Flow of Dilute Polymer Solutions: Chain Conformations and Degradation of Drag Reducers

Witold Brostow,*,† **Hamide Ertepinar,**‡ **and R. P. Singh**§

Center for Materials Characterization and Department of Chemistry, University of North Texas, Denton, Texas 76203-5308, Fen Edebiyat Fakültesi, Karadeniz Üniversitesi, Kimya Bolümu, 61080 Trabzon, Turkey, and Materials Science Centre, Indian Institute of Technology, Kharagpur 721 302, India

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ABSTRACT: A model of flowing solutions that takes into account the structure, orientation, and mechanism of action of drag reducers is analyzed. For each polymer chain that causes drag reduction (DR), the model assumes the existence of two kinds of sequences that interact with the flow in different ways. The resulting solution structure seems to agree with the available experimental evidence on DR. A theoretical analysis of conformational states is provided. Computer calculations for model chains show the effects of varying solvent quality, polymer concentration, and free volume in the system. The results of the computer work provide clear criteria for choosing drag reducers with high efficacy λ. The model is represented by equations in terms of the parameters that determine DR. Among other things, the theory provides a relation between the DR efficacy and time t, this for unary as well as multicomponent drag reducers. Calculations performed for a variety of DR agents in aqueous solutions show that the predicted $\lambda(t)$ values agree with the measured ones within limits of the experimental accuracy. The parameters obtained can be used to optimize multicomponent DR agents. While our primary interest in the present paper is in polymers, it is at least possible that nonpolymeric drag-reducing agents act by a similar mechanism.

1. Introduction and Scope

The present paper is concerned with *drag reduction* in flowing polymer solutions. It is convenient to distinguish between the phenomenon itself, abbreviated DR, and its quantitative measure, represented by λ. The definition is

$$\%\ \lambda = (1 - f/f_1) \times 100 \qquad (1)$$

where f is the frictional coefficient (friction factor, drag coefficient) for solution and f_1 is the respective coefficient for pure solvent. Fairly high values of λ such as 70% are possible, and in fact we intend to report experimental results of this kind in the following paper.[1] λ decreases with time t, and in this paper we shall be concerned also with $\lambda(t)$ dependence.

Drag reduction has a number of applications, listed in an earlier paper by one of us.[2] Our present work seems to indicate that there are other potential applications *not yet* realized in practice. Even more important, therefore, is the understanding of the *nature* of DR: why and how it occurs. While much effort to achieve this has been expended, Donohue, Tiederman, and Reischman[3] evaluate the situation as follows: "The mechanism by which this reduction in frictional drag occurs has been the subject of much discussion; however, as yet no completely satisfactory explanation has been offered". In a very detailed review, Virk[4] states that "the mechanism of drag reduction is still rather obscure and our discussion involves speculation and is likely to contain some erroneous impressions". Equally honestly, Gramain and Boreill[5] say that "...the basic mechanisms of drag reduction are still unresolved". Reischman and Tiederman[6] "...conclude that the mechanism by which the polymer additives make their presence felt so strongly in the buffer region is still not thoroughly understood". Berman[7] reviewed research on DR and concluded that "...a detailed understanding of the nature of drag reduction is still lacking". Darby[8] said: "The mechanism by which drag reduction occurs has, likewise, not been firmly established". Kim and his colleagues[9] have reached the same conclusion: "However, molecular understanding of the polymer role in drag reduction process is still primitive". While various drag-reducing agents,[10–22] including some surfactants,[23,24] exist and give sometimes fairly good results, it is clear from these quotations that our understanding of DR has to be improved considerably to achieve a satisfactory level of boundary layer control.

Given the utility of the phenomenon, numerous—sometimes mutually conflicting—explanations have been advanced. Often explanations of drag-reducing activity of polymers are based on the *random flight* or freely jointed model of polymer chains. That model assumes that a chain consists of r bonds, each of fixed length and jointed in linear succession, the angles at the bond junctions being free to assume all values with equal probability; see Flory[25] or Forsman.[26] Rotations about bonds are likewise free, what produces virtually full flexibility of the macromolecule. An example of this approach is the cascade theory of DR,[27,28] limited from the start to linear flexible chains in good solvents, with an interesting assumption that the chains are characterized by an elastic modulus. The behavior beyond the elastic threshold has not been treated.

The random flight model has explained successfully a number of *equilibrium* chain properties, and this is presumably the reason why it has been also applied to explain *flow* properties. However, several decades ago Debye proved theoretically[29] that a freely jointed polymer chain in a flowing solution will *rotate* as a whole—rather than orient itself in the direction of the flow. Moreover, even for equilibrium properties Flory[30] pointed out in 1956 that values of configurational dimensions of polymers in dilute solutions are often *twice* those calculated assuming free rotation about all single bonds; this was the starting point for his statistical-mechanical theory of polymeric systems involving rigidity.[30,31] Hence the assumption of the random flight chain, its success for some equilibrium properties notwithstanding, is not sufficient as a basis for understanding drag reduction or other aspects of flow of

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* To whom correspondence should be addressed.
† University of North Texas.
‡ Karadeniz Üniversitesi.
§ Indian Institute of Technology.

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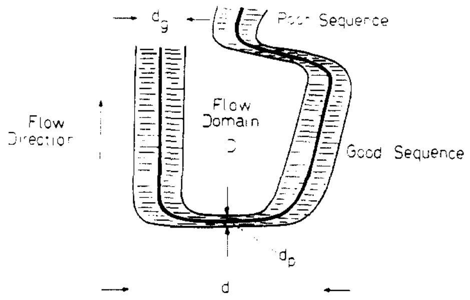

Figure 1. A schematic representation of domains created in the hydrodynamic volume of a part of a flowing polymer chain in solution. Two-dimensional cross-section. d_g = diameter of a good sequence; d_p = diameter of a poor sequence; d = average diameter of the domain D. Flow direction shown by an arrow.

polymer solutions. While various approaches deal for instance to a certain degree with the excluded volume, there is none that would account for specific solvent interactions with the polymer backbone. Further, it should be noted that *not* all drag-reducing agents are polymer chains; the explanation of the DR phenomenon should be general enough to take these other kinds of drag reducers into account also.

Flory has taught us how important it is to infer from a body of experimental data a model that would include the essentials—and that would not include anything else. A model of drag reduction that does not involve the assumption of the freely jointed chain has been advanced in ref 2. In the present paper we analyze that model in more detail (section 2). We consider conformational states and vary on a computer solvent quality, polymer concentration, and free volume in the system (section 3). Further, we extend the model to DR agents consisting of more than one component and use accurate experimental data on the time dependence of DR to see the extent of their agreement with the $\lambda(t)$ values predicted from the theory (section 4). Thus, we are mainly concerned here with the understanding of the DR phenomenon and the validity of the model that explains it. As already mentioned, more experimental results will be reported later.[1]

2. Structure of Flowing Solutions

Forsman[26,32] established the existence of an intimate connection between conformational statistics and chain dynamics. In turn, these two aspects have to be considered in conjunction with the role of the solvent. Alig, Wartewig, and collaborators[33-37] studied ultrasonic absorption and shear viscosity of a number of solutions of homo- and copolymers. Polymer + polymer as well as polymer + solvent interactions turned out to be important. For instance, the frequency dependence of the excess sound absorption of poly(vinyl chloride) is distinctly different in different solvents. Particularly pertinent for perceiving the role of the solvent are experimental results of Zakin, Hunston, and their colleagues[10-12] showing that the polymer concentrations required for equal drag reduction λ are several times *greater* in poor solvents as compared to a good solvent. Moreover, the same authors have found that, under given flow conditions, more mechanical degradation was observed in poor solvents than in a good solvent.

In view of the above, consider a model of conformations proposed in ref 2 which will now be analyzed in some detail. For this purpose we provide a graphical representation in Figure 1. Consider first a polymer chain in a solvent in a static situation. As any such chain, it has many reversals of direction; see for instance section 12.2 in ref 38. Segments of the chain interact with solvent molecules to a greater (good solvent) or lesser (poor solvent) extent. Now, when flow begins, deformation takes place, this both for the chain and the solvent molecules. Consequences of that deformation for a pure liquid were examined in some detail by one of us and Szymanski,[39] while deformation of chains under external mechanical forces was studied by molecular-dynamics computer simulation by one of us and Turner.[40] Thus, we have now a reasonably good idea how the system of chains in a solvent will behave. There are always interactions between solvent molecules and polymer segments. When flow begins, some solvent molecules will move *in unison* with the nearest polymer segment. The number of molecules so moving depends on two key factors: the relative strength of the polymer + solvent interactions (parameter X_{12}; see below), and the location of a given segment—and of its near neighbors along the polymer backbone—with respect to the flow.

Consider a rectilinear sequence in the chain along the backbone, that is, a sequence of segments between two changes of direction. Take first a sequence that happens to be aligned with the flow direction. The solvent molecules in the proximity of the sequence are similarly aligned. When shearing forces will start operating, the polymer sequence and the surrounding solvent molecules will start moving as a single unit. One can define a diameter d_g of that unit in the direction locally perpendicular to the chain backbone. By contrast, consider now a sequence of segments that is perpendicular to the flow. Even if in the static situation the number of solvent molecules attached to each segment was the same as for the other sequence, shearing forces will separate many of these molecules from the sequence. Consequently, the diameter of the second sequence will be different, d_p, and in general $d_g > d_p$. In a good solvent we shall have more sequences of the g type (earlier called extended), and in a poor one more of those of the p type (earlier called compact), hence the symbols for these indices. Of course, orientations with respect to the flow other than strictly parallel and strictly perpendicular are also possible, but for simplicity we divide all sequence orientations into these two broad categories. We do this also because some orientations that are not quite parallel will become closer to parallel under the action of flow forces; de Gennes[41] and more recently Gotlib and Rystov[42] discuss how a polymer molecule can unwind from a coil structure to a more extended or stretched conformation. The structure resulting from our considerations is shown in Figure 1, where good and poor sequences can be distinguished easily. Qualitatively, the chain part shown in Figure 1 can be at rest as well as in flow, although the number of good sequences in the entire chain will not be the same in these two situations.

The model shown in Figure 1 represents of course only a two-dimensional cross-section through the solution. Consider a region between two good sequences, such as marked by the letter D in the figure. Above it and below it we shall have similar good sequences, also approximately aligned in the flow direction. As a consequence, a *domain* is formed. Clearly, because of the solvent molecules in between, the domain diameter d in the direction perpendicular to the flow is $d > 2d_g$. When the flow starts, domains offer *resistance* to vortex formation, with evident consequences for the turbulence. Further, chains gradually become less entangled and intertwined, more elongated, and thus new domains can be created. During the flow, sequences in the chain can undergo extension and contraction and act as *energy sinks* interacting with the turbulent flow. The magnitude of this interaction depends for each sequence on its character (good or poor) and also on its instantaneous location with respect to local eddies. The same chain sequences, plus fully rigid drag-reducing agents if present, act to preserve the integrity (although not the dimensions) of the domains. Hence central to the model of drag reduction formulated in ref 2 are *two roles* performed by the domains: resisting vortex formation and acting as energy sinks with respect to turbulence.

Domain formation is aided by the well-known tendency of macromolecules (or at least of their parts) to aggregate in solution. A method of computer simulation of light scattering by polymer solutions was developed[43] because of anomalous particle scattering factors—explained by concurrent action of sequences from at least two chains forming a single scatterer. Excess low-angle light scattering in semidilute solutions was reported by Koberstein, Picot, and Benoit.[44] The phenomenon, ascribed to density fluctuations due to long-range heterogeneities (LRH), is being studied by Springer and collaborators.[45,46] One of the conclusions of Springer is that the mean correlation length of LRH does not change with polymer concentration.

We note that the existence of poor sequences, oriented more or less perpendicularly to the flow, is also useful—although not quite essential—to the domain formation. In other words, the nearly parallel-to-flow units are those that are necessary for the domain creation. Our model is *general* indeed, and these units do not need to be sequences of macromolecular chains; asbestos fibers, for instance, can do a similar job. The diameter of an asbestos fiber is distinctly larger than that of a polymer (for instance, carbon) chain, but in our model the corresponding diameter is d_g, not just the thickness of the "nude" chain. The approximately perpendicular units, be they poor polymer chain sequences or again asbestos fibers that somehow acquired such an orientation, improve the domain stability.

It appears that our mechanism of drag reduction agrees with experimental as well as theoretical evidence. Some experimental findings reported in the literature were confronted with the model when it was originally proposed.[2] Let us now consider important facts pertaining to other aspects of DR. First of all, the model does not contradict the theoretical work of Debye:[29] we do not deal with completely flexible chains, since we have taken into account polymer + solvent interactions, as indeed should be done. Moreover, the model agrees with the finding of Flory[30] that dimensions of polymer chains in solution often exceed those calculated from the random flight model; our mechanism of chain solvation is operative here. Still further, Donohue, Tiederman, and Reischman[3] studied low-speed streaks originating from conduit wall. Their motion pictures show streaks that lift and then after neither oscillating nor bursting return to the wall. These are precisely our domains at work, reflecting the streaks back to the wall. An explanation of drag reduction by Virk[4] in terms of an "elastic sublayer" used to be quite popular; we do not invoke such an explanation, while Reischman and Tiederman[6] found by velocity measurements that "There is no evidence that the viscous sublayers of the drag-reducing channel are thicker than those in solvent flows". Bewersdorff,[14] while not negating the existence of DR with changes in the turbulence structure only in the near-to-wall region, has established that DR does occur if the polymer forms a liquid thread that is conveyed into the core region of the flow; that is, no significant part of the injected polymer is present in the near-to-wall region.

We also know that there is an onset point for drag reduction, below which that phenomenon will not occur. Hunston and Reischman[47] have demonstrated that that point is determined by molecules with the highest molecular weight in the polymer sample. Moreover, they have found that the onset point decreases with increasing M. Clearly, longer chains—because of the ability to form longer good sequences as well as because of larger hydrodynamic volumes—are more effective as domain formers.

A very interesting phenomenon was observed by Kim and collaborators:[9,18,48] while poly(acrylic acid) (PAA) in water loses fairly rapidly its DR efficacy with flow time, addition of NaCl during flow restores DR, while adding NaCl before the flow start results in maintaining the same DR level for several minutes. Clearly, the fall of DR in the absence of sodium chloride cannot be ascribed to chain degradation. Kim et al. suggest that the shearing forces possibly enhance interchain association, facilitating hydrogen bonding between the chains; addition of NaCl would then cause dissociation of these aggregates. More generally, they say[18] that "...drag reduction recovery is probably a consequence of environmental changes in the deformed chains by the addition of the salt". Their picture is quite consistent with ours: under the action of the shearing forces, numerous interactions between chain segments and solvent molecules are broken, resulting in some good-to-poor sequence conversion. Addition of NaCl in advance prevents this from happening, while later addition restores original interactions. Hydrogen bonding and its blocking by NaCl might well be operative here. We remember that one is dealing here with chain + solvent entities and not just "nude" chains. In fact, in their third paper[48] Kim and collaborators obtained transmission electron micrographs (TEMs) of PAA stained with uranyl acetate: from the unsheared solution a fluffy film with a texture of expanded molecular network, which was obviously well filled with the solvent before; from the sheared solution a much more compact structure, forming a solid powder and with a higher glass transition temperature. TEM thus provides a direct experimental evidence for the role of solvation as defined in our model.

Kim et al.[18,48] have also found that at higher polymer concentrations DR tends to *increase* with shearing. Another role of the turbulence forces shows up here: deformation produces a decrease in chain overlap and thus promotes the creation of new domains.

3. Computer Study of the Chain Conformation Model

To see still further consequences of the model, consider a solution containing N_1 solvent molecules plus N_2 polymer molecules. Without a loss of generality, we can take one polymer chain plus N_1/N_2 solvent molecules. While we are dealing with flow, Wolf[49] argued convincingly that an *equilibrium* approach can be applied to flowing polymer solutions. He treated phase separation in such solutions by a thermodynamic theory based on the Flory–Huggins equation, predicting that shear dissolution can occur at low shear rates and shear demixing at high shear rates. Wolf's prediction was confirmed experimentally; in fact both kinds of behavior were found in a single system.[50,51] A similar approach has been taken by Rangel-Nafaile, Metzner, and Wissburn,[52] who have combined equilibrium variables of temperature and composition with a measure of molecular deformation resulting from the flow. The problem we shall now consider happens to be simpler: we deal with a particular conformational state of a chain.

While we are primarily interested in a system of one chain + solvent molecules that has already been affected by flow forces (elongation, a decrease in overlap, partial dissociation of attached solvent molecules, and so on) and is now in motion, the ensuing analysis is also applicable to a similar system at rest.

We are dealing with chain conformations in terms of two kinds of sequences, good and poor. That is, we have a two-state model; its history in science goes back to the doctoral thesis of Ising.[53] Our problem is more complex than his because of the connectedness of sequences in the polymer chain. We need the following definitions:

$$b = b_g + b_p \tag{2}$$

$$r = br_b \tag{3}$$

Here b is the total number of sequences in a chain (for simplicity, as well as to improve perspicuity of the results, we consider monodisperse systems or single chains), b_g is the number of good sequences in the chain (see again Figure 1), and b_p is similarly the number of poor sequences. The degree of polymerization is r; similarly as Rice and his colleagues[54] dealing with helical chain sections of two kinds, we assume the same average number of base units r_b in good as well as in poor sequences.

A series of sequences, say gpgpgpgpgg, is different than ggggppppgg, although both contain the same numbers of good and of poor sequences. We shall call, in obvious notation, the numbers of pairs of neighboring sequences N_{gg}, N_{pp}, and N_{gp}. Thus, in both series we have $b = 10$, $b_g = 6$, and $b_p = 4$. In the latter series we also have $N_{gg} = 4$, $N_{pp} = 3$, and $N_{gp} = 2$. From combinatorics we have

$$N_{gg} + N_{pp} + N_{gp} = b - 1 \approx b \tag{4}$$

For long chains, neglecting unity again, we also have relations already provided (albeit with somewhat different notation) in ref 55:

$$2N_{gg} + N_{gp} = 2b_g \tag{5}$$

$$2N_{pp} + N_{gp} = 2b_p \tag{6}$$

Instead of N_{gp}, it is sometimes convenient to use a fraction x_{gp}, namely

$$x_{gp} = N_{gp}/(N_{pp} + N_{gp}) = N_{gp}/[b_p + (N_{gp}/2)] \tag{7}$$

As others,[49,52] we use a theory of Flory, but a version taking into account explicitly free volume effects. Following Flory,[56,57] we write the partition function Q as

$$Q = Q^{comb}Q^{fv}Q_c \tag{8}$$

where Q^{comb} is the combinatorial factor, Q^{fv} the free volume factor, and Q^c the configurational factor.

For our purposes, the most important is Q^c. By using standard methods of statistical mechanics, we write for the two-state chain model[55]

$$Q^c = \sum_{b_g,b_p,N_{gp}} \Omega \exp\left[-\frac{1}{kTv_s}\left[\frac{N_1 z\eta_{11}}{2N_2} + r_b(z-\zeta)(b_p[(1-x_{gp})(1-\nu_m) + x_{gp}(1-\nu_t)]) + \left(\eta_{12} - \frac{\eta_{11}}{2}\right) + {}^1/_2 r_b(z-\zeta)b_p[(1-x_{gp})\nu_m + x_{gp}\nu_t]\eta_{22}\right]\right] \tag{9}$$

Here Ω is the number of ways of realizing a configuration containing b_g sequences of the g type and b_p sequences of the p type; k is the Boltzmann constant; T is the thermodynamic temperature; v_s is the segment volume; z is the coordination number for polymer segments as well as for solvent molecules; and ζ is the internal coordination number of the polymer, that is, the number of nearest-neighbor sites occupied by segments *directly connected* to a given segment, averaged over all segments of the chain. $\eta_{yy'}$ parameters are defined so that the average interaction energy $u_{yy'}$ per pair yy' is given by $-\eta_{yy'}/v_s$; therefore for attractive interactions $\eta_{yy'}$ is positive (η should not be confused with the viscosity; we simply use the same symbols as Flory[56,57]). The average number of interactions per segment is then $(z - \zeta)$. We define as $(z - \zeta)\nu_m$ the number of interactions with other polymer chains for a segment in a p type sequence surrounded by p type sequences, and similarly $(z - \zeta)\nu_t$ is the number of interactions for a p type sequence adjacent on both its sides to g type sequences.

We see that eq 9 takes into account essential aspects of the internal structure of the chains, solvent structure, and all types of interactions (1 + 1, 1 + 2, and 2 + 2) present in solution. By taking into account the Flory formula for Ω and extremizing eq 9, we obtain a pair of equations:[55]

$$\ln\frac{b_p(b - b_p - N_{gp}/2)}{(b - b_p)(b_p - N_{gp}/2)} + \frac{(z-\zeta)r_b}{kTv_s}\left[\nu_m - 2(\nu_m - \nu_t) \times \left(\frac{N_{gp}/2}{b_p + N_{gp}/2}\right)^2\right](\eta_{11} + \eta_{22} - 2\eta_{12}) = 0 \tag{10}$$

$$\ln\frac{(b_p - N_{gp}/2)(b - b_p - N_{gp}/2)}{(N_{gp}/2)^2} + \frac{r_b}{kTv_s}(z-\zeta)(\nu_m - \nu_t) \times \left(\frac{b_p}{b_p + N_{gp}/2}\right)^2(\eta_{11} + \eta_{22} - 2\eta_{12}) = 0 \tag{11}$$

Equations 10 and 11 can be solved simultaneously for two unknowns, b_p and N_{gp}. We recall that these two quantities are related to other parameters defining the chain structure by eqs 2–6.

Once a definite polymeric drag reducer has been chosen, two parameters belonging to our characteristics are fixed: the molecular mass M and ζ, since the latter is defined by the degree of branching. This, however, still allows us choices of a number of parameters: free volume in the liquid, coordination number, and solvent quality, at least. Temperature T might be imposed by process conditions, or choices might be possible. We know from work of Zakin, Hunston, and their colleagues[10–12] that the solvent quality (in our terms the strength of polymer + solvent interactions) is highly important. In view of eqs 10 and 11 and following Flory[56,57] we introduce

$$X_{12} = z(\eta_{11} + \eta_{22} - \eta_{12})/2v^{*2} \tag{12}$$

Here v^* is the characteristic (hard-core, incompressible) volume; that is

$$v = v^* + v^f \tag{13}$$

where all quantities in eq 13 pertain to 1 g, so that v is the specific volume and v^f the respective free volume. Thus, we have only one parameter representing the solvent quality, rather than three. X_{12} is related to χ in the Flory–Huggins theory. However, χ contains free volume contributions; X_{12} does not, this because of the Q^{fv} term in the partition function eq 8. Calculations made by one of us[58] for a number of polymer + solvent systems have shown that X_{12} is not composition dependent, while χ typically is. The relation between the two energy parameters (obtainable by combining eqs 14, 15, and 18

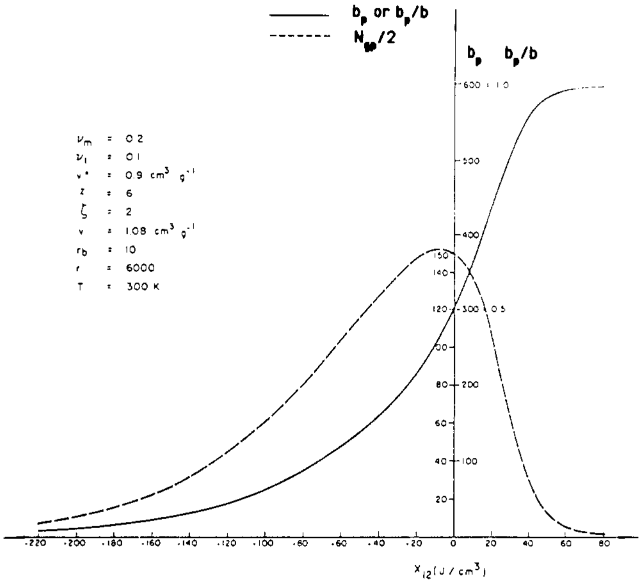

Figure 2. Plots of the number of neighboring sequences of two different kinds $N_{gp}/2$ and of the fraction of poor sequences b_p/b vs. the interaction energy density X_{12}.

in ref 58) is

$$X_{12} = \varphi_2^{-2}[1 + (s_1/s_2 - 1)\varphi_1]^2 v \{\chi N_A k T \varphi_2^2 / v_1^* P_1^* (3\tilde{T}_1 \ln [(\tilde{v}_1^{1/3} - 1)/\tilde{v}^{1/3} - 1)] + \tilde{v}_1^{-1} - \tilde{v}^{-1}\} \quad (14)$$

Here φ_i and s_i are respectively the volume fraction and the number of interaction sites per segment of the ith component. N_A is the Avogadro number. The reduced parameters are defined as

$$\tilde{v} = v/v^*; \quad \tilde{T} = T/T^*; \quad \tilde{P} = P/P^* \quad (15)$$

Parameters without indices pertain to the solution as a whole. T^* and P^* are characteristic parameters for a given substance. Equation 14 is general. For dilute solutions in which drag reduction takes place we can simplify it by assuming $v = v_1$ and $\tilde{v} = \tilde{v}_1$; then

$$X_{12} = \chi N_A k T v / v^{*2}[1 + (s_1/s_2 - 1)\varphi_1] \quad (16)$$

There are several ways[58,55] of evaluating the s_1/s_2 ratio. Definition 12 shows that X_{12} values close to zero, or even better negative, correspond to good solvents, while the larger is a positive value of X_{12}, the poorer the solvent.

To acquire a good understanding of chain conformations possible, we have solved on a computer a large number of pairs of eqs 10 and 11, varying one parameter at a time and keeping other parameters constant. As can be seen in Figure 1, particularly important for our model is the number of poor sequences in the chain b_p and also the distribution of two kinds of sequences along the backbone as characterized by N_{gp}. We provide selected results below. In one such series of computations we have varied the interaction energy density X_{12}. Experimental values for a number of solvent + polymer pairs are listed by Flory.[57,59] For instance, for cyclohexane + polystyrene, X_{12} = 67 J·cm^{-3}; for ethylbenzene + polystyrene, X_{12} = 8.8 J·cm^{-3} (we recall that in toluene, just one methylene group less, polystyrene acts as a drag reducer); for n-octane + polyisobutylene, X_{12} = 4.4 J·cm^{-3}. We have covered a large interval of X_{12} values, from +80 to −220 J·cm^{-3}. The resulting curves of $N_{gp}/2$ and b_p as a function of X_{12} are shown in Figure 2. The parameters used in that computation are listed in an insert in the same figure. Since we have r = 6000 and r_b = 10, b_p = 600 corresponds to b_p/b equal to unity. Inspection of Figure 2 shows that an increase of the interaction energy density, that is, the solvent becoming poorer, is accompanied by a conversion in the chain structure, leading eventually to the entire chain consisting of poor sequences only. The number of mixed pairs has a maximum near the value of X_{12} = 0. These are expected results, but they prove the physical significance of the parameters of the theory and the internal consistency of the model; in other words, the model works as it should.

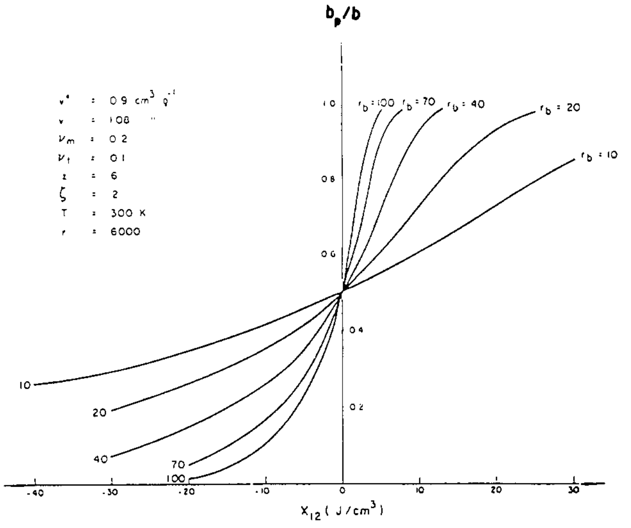

Figure 3. Plots of the fraction b_p/b vs. the interaction energy density X_{12} for different average lengths r_b of sequences.

In another series, we also had the interaction energy density as the independent variable, but we studied the effect of varying the sequence length on the fraction b_p/b of poor sequences. The results are shown in Figure 3; values of the parameters used are listed in an insert in the figure. We find that if the average sequence is long, r_b = 100, then the conversion of the chain to a completely poor one occurs much faster upon increasing a positive value of X_{12}. In very good solvents, with negative values of X_{12}, the disappearance of poor sequences is also faster. For r_b = 20 it takes X_{12} close to +30 to convert all sequences into poor ones. We note that the curve branches for positive and negative X_{12} values are *not* superimposable on each other as mirror images.

We have also studied the effect of polymer concentration c on chain conformations. Since parameters ν_m and ν_t increase along with c, we show in Figure 4 curves of b_p/b vs. ν_m for various X_{12} values. We find that for X_{12} = 0 there is no dependence. For very good solvents, $X_{12} < 0$, the increase in polymer concentration actually decreases the fraction of poor sequences. As expected, the poorer the solvent, the faster an increase in polymer concentration increases the fraction of poor sequences. For values of X_{12} such as 10 or 20 J·cm^{-3}, we find that our curves correspond to the semiempirical equation of Rudin and Wagner,[60] namely

$$\alpha^3 = \beta_0/[1 + c(\beta_0 - 1)/c_\Theta] \quad (17)$$

where α is the Flory expansion factor, β_0 a constant, and c_Θ the polymer concentration at the Θ point. However, for X_{12} = 40 J·cm^{-3}, the curve becomes convex rather than concave. We see that the solvent quality determines not only the values but also the form of the concentration dependence.

We now go on to discussing the effect of free volume. A convenient quantity is the reduced volume, defined by the first of eqs 15, which we shall use as the independent variable. In other words, $\tilde{v} = 1 + v^f/v^*$. Typical values

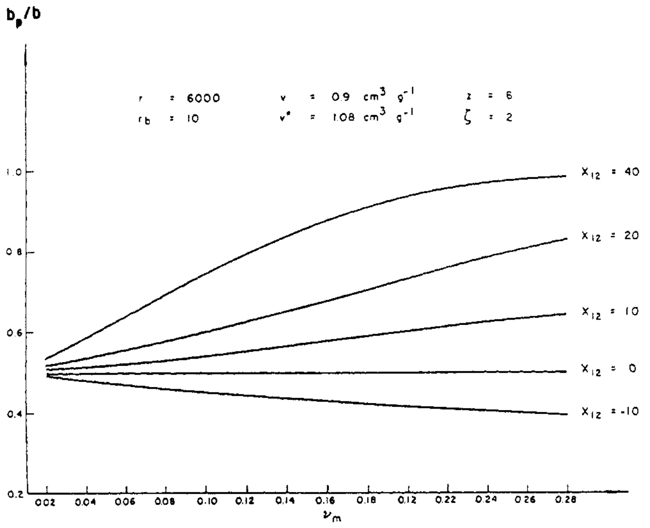

Figure 4. Plots of b_p/b vs. the concentration term ν_m for various values of the interaction energy density.

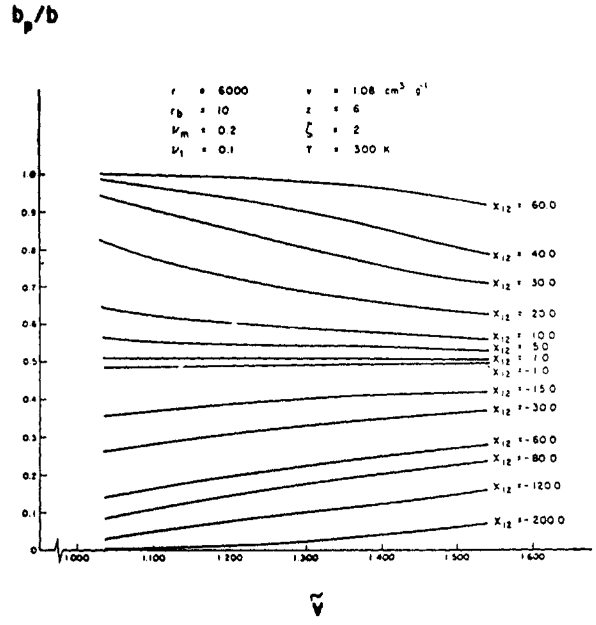

Figure 5. Plots of b_p/b vs. the reduced volume $\tilde{v}$ for various solvent qualities.

of $\tilde{v}$ for liquids used as polymer solvents are between 1.1 and 1.3.[56,58] Given low concentrations of drag reducers, the respective values for solutions are very near to those for solvents, a fact already used to derive the approximate eq 16. Plots of b_p/b vs. $\tilde{v}$ for various X_{12} values are shown in Figure 5. There is little effect for $X_{12} \approx 0$. For very high negative values of X_{12} (not very realistic ones, but explored so as to have a complete picture) an increase in reduced volume increases the fraction of compact sequences. In the range of positive values of X_{12} an increase in $\tilde{v}$, that is, in free volume, lowers b_p/b. For X_{12} around 40 J·cm^{-3} there is a quite strong effect. This is quite an important finding: apparently we can salvage a situation when the solvent is poor for a polymer we want to use as a drag reducer by increasing free volume.

One more parameter that one might be able to manipulate is the liquid coordination number z. We have explored the effect of this parameter also. The results are shown in Figure 6. It turns out that the effects are small, except for very low coordination numbers ($z = 4$ is the lowest possible value for a liquid[61]). Thus, our computations demonstrate that varying the coordination number in real solutions for improving drag reduction is not worthwhile.

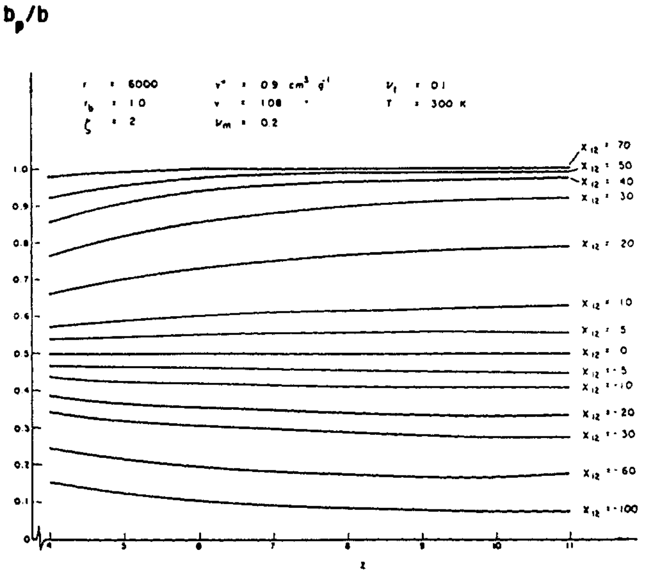

Figure 6. Plots of b_p/b vs. the liquid coordination number z for various solvent quantities.

Since a high proportion b_p/b of poor sequences destroys the drag-reducing domains or else inhibits their creation, particularly useful are our findings on the effect of free volume on b_p/b: *an increase in* v^f *lowers* b_p/b. Thus, for a given drag reducer, there are several ways of increasing its efficacy by increasing free volume. The first and simplest is to increase the temperature. However, we are increasing the thermal energy at the same time; the consequences are often undesirable and will be analyzed in later papers. There is also an increased energy cost; for this reason alone we do not recommend it for the Alaska pipeline. The second method consists in using a *mixed* solvent, where to a given liquid we add a certain amount of another one, the latter with higher $\tilde{v}$ (that is, v^f) than the main component. Often, even if the difference between $\tilde{v}$ values is not that large, the very *disruption* of structure of the main solvent produces positive excess volume $\tilde{v}^E$ (for definitions of excess functions see, e.g., ref 38); thus $\tilde{v}^E >$ 0 and additional space appears between the molecules. This second possibility represents the best option. The third possibility is to manipulate *branching*; the effects of branching on free volume are discussed in ref 62. However, one has to be very careful in this last case. In a *solid* polymer short and frequent branches as well as long and infrequent branches increase v^f. However, in *solution* short branches located at small intervals from each other along the polymer backbone will only cut the domains in pieces or at best decrease their sizes and numbers. It is only long and infrequent branches that can create additional domains and aid in DR process.

From the results reported in this section one can infer the following *criteria* for the achievement of high drag reduction efficacy:

(1) Polymers should be chosen so that the liquid is a good solvent for a given polymer. For reasons discussed above, the Flory interaction energy density X_{12} (determinable as described in refs 56–59) serves best to characterize the solvent quality. The Flory–Huggins parameter χ can be used when X_{12} values are not available—see again approximate eq 16.

(2) While an increase in polymer concentration c increases drag reduction, for $X_{12} > 0$ there is a concomitant conversion of good sequences into poor ones. Thus, an

increase in c produces higher λ, but at a rate less than linear. With the solvent quality known, curves shown in Figure 4 enable an assessment of how much of a polymer concentration increase is worthwhile.

(3) An increase in free volume v^f or reduced volume $\tilde{v}$ fortifies the drag reduction effect. This can preferably be achieved by adding a second solvent. The choice of that solvent should be based on maximizing the reduced excess volume $\tilde{v}^E$ in the binary main solvent + secondary solvent system. Numerous excess volume data for liquid pairs are available in the literature.

Data available in the literature support the criteria just formulated. We already referred above to the results of Zakin, Hunston, et al.,[10-12] who demonstrated the role of solvent quality both for DR itself and for change of DR with time due to chain degradation. Moreover, Ballauf and Wolf[63] found that degradation of polystyrene takes place in *trans*-decalin (a Θ solvent) while none was observed in toluene (a very good solvent). In future papers we shall test further the applicability of the criteria now formulated against experimental data.

4. Time Dependence of Drag Reduction

After finding a suitable drag reducer, the second key problem is the shear stability of the additive in turbulent flow. As discussed above, mechanical degradation in flow (MDF) is also related to solvent quality.

Incidentally, MDF in *laminar* flow is also possible, but this has only been observed in moderately concentrated solutions of unusually poor solvents.[64]

An analysis of the time dependence of drag reduction was performed in ref 2. However, this was limited to one-component drag reducers and purely polymeric ones. We shall now present a more general approach, which strictly reduces to the earlier one for unary monodisperse drag-reducing agents. The starting point is the proportionality between the drag reduction efficacy λ and the *effective* number-average molecular mass M, namely

$$\lambda/\lambda_0 = M/M_0 \tag{18}$$

where the index 0 pertains to the beginning of the flow. The fact that DR decreases due to the chain scission was shown directly by gel permeation chromatography determination of molecular mass distribution changes with time by Hunston and Zakin[12] and similarly by Ballauf and Wolf.[63] The word "effective" requires an explanation. We recall the experimental finding of Hunston and Reischman[47] that only chains with relatively high molecular weights participate in DR. Moreover, there is the increase in DR with time observed by Kim and collaborators,[9,48] explained by us in terms of lowering the chain overlap by flow forces. Thus, M represents an effective value for the *participants in drag reduction*: chains that are not too short and that can create domains; chains that are not prevented from forming the domains because of extensive overlap; and also possibly nonpolymeric DR agents that produce effects equivalent to a polymer chain of a certain molecular weight. Incidentally, the problem of chain overlap in dilute polymer solutions is the object of a separate study.[65] In the following when we talk about M values and related quantities, we mean these effective values. We cannot obtain effective values for multicomponent drag reducers from values for unary DR agents, since the effects are evidently not additive in any simple way. However, as shall be seen below, we can make approximate predictions.

At the beginning of the flow the number of chain molecules per unit volume is

$$N_2/V = cN_A/M_0 \tag{19}$$

Experimental evidence shows (see refs 10–12 and also our results below) that the degradation process does not go on indefinitely but stops at a value M_∞. Also, Kim et al.[9] found that when they started with a relatively low molecular weight, DR hardly changes with time; apparently their M_0 was only insignificantly higher than M_∞. At the time $t = \infty$ (or in practice at the time when MDF has stopped) we have

$$N_2 = cN_A/M_\infty \tag{20}$$

From the above equations, for the number of bonds $a(t)$ broken per unit volume at time t we obtain

$$a(t) = cN_A(1/M - 1/M_0) \tag{21}$$

As a special case of eq 21 we have a formula for a_∞ in terms of M_∞.

Further, we note that the points on the chain where changes of direction occur are more vulnerable to chain scission (see again Figure 1). Depending on specific location, some of them might be protected from degradation by surrounding domains, while some others will undergo scission during flow. The average number of points of the latter kind per chain will be denoted by W. Clearly, W is proportional to N_{gp}, or approximately proportional to an average value of N_{gp} for a binary polymeric drag reducer. Moreover, in view of our definitions

$$M_\infty = M_0/(1 + W) \tag{22}$$

For a multicomponent drag reducer the parameter W represents also an effective value. For a unary and purely polymeric drag-reducing agent, W can be related[2] to the drag reducer concentration c, the energy U_d coming from turbulent flow that produces degradation, and the energy ϵ necessary to break one bond. Specifically

$$M/M_0 = [1 + M_0U_d/cN_A\epsilon]^{-1} \tag{23}$$

Then, since U_d is time dependent, with its final value $U_\infty = U_d(\infty)$, while evidently ϵ is not, we have

$$W = M_0U_\infty/cN_A\epsilon \tag{24}$$

A part of the energy furnished to the drag-reducing agents during flow is *not* spent on degradation but rather on orientational changes and in polymeric drag reducers also on chain relaxation. A detailed analysis of these two kinds of energy expenditure[2] which is also applicable to our more general case involving effective quantities leads eventually to the formula

$$U_d = U_\infty(1 - e^{-ht}) \tag{25}$$

where h is a parameter that depends on the total concentration of the drag reducers (another effective value), on the solvent quality parameter X_{12}, and on free volume. The use of eqs 22–25 and substitution of the result into eq 18 lead to

$$\lambda/\lambda_0 = [1 + W(1 - e^{-ht})]^{-1} \tag{26}$$

which is the desired result.

We have tested eq 26 against experimental results for a number of liquid + drag reducer systems; in part, results reported in ref 20 were used. The data were all obtained in a turbulent flow rheometer that required only 150 cm^3 of the liquid and thus only a few milligrams of a drag

Table I
Drag Reducers, Their Composition, Efficacy, Parameters in Eq 26, and Agreement between Values Obtained from Eq 26 and Experimental Values

no.	composition[a]	$\lambda_0/\%$	W	h × (no. of passes)	σ	$D/\%$
1	20 ppm GG	12.9	0.526	9.288	0.0263	0.0191
2	10 ppm PGG + 10 ppm PAM	46.2	1.885	18.41	0.0195	0.0149
3	15 ppm PGG + 5 ppm PAM	20.3	0.483	3.548	0.0268	0.0179
4	10 ppm PXG + 10 ppm PAM	45.5	1.706	18.48	0.0143	0.0122
5	10 ppm GXG + 10 ppm PAM	41.7	4.483	49.78	0.0466	0.0371
6	25 ppm AF + 25 ppm PGG	36.9	1.401	4.373	0.0116	0.0080
7	25 ppm AF + 25 ppm GXG	27.3	1.956	13.34	0.0234	0.0162
8	25 ppm AF + 25 ppm PXG	20.0	0.857	2.329	0.0124	0.0088
9	25 ppm AF + 50 ppm GXG	29.6	2.311	9.488	0.0147	0.0116

[a] Code symbols for drag reducers: GG = guar gum; PGG = guar gum purified according to ref 67; PAM = polyacrylamide, Hoechst, France, Bozofloc N-46 BT, $M \approx 6.0 \times 10^6$; PXG = purified xanthan gum; GXG = xanthan gum grafted according to ref 68; AF = crysolite asbestos fiber, TBA Industrial Products Ltd., Great Britain, Cassiar A65, diameter 30–40 nm, aspect ratio 4 × 10^4.

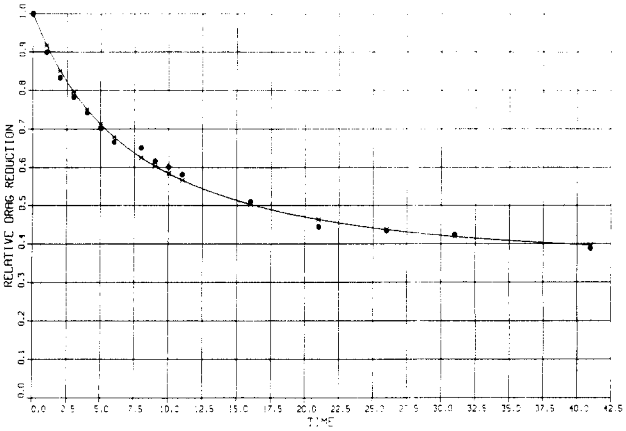

Figure 7. Time dependence of relative drag reduction efficacy λ/λ_0 for purely polymeric sample 4; for parameters see Table I. Experimental values: (●); calculated values: (—) and (*).

reducer. The rheometer is basically a motor-driven glass syringe with the delivery rate determined by a motor speed controller. All measurements were made as a function of the pass number (which represents t in the equations above) at a constant Reynolds number $Re \approx 1.40 \times 10^4$. Pressure drops were measured with Statham universal transducers with a 10-psi ($\approx$0.070 J·cm^{-3}) pressure diaphragm, which provided quite satisfactory accuracy. As stated in section 1, our aim is to understand and control drag reduction in general, not only for polymers as drag reducers. Therefore, we studied also drag reducers containing crysolite asbestos fibers; these fibers act as drag reducers.[66] Effective procedures for preparing well-dispersed fiber suspensions were described earlier.[20] Both the kind of drag reducer, unary or binary, and concentration were varied. However, because of the general nonadditivity of DR effects, the role of concentration will be considered more in detail in a later paper.[1]

As an example, we show in Figure 7 degradation as a function of time for a drag reducer, sample 4, consisting of two polymers: polyacrylamide (PAM) and purified xanthan gum. Characteristics of the materials are provided in the footnote to Table I. For this system X_{12} is not known, nor is it known for subsequent systems, while v^f for all these aqueous solutions is virtually the same. Equation 24 was applied, with the two unknowns, W and h, obtained by solving an overdetermined system of nonlinear equations (Subroutines ZXSSQ or UNLSF from IMSL, Houston, TX). Figure 7, obtained from the data by using DISSPLA, shows that the calculated and measured values of drag reduction efficacy ratio λ/λ_0 *coincide* within limits of the experimental accuracy. This is confirmed by the root-mean-square deviation σ and the average deviation D listed in the table. D, in percent, is defined as

$$\% D = (100/n)\sum_i [(F_i^{\text{exptl}} - F_i^{\text{calcd}})/F_i^{\text{exptl}}] \qquad (27)$$

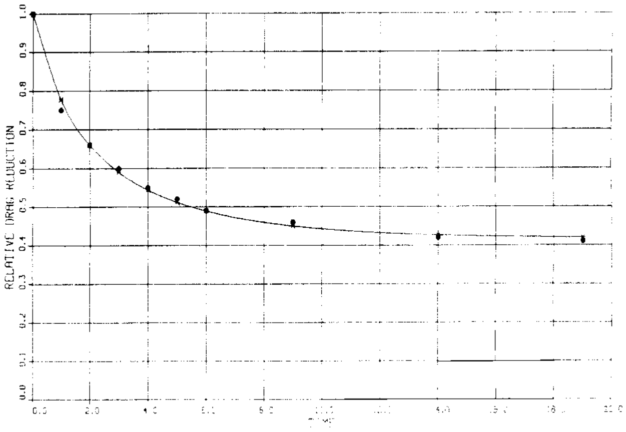

Figure 8. Time dependence of relative drag reduction efficacy λ/λ_0 for a partly nonpolymeric drag reducer, sample 6; for parameters see Table I. Experimental values: (●); calculated values: (—) and (*).

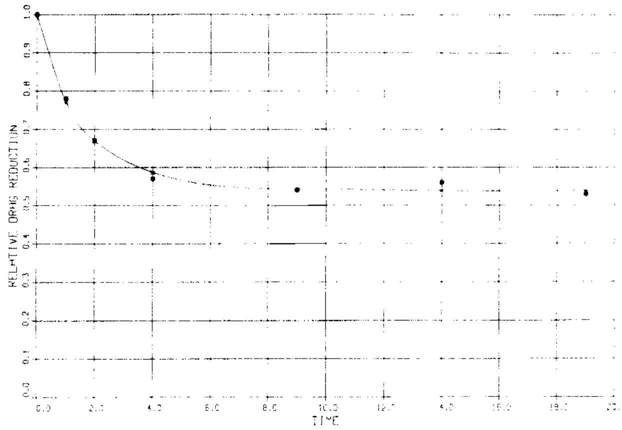

Figure 9. Time dependence of relative drag reduction efficacy λ/λ_0 for a partly nonpolymeric drag reducer, sample 8; for parameters see Table I. Experimental values: (●); calculated values: (—) and (*).

Characteristics of other drag reducers, the respective parameters in eq 26, and values of σ and D are listed in the same table. In view of our objectives, particularly interesting are the data when the drag reducer is not only a polymer. In Figures 8 and 9 we show the time dependence of λ, or the progress of degradation, for two polymer additives, samples 6 and 8, both containing asbestos fibers. There is an important difference between the two drag-reducing agents, since the efficacy of sample

6 is approximately twice that of sample 8. However, it is clear from the two figures, as well as from the data listed in Table I, that eq 24 is obeyed here equally well as for purely polymeric drag reducers. In fact, that equation works well for *all* drag reducers studied. This tends to support our claim that our mechanism of drag reduction is universal; we mean here of course the domain formation, while the specific way domains are formed by polymer chains has been discussed in connection with Figure 1.

It is evident from Table I that values of the parameters W and h are determined by molecular structures and compositions of drag-reducing agents. For instance, agents 2 and 3 have the same total concentration of the binary drag reducer, but we have twice the amount of PAM in agent 2. We find that PAM has more vulnerability points W than PGG and also that PAM degrades faster. Further, GXG degrades at many locations and fast, as can be seen from the results for agents 4 and 5. In fact, agent 5 degrades fastest of all, although it has a relatively high value of λ_0. By comparing agents 6, 7, and 8, we find that GXG again causes a high W value and also fast degradation (that is, very high h). We find that a given constituent of multicomponent drag-reducing agents behaves in a predictable way, always causing similar effects when present.

5. Some Concluding Remarks

There is no question that eq 26 represents very well the effect of time on drag reduction efficacy, this independently of the initial magnitude of λ, for pure and mixed drag reducers, purely polymeric as well as containing fibrous agents. From this and from the computations reported in section 3 we can infer also the following: lower b_p/b means not only higher drag reduction efficacy but also lower W and thus slower degradation. Thus, the criteria formulated at the end of section 3 for choosing agents with high λ should be also helpful for developing drag reducers with high shear stability.

W and h values listed in Table I not only prove the physical significance of these parameters but also provide us with a guidance for selecting constituents of multicomponent drag reducers and choosing their concentrations. Quite instructive here is the comparison of DR agents 7 and 9. Apparently, doubling the GXG increases the initial value λ_0 only little. The average number of vulnerability points increases (we have the same amount of the fibrous component and more of a degradable polymer), while the degradation rate h decreases, but not that much, and we conclude that using twice the amount of the polymer is not worthwhile.

Fibrous drag reducers can form easily domain walls along the flow direction, but only with difficulty walls perpendicular to flow. From this we infer that, for a fixed total concentration c_{total} of a drag reducer, λ will be higher if the reducer consists of both fibers and polymer chains rather than only of fibers. These and other conclusions from the present work will be analyzed further in future papers.

Given our parameter W, it is interesting to find out locations of scission points along a chain. We are performing computer simulations by molecular dynamics, following an adaptation of this procedure to polymeric systems by Cook and Mercer[69] and its use by us.[40] In agreement with our model, the scission points do not occur at random but are located near to the joints between flexible and nonflexible sequences within a chain.[70]

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