tension being borne by it at that point is immediately transferred to the “original” chain, making it as vulnerable as the linear PAA structure. Thus, the proposed associative bond breaking-reformation process does not appear to be the appropriate mechanism.

Here we present an alternative mechanism for the higher shear stability of the ladderlike structures, e.g., of the kind investigated by Ting and Little.¹¹ As such structures are also formed in interpolymer complexes under intense flow conditions by an extremely rapid “zipping up” action,¹³ the mechanism proposed here would also explain their higher shear stability as compared to the precursor linear molecules. We propose strategies for optimum design of such molecular systems. Since the process of bond breaking—reformation is not a necessary requisite for this mechanism, we argue that associative bonding is not essential and permanent covalent bonds resulting in similar structures would perform equally well, if not better.

We first briefly review the current theories for shear induced scission of linear macromolecules. In Sec. III, we present a methodology to examine stress development in fully extended linear bead-rod chain in elongational flows, in presence of hydrodynamic shielding. In Sec. IV, we use

^{a)} Author to whom all correspondence should be addressed.

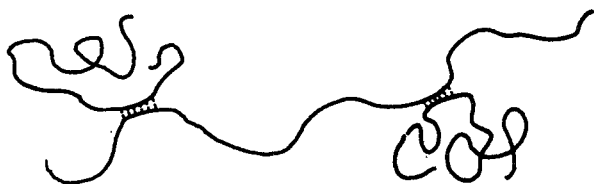


FIG. 1. Typical structure formed by reversible bonding between chains at random active sites along the chains.

this to analyze the following structures for their shear stability (i) a simple linear molecule, and a complex molecule consisting of two bead rod chains of (ii) equal and (iii) unequal lengths, extended and running parallel to each other. By consideration of such systems of different chain lengths, the optimum structure which provides the maximum shear stability and drag reduction efficiency are arrived at. Our conclusions are summarized in Sec. V.

II. FRACTURE OF STRETCHED LINEAR CHAIN MOLECULE

Frenkel¹⁴ considered a polymer molecule under flow to be straightened out in the direction of the flow with the chain ends curled up. He concluded that hydrodynamic forces on long chain polymers may be sufficient to break the covalent bonds, and the most probable place for a chain to break is at its center. Bueche¹⁵ arrived at the same result by calculating the force required to pull a chain segment through the many entanglements of the chain in a polymer melt under shear flow. Levinthal and Davidson¹⁶ calculated the maximum force experienced by a long thin rodlike molecule during laminar flow through a tube. For flow of DNA molecules, they found agreement between their experimental results and the predictions of the critical flow rate below which the molecules are not affected. The group of Zimm^{17,18} also predicted and experimentally verified breaking of the molecules in half. Odell and Keller¹⁹ presented a simple analysis for fracture of an isolated, bead-rod chain model polymer molecule. They considered a steady elongational flow of strength ($\dot{\epsilon}$) greater than a critical value ($\dot{\epsilon}_c \sim \tau^{-1}$, where τ is the longest relaxation time of the chain molecule), when the chain is fully extended.^{20,21} They concluded that tension is maximum in the central bonds of a chain, and is given for a chain of ($n = 2N_1 + 1$) beads (Fig. 2) by

$$T_{(c)}^0 K = \zeta b \dot{\epsilon} N_1^2 / 2, \quad (1a)$$

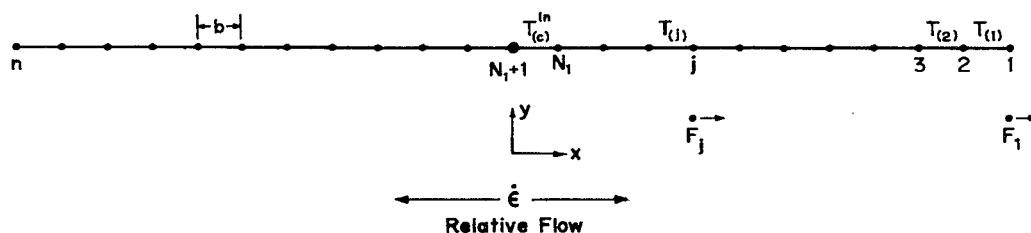


FIG. 2. Bead-rod model for fully extended linear chain in elongational flow Ref. 19.

where $\zeta = 6\pi\eta a$ is the Stoke's friction factor of the bead, η being the solvent viscosity and a the bead radius. b is the separation between adjacent bead centers. If this force exceeds the bond strength T_f , then chain scission at the central rods would occur. Many experimental studies of shear degradation of nearly monodisperse polymers during a variety of flows^{19,22-30} confirm the backbone scission at the chain center. Further, in stagnant elongational flows, the minimum elongation rate required for fracture of a given polymer is found to vary as inverse square of the molecular weight [$\dot{\epsilon}_f \sim n^{-2}$, Eq. (1a)].^{19,22}

Considering incomplete extension of the chains in transient elongational flows, Rabin³¹ used Ryskin's yo-yo model,³² to obtain the following scaling law:

$$\dot{\epsilon}_f \sim n^{-1.1} \quad (1b)$$

in agreement with transient flow experiments of Merrill³³ and Nguyen and Kausch.^{27,28} Odell *et al.*²² presented a comprehensive analysis of the reported experiments, and suggested that the contrast with his theory was due to the flow modifying effect (e.g., reduction in the turbulence) of the added polymer. Rabin³¹ also predicted that higher strain rates would be required for scission during transient flows, and that the scission would be less precisely central. Some studies show fracture products broadly distributed in size.^{27,34,35} Reese and Zimm³⁶ recently attributed this to the existence of folds in the flexible molecules due to incomplete extension of the molecules under transient extensional flow. Thus, even as the overall molecular axis gets aligned along the flow, the points of maximum stress are not at the molecular centers. Further, Nguyen and Kausch²⁷ suggested that the rate of chain scission may be controlled by the free energy stored in the deformed molecules, rather than by the frictional hydrodynamic forces.

Thus, the mechanism of chain scission seems to be dependent on the flow situation. The experimental results that we cite in this paper are based on turbulent flows (drag reduction). Here, though polymer molecules experience significant extensional flow, the chain extension is perhaps far from complete, and the actual flow situation is very complex.^{4,27,38} For simplicity, in this work we carry out a theoretical analysis of stresses on fully extended bead-rod molecules in steady elongational flows. We expect that the results would be valid even for turbulent flows qualitatively, in respect of our central physical idea here that the shear stability of polymers can be enhanced by employing struc-

tures that reduce the drag force contribution to the otherwise most vulnerable backbone center.

III. EFFECT OF HYDRODYNAMIC INTERACTION BETWEEN BEADS

As in Odell and Keller,¹⁹ we consider the molecule to be completely stretched in the elongational flow field

$$\mathbf{V}^u = \dot{\epsilon} \times \hat{\mathbf{e}}_x, \quad (2)$$

where $\hat{\mathbf{e}}_x$ is the unit vector along the x -axis, i.e., the molecular axis. The Stoke's viscous stresses on the i th bead at \mathbf{r}_i is given as

$$\mathbf{F}_i = \zeta \mathbf{V}(\mathbf{r}_i) \quad i = 1, 2, \dots, n. \quad (3)$$

Here $\mathbf{V}(\mathbf{r}_i)$ is the fluid relative velocity experienced by the i th bead. While Odell and Keller¹⁹ assumed $\mathbf{V} = \mathbf{V}^u$ (i.e., the velocity field is unaffected by the presence of the beads), we consider that the velocity field at any position \mathbf{r}_i is changed³⁸ due to presence of the j th beads by an amount $\Delta \mathbf{V}_i$ given by

$$\mathbf{V}_i = \mathbf{V}_i^u + \Delta \mathbf{V}_i, \quad (4)$$

$$\Delta \mathbf{V}_i = - \sum_{j \neq i} \Omega_{ij} \cdot \mathbf{F}_j, \quad (5)$$

where $\Omega_{ij} = (1/8\pi\eta r_{ij})(\mathbf{I} + \hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij})$ is the Oseen tensor, \mathbf{I} is the identity tensor, $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$ is the separation between the i and j th beads, and $\hat{\mathbf{r}} = (\mathbf{r}_j - \mathbf{r}_i)/r_{ij}$ is the unit vector along $(\mathbf{r}_j - \mathbf{r}_i)$. Since \mathbf{F}_j are not known *a priori* [Eqs. (3)–(5)], a set of simultaneous equations is obtained as follows. Combining Eqs. (2)–(5), we get

$$\mathbf{F}_i = \zeta \dot{\epsilon} x_i \hat{\mathbf{e}}_x - \frac{3}{4} \sum_{j \neq i} \frac{a}{r_{ij}} [\mathbf{F}_j + (\mathbf{F}_j \cdot \hat{\mathbf{r}}_{ij}) \hat{\mathbf{r}}_{ij}]. \quad (6)$$

Substituting

$$\hat{\mathbf{r}}_{ij} = \frac{1}{r_{ij}} [(x_j - x_i)\hat{\mathbf{e}}_x + (y_j - y_i)\hat{\mathbf{e}}_y] \quad (7)$$

with

$$r_{ij}^2 = (x_j - x_i)^2 + (y_j - y_i)^2, \quad (8)$$

and introducing dimensionless parameters by dividing distances by b , and drag forces and tensions by $(\zeta \dot{\epsilon} b)$, and denoting these as $\bar{\mathbf{r}}$, $\bar{\mathbf{F}}$, and \bar{T} , we separate x and y components of Eq. (6) to get

$$\begin{aligned} \bar{F}_i^x = \bar{x}_i - \frac{3a}{4b} \sum_{j \neq i} \frac{1}{\bar{r}_{ij}} [\bar{F}_j^x + (\bar{F}_j^x \cos \theta_{ij} \\ + \bar{F}_j^y \sin \theta_{ij}) \cos \theta_{ij}], \end{aligned} \quad (9a)$$

$$\begin{aligned} \bar{F}_i^y = -\frac{3a}{4b} \sum_{j \neq i} \frac{1}{\bar{r}_{ij}} [\bar{F}_j^y + (\bar{F}_j^x \cos \theta_{ij} \\ + \bar{F}_j^y \sin \theta_{ij}) \sin \theta_{ij}], \end{aligned} \quad (9b)$$

where

$$\cos \theta_{ij} = (\bar{x}_j - \bar{x}_i)/\bar{r}_{ij}, \quad (10a)$$

$$\sin \theta_{ij} = (\bar{y}_j - \bar{y}_i)/\bar{r}_{ij}. \quad (10b)$$

Equations (9) are written in the matrix form as

$$[\mathbf{A}]\{\bar{\mathbf{F}}\} = \{\mathbf{p}\}, \quad (11)$$

where

$$\{\bar{\mathbf{F}}\}^T = \{\bar{F}_1^x, \bar{F}_1^y, \bar{F}_2^x, \bar{F}_2^y, \bar{F}_3^x, \bar{F}_3^y, \dots, \bar{F}_n^x, \bar{F}_n^y\}, \quad (12)$$

$$\{\mathbf{p}\}^T = -\{\bar{x}_1, 0, \bar{x}_2, 0, \bar{x}_3, 0, \dots, \bar{x}_n, 0\} \quad (13)$$

for $i \neq j$,

$$A(2i-1, 2j-1) = \frac{3a}{4b} \frac{1}{\bar{r}_{ij}} [1 + \cos^2 \theta_{ij}],$$

$$A(2i, 2j-1) = \frac{3a}{4b} \frac{1}{\bar{r}_{ij}} \sin \theta_{ij} \cos \theta_{ij},$$

$$A(2i-1, 2j) = \frac{3a}{4b} \frac{1}{\bar{r}_{ij}} \sin \theta_{ij} \cos \theta_{ij},$$

$$A(2i, 2j) = \frac{3a}{4b} \frac{1}{\bar{r}_{ij}} [1 + \sin^2 \theta_{ij}],$$

and for $i = j$,

$$A(2i-1, 2i-1) = 1,$$

$$A(2i, 2j-1) = 0,$$

$$A(2i-1, 2j) = 0, \quad (14)$$

$$A(2i, 2j) = 1.$$

Numerical solution of Eq. (11) yields the required force components \bar{F}_i^x and \bar{F}_i^y . For the given flow field, \bar{F}_i^y are an order of magnitude smaller than \bar{F}_i^x . For the symmetric molecules considered here, our interest is confined to tension in the rods along x -axis, i.e., \bar{F}_i^x alone.

IV. RESULTS AND DISCUSSION

A. Linear chain

We first consider the fully extended linear chain of $(2N_1 + 1)$ beads (Fig. 2). On incorporating the hydrodynamic interactions, the dimensionless parameters of the system are (a/b) and N_1 . The computing of tension $\bar{T}_{(j)}$ in the desired rod (j) is straightforward

$$\bar{T}_{(j)} = \left| \sum_1^j \bar{F}_i^x \right| = \left| \sum_{j+1}^n \bar{F}_i^x \right|. \quad (15)$$

Clearly, the tension is maximum in the central rods $[\bar{T}_{(c)}^{\text{ln}}]$. Our results for this are plotted (Fig. 3) as the shielding factor, defined as $S_1 = \bar{T}_{(c)}^{\text{ln}}/\bar{T}_{(c)}^{0K}$, which is representative of the extent to which the drag force experienced by the chain beads is reduced by presence of other beads of the chain. Thus, $S_1 = 1$ corresponds to the Rouse limit³⁹ examined by Odell and Keller.¹⁹ We find that for a given N_1 , the extent of shielding $(1 - S_1)$ is more for larger beads (Fig. 3). The Rouse limit thus overestimates the stress even in the completely stretched state of the molecule considered here. This has implication in calculation of the stretch-coil transition where the relevant relaxation time has been taken as the

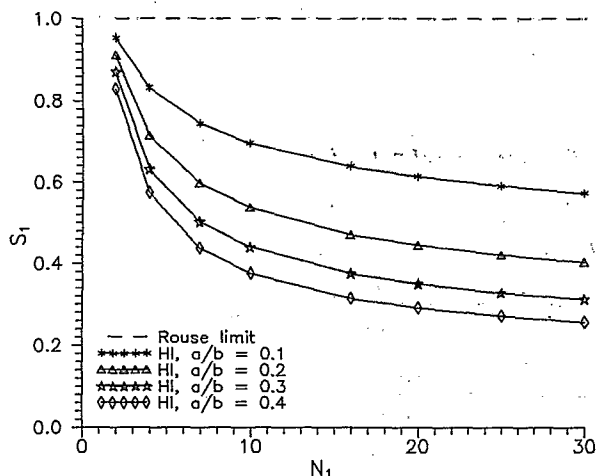


FIG. 3. Dependence of the hydrodynamic shielding factor for fully extended linear chain, on the chain length and (a/b) .

Rouse relaxation time.²¹ Further, we find from Fig. 3 that with increase in N_1 , the extent of shielding increases continuously. No limiting value of S_1 is reached because the hydrodynamic interaction between beads i and j decreases only as $1/r_{ij}$, and the series $\sum_j 1/j$ in Eq. (9) is divergent. However, with increase in N_1 , the dependence of S_1 on N_1 becomes small, indicating that $\bar{T}_{(c)}^{\text{ln}} \sim (N_1)^2$ is approached even when the hydrodynamic interactions are considered. The situation is analogous to that encountered in the classical treatments of rigid rodlike and wormlike chains.^{40,41}

B. Perfect ladderlike polymer

Here we model a ladderlike polymer in elongational flow as being made up of two fully stretched bead-rod chains of equal lengths ($2N_1 + 1$ beads each), arranged parallel to each other, and connected through many tie rods [Fig. 4(a)]. The separation between the comprising chains is c , and in this work we use $c = b$. We compare this ladderlike polymer with a single linear chain of the same length (Fig. 2). The sum of drag forces experienced by the two chains [$2\bar{T}_{(c)}^{\text{ld}}$] in the ladder polymer would obviously be more (because of the larger surface) than $\bar{T}_{(c)}^{\text{ln}}$ experienced by an isolated linear chain. However, due to the additional hydrodynamic shielding provided by the two individual chains to each other in the ladderlike polymer, it is expected that

$$\bar{T}_{(c)}^{\text{ld}} \leq \bar{T}_{(c)}^{\text{ln}}$$

or, the additional shielding factor, $S_2 = \bar{T}_{(c)}^{\text{ld}}/\bar{T}_{(c)}^{\text{ln}} \leq 1$. Indeed, from the calculated results are presented in Fig. 5, we find that for any given N_1 , $S_2 < 1$, i.e., the maximum tension is smaller in the ladder polymer, or, they are more stable than each of the comprising individual isolated chains. Further, the extent of shielding is higher for longer polymer, and larger (a/b) . When polymers are used as drag reducing additives, their utility may be determined by their maximum stretched length that would not degrade under given flow conditions.²⁻⁴ With this in mind, we compare for many val-

ues of given maximum permissible tension [$\bar{T}_{(c)}^{\text{ln}} = \bar{T}_{(c)}^{\text{ld}} = \bar{T}_f$], the corresponding maximum permissible extended molecular sizes N_1^{ln} and N_1^{ld} for the linear and the ladder polymer. The results are presented as $N_{\text{enh}} = (N_1^{\text{ld}}/N_1^{\text{ln}})$ vs N_1^{ln} in Fig. 6. We see that for any maximum permissible N_1^{ln} (depending on a given \bar{T}_f) for the linear polymer, a higher N_1^{ld} is permissible in the case of a ladder polymer. We find that the gains are larger in the case of larger (a/b) , and the molecular length can be increased by as much as 35%, without enhancing the shear degradation. Clearly, such gains would be higher if the macromolecule is made by aligning more than two chains alongside.

We now present some practical ways of achieving such effects. First example is the Na-PAA polymer of Ting and Little¹¹ discussed in the Introduction. In this case, the advantages of the ladderlike structure are even higher because in forming the additional parallel chain of associating bonds, no additional drag is introduced as no new molecular chain is introduced.

An important consideration of the above model is that both the constituent chains must be perfectly taut so as to equally share the tension. While this is achieved in conventional ladder polymers made up of covalent bonds,⁴² these are often difficult to obtain in high molecular weights necessary for application as flow modifying additives. Even if possible, their solubility in solvents of interest may be small or none. Further, the rigidity of these structures may also result in significant increase in solution viscosity, thereby offsetting the advantage gained for applications such as drag reducing additives. We note that the function of the tie-rods in the above model [Fig. 4(a)] is only to retain the component chains together, and they are not load (drag tension) bearing. Hence, an alternative way to achieve such structures would be through interpolymer complexation. As discussed by Hudson *et al.*¹³ during their studies on elongational flow and Kim *et al.*⁴³ during their studies on turbulent flow, such associations at many sites along the chain length would provide the tie rods, resulting in structures as if the chains have been "zipped" together to form rigid ladderlike structures.

C. Staggered ladderlike associating polymers

During interpolymer associations between polymer chains extended under flow, the individual chains may be of unequal lengths, thus resulting in incomplete "zipping" [Fig. 4(b)]. Even in the case of equal lengths, the complexation need not be end-to-end. Hence, the structures formed would be ladderlike only along the zipped portions of the chains, while remaining lengths of the individual chains may appear attached to the ladder ends [Fig. 4(c)].

For the purpose of the present model, the two structures in Figs. 4(b) and 4(c) are equivalent. For calculation of tension $\bar{T}_{(j)}$ in the rods ($j = 1, 2, \dots$), one begins from the chain end ($j = 1$), adding up the drag force on each bead. Thus, $\bar{T}_{(j)}$ increases with j as one approaches the chain center, but until reaching a local maxima at the branch point ($\text{br} = N_1 - N_2$) [see Figs. 4(b) and 4(c)],

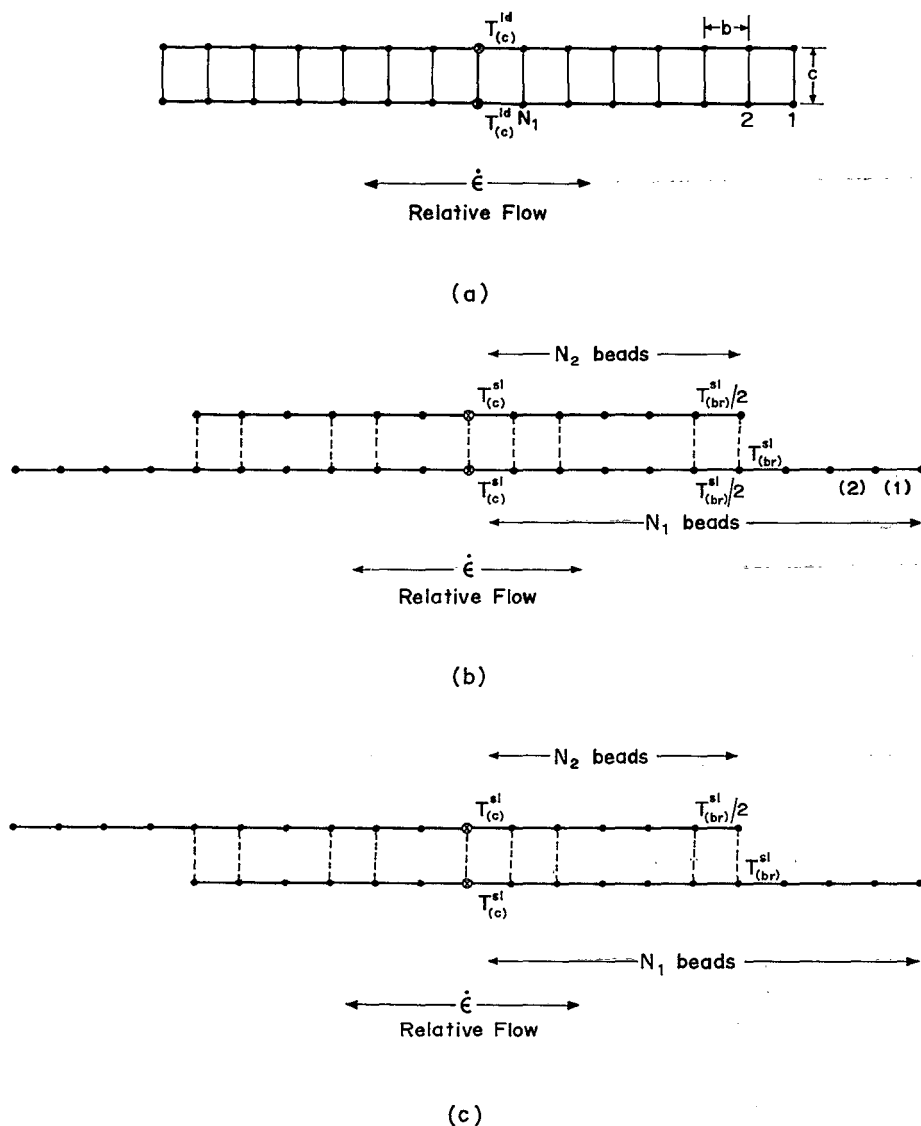


FIG. 4. (a) Model of a perfect ladderlike polymer, and (b) and (c) "zipped" staggered ladderlike structures formed by interpolymer associations between polymer chains extended under flow.

$$\bar{T}_{(br)}^{sl} = \left| \sum_{i=1}^{br} \bar{F}_i^x \right|. \quad (16)$$

This represents a local maxima since on proceeding further towards the center, this tension is considered to be borne equally by the two chains

$$\bar{T}_{(br+1)}^{sl} = \bar{T}_{(br)}^{sl}/2 + \bar{F}_{br+1}^x \quad (17)$$

representing a decrease [i.e., $\bar{T}_{(br+1)}^{sl} < \bar{T}_{(br)}^{sl}$, since $\bar{F}_{br+1}^x \ll \bar{T}_{(br)}^{sl}/2$ for long chains]. Proceeding further towards the center, the tension increases again, reaching another maxima at the chain center

$$\bar{T}_{(c)}^{sl} = \bar{T}_{(br)}^{sl}/2 + \left| \sum_{i=1}^{N_2} \bar{F}_{br+i}^x \right|. \quad (18)$$

Of the two tensions $\bar{T}_{(br)}^{sl}$ and $\bar{T}_{(c)}^{sl}$, it is the larger which is the critical (and called \bar{T}_{cr}^{sl} here) in determining chain frac-

ture. If the second term on right-hand side of Eq. (18) is smaller than $\bar{T}_{(br)}^{sl}/2$, then $\bar{T}_{cr}^{sl} = \bar{T}_{(br)}^{sl}$. Clearly, this would happen if N_2 is small [Eq. (18)], or, complexation is restricted to small lengths near chain center. This is interesting since it implies that the tension need not be maximum in the central rod even in symmetrical molecules! On the other hand, if N_2 is large (i.e., if zipping extends over most of the length of the chains), then $\bar{T}_{(br)}^{sl}$ would be small as only a few end beads ($N_1 - N_2$) contribute to it [Eq. (16)], and stress at the chain center would be critical. The computations presented in Fig. 7, for a given N_1 and (a/b) , and for different values of N_2 , are in conformity with this.

In Fig. 8 we plot \bar{T}_{cr}^{sl} vs N_2/N_1 for various values of N_1 and (a/b) . Note that $N_2/N_1 = 0$ corresponds to a single linear chain of the same overall extended length, and $N_2/N_1 = 1$ corresponds to the perfect ladder case, presented in Secs. IV A and IV B, respectively. We find that introduction of complexation by a chain of length N_2 symmetrically about

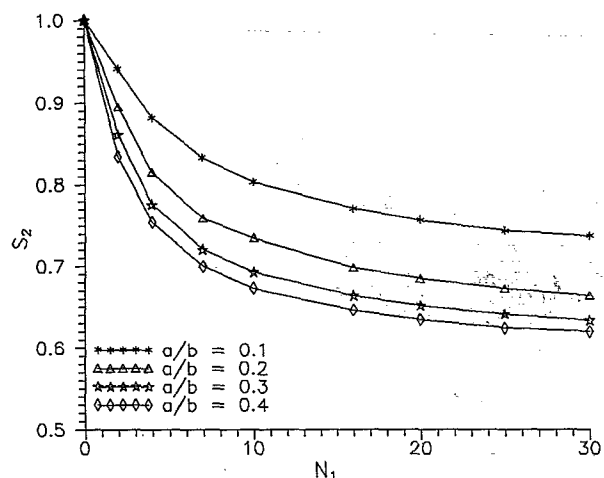


FIG. 5. Fractional maximum tension in the ladderlike polymer [Fig. 4(a)] as compared to linear chain (Fig. 2) of same N_1 and (a/b) .

the center of chain of length N_1 [Fig. 4(b)] results in reduced maximum tension compared to the linear chain alone ($N_2/N_1=0$). Thus, it can be viewed as local load sharing at the stressed chain center resulting in enhanced shear stability of the chain. Interestingly, a minimum in \bar{T}_{cr}^{sl} is reached at $N_2/N_1 \sim (0.6-0.7)$, more or less irrespective of N_1 , but slightly dependent on a/b . The minimum in tension \bar{T}_{cr}^{sl} achieved this way is to a value about 0.6 and 0.56 of the corresponding linear chain values $\bar{T}_{(c)}^{ln}$, for $(a/b)=0.1$ and 0.4, respectively. Alternatively, for a given maximum permissible tension \bar{T}_f (and hence, a given level of shear degradation), a higher overall chain length is permissible for the staggered ladder polymer as compared to a linear chain. For large N_1 of interest, the ratio (N_1^{sl}/N_1^{ln}) of such maximum permissible lengths, such as determined from Fig. 8 is ~ 1.33 for $(a/b)=0.1$ and in the range 1.4–1.45 for $(a/b)=0.4$. It suggests that if optimized, structures with up to 45% higher maximum extended length can be obtained, without reducing

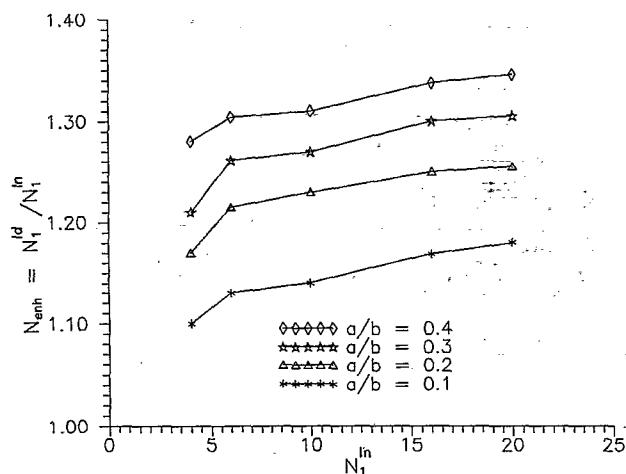


FIG. 6. Maximum N_1 permissible in the case of a ladderlike polymer as compared to a linear polymer, for same \bar{T}_f .

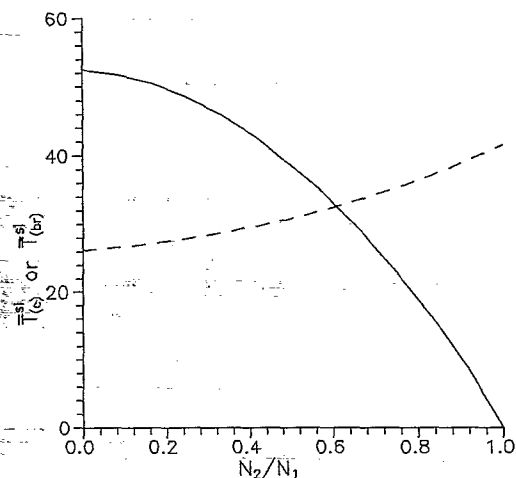
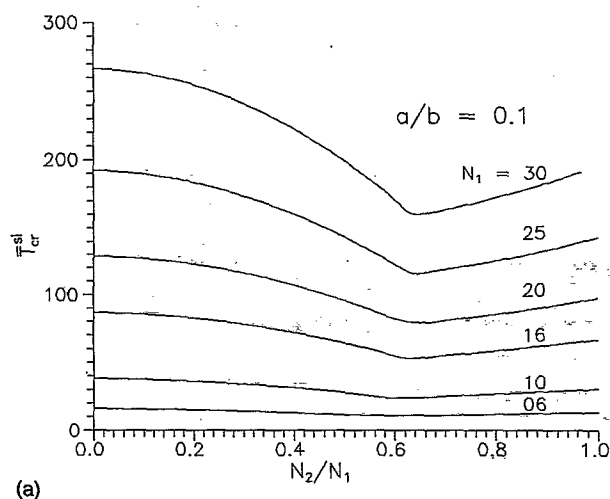
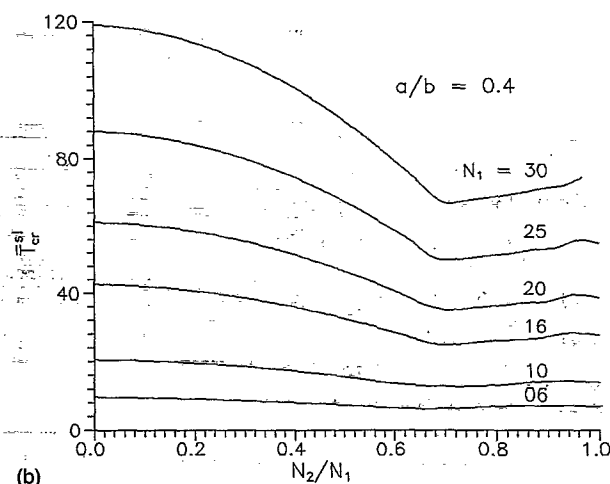


FIG. 7. $\bar{T}_{(br)}^{sl}$ (---) and $\bar{T}_{(c)}^{sl}$ (—) for staggered ladderlike polymer [Figs. 4(b) and 4(c)] with $N_1=12$ and $(a/b)=0.1$.



(a)



(b)

FIG. 8. \bar{T}_{cr}^{sl} vs N_2/N_1 for staggered ladderlike polymer [Figs. 4(b) and 4(c)], for (a) $(a/b)=0.1$ and (b) $(a/b)=0.4$.

the shear stability. While formation of only such optimum structures [Fig. 4(b)] in a turbulently flowing solutions of these associating polymers is not likely, it is notable that the structures as in Fig. 4(c) are essentially equivalent. Such structures are more shear stable than the comprising isolated polymer chains, so long as at least the tension at their individual chain centers are now reduced by zipping. Of course, the shear stability gain can be maximized if we can obtain structures such as in Figs. 4(b) and 4(c) with $N_2/N_1 \sim 0.6-0.7$.

V. CONCLUSION

A mechanistic analysis is presented to examine the effect of hydrodynamic interactions on the fracture of fully extended linear and ladderlike polymers in intense flow fields. Incorporating the hydrodynamic interactions between beads in a linear polymer results in reduction in the maximum drag tension. This reduction is more at higher chain length and (a/b). It is shown that ladder and staggered ladder polymers are more shear stable than linear polymers of the same extended chain length. In other words, extended chain length that is permissible (at a given drag tension) is up to 45% larger than the corresponding length for a linear polymer. This has interesting implications in their application as turbulent drag reducers, since their efficiency may be determined by the extended chain length.² Such mechanisms may also be prevalent in the reported higher shear stability of the associating polymers.

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