Water-Soluble Copolymers. 31. Effects of Molecular Parameters, Solvation, and Polymer Associations on Drag Reduction Performance

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ABSTRACT: The relationships between drag reduction performance and polymer parameters including chemical structure, molecular weight, hydrodynamic volume, associations, and solvent nature were examined using synthetic water-soluble copolymers. Copolymer models were tailored to be systematically responsive to changes in electrolyte addition and included polyelectrolytes, polyampholytes, hydrophobically modified polymers, and uncharged, hydrophilic polymers. Commercial poly(ethylene oxide) (PEO) and copolymers of acrylamide with the comonomers sodium 3-(acrylamido)-3-methylbutanoate (NaAMB), sodium 2-(acrylamido)-2-methylpropanesulfonate (NaAMPS), [2-(acrylamido)-2-methylpropyl]dimethylammonium chloride (AMPDAC), and diacetone acrylamide (DAAM) synthesized in our laboratories were tested for drag reduction effectiveness using a rotating disk and a tube flow apparatus. Hydrodynamic volume as determined by viscometry and light scattering was monitored in deionized water and 0.514 M NaCl for particular compositions and molecular weights. Drag reduction performance was greatly affected by the nature of polymer/polymer and polymer/solvent interactions, generally increasing with hydrodynamic volume. Enhanced drag reduction behavior observed for the associating DAAM copolymers is proposed to be due to changes in water structuring in turbulent flow.

Introduction

The reduction of drag in turbulent flow produced by addition of small concentrations of high molecular weight polymers has been studied for over 40 years.[1] Studies of polymers of varying structures have shown that drag reduction (DR) can be profoundly affected by changes in molecular parameters such as molecular weight, aggregation, or chain flexibility. However, a quantitative understanding of these effects has not yet been obtained and experimental studies involving changes in macromolecular properties have sometimes yielded conflicting results.[2-5]

The relationship between polymer coil size and DR effectiveness has been clearly demonstrated. However, it is unclear whether the parameter providing best correlation is molecular weight (MW), chain length (N), radius of gyration (R_g), or hydrodynamic volume (R_h or $[\eta]$).[4-7] The effect is complicated by the polydispersity of polymer samples and by the fact that polymer chemical composition also alters DR performance.[8-12]

The importance of molecular associations in DR experiments has long been recognized.[13] Researchers have reasoned that since high MW polymers are the most efficient drag reducers, higher MW aggregates might provide an even greater effect. Some researchers have suggested that macromolecular aggregates must be present for DR to occur.[14] They postulate that in cases where aggregates are not evident under laminar conditions, the high shear of turbulent flow might induce association. Other studies have indicated that drag reduction is possible in polymer solutions where no associations are present.[15] Results of studies of this type have shown that, in general, the presence of macromolecular associations enhances drag reduction when the association produces an aggregate of increased length or volume.[16-24] Kowalik et al.[17] reported that intrapolymer associations generally decreased performance, while interpolymer complexes in dilute solution increased drag reduction capability. Kim and co-workers[19-22] found that aggregates of collapsed structure occupying a smaller volume than expanded individual coils displayed lower DR effectiveness. Studies of associations of polymer molecules with dyes[23] or soaps[24] also revealed enhanced DR for expanded aggregates.

The effect of chain flexibility on DR effectiveness is also a function of polymer concentration, flow rate, and testing geometry.[4] Under some flow conditions flexible chains are more efficient, while under others rigid rods appear to perform better. Parker and Hedley[25] suggested that DR effectivenss depends not on chain structure or stiffness but rather on the maximum dimension of the coil at a given flow rate and its relation to the size of turbulent disturbances.

The effect of solvent is also related to polymer hydrodynamic volume. It has been shown that polymers more effectively reduce drag in good than poor solvents[26] and that polyelectrolytes are more efficient drag reducers in their expanded forms.[6] Hlavacek et al.[27,28] postulated that the effect of polymer on solvent structure may be more important than the effect of solvent on polymer conformation in drag reducing solutions. They postulated that DR results from changes in solvent structure rather than from the actions of individual polymer molecules, reasoning that polymer concentration is insignificantly small in comparison to solvent. Solvent stabilization and turbulence suppression may occur when solvent is "bound"[29] to the polymer chain or when a chain pervades two or more solvent microdomains simultaneously.

Certainly, such proposals merit strong consideration and further study since the effects of dissolved macromolecules on water structure have been well documented both in terms of bound water and in studies of polymer conformation and flow properties.[29-35] Hydrophobic bonding and formation of "icelike" structures in water surrounding hydrophobic sections of water-soluble polymers are integrally involved in the flow behavior of dilute solutions of water-soluble polymers. Under turbulent flow conditions, polymer/solvent interactions may be profoundly altered and this may have a direct influence on drag reduction performance.

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An earlier study of the DR performance of water-soluble copolymers synthesized in this laboratory[8] showed that slight modifications of polymer chemical composition could greatly affect polymer drag reduction performance. Drag reduction (DR) effectiveness was found to be a function of polymer coil dimensions that depend upon polymer structure, polymer/polymer interactions, and polymer/solvent interactions. The effects of molecular parameters are further examined in the present study using copolymer models with specific structural variations tested in solvents of varying ionic strength. The types of copolymers studied include uncharged, hydrophilic polymers (polyacrylamide), polyelectrolytes (poly[acrylamide-*co*-sodium 3-(acrylamido)-3-methylbutanoate]), polyampholytes (poly[sodium 2-(acrylamido)-2-methylpropanesulfonate-*co*-[2-(acrylamido)-2-methylpropyl]dimethylammonium chloride]), and hydrophobically modified acrylamide copolymers [poly(acrylamide-*co*-diacetone acrylamide)].

Experimental Section

Different molecular weight grades of poly(ethylene oxide) (PEO) were purchased from Union Carbide. Synthesis and characterization methods for homopolyacrylamide (PAM) and copolymers of acrylamide with sodium 3-(acrylamido)-3-methylbutanoate (NaAMB) and diacetone acrylamide (DAAM) were described in the previous study.[8,36,37] Synthesis and characterization of the polyampholyte model copolymers (ADAS) of [2-(acrylamido)-2-methylpropyl]dimethylammonium chloride (AMPDAC) with sodium 2-(acrylamido)-2-methylpropanesulfonate (NaAMPS) and terpolymers (ADASAM) of AMPDAC with NaAMPS and AM were also reported previously.[38,39]

Zero shear intrinsic viscosity, $[\eta]$, was obtained using four-bulb shear dilution viscometers and/or a Contraves low shear 30 rheometer. Solution studies were performed in 0.514 M aqueous NaCl solution containing 0.01% NaN_3 as a biocide at 25 °C. Classical light scattering studies were performed using a Chromatix KMX-6 low angle laser light scattering spectrophotometer utilizing a 2-mW He–Ne laser operating at 633 nm. Weight-average molecular weight, M_w, and second virial coefficient, A_2, were obtained for each copolymer. Specific refractive index increment, dn/dc, was determined from a Chromatix KMX-16 laser differential refractometer.

Quasielastic light scattering studies, yielding translational diffusion coefficient, D_0, and hydrodynamic diameter, d_0, were performed using the KMX-6 in conjunction with a Langley-Ford Model LFI-64 channel digital correlator. The apparatus was interfaced with a Hewlett-Packard 85 computer for numerical analysis. The autocorrelation function was evaluated following the method of cumulants.[47] Hydrodynamic diameter was calculated from D_0 using the Stokes–Einstein relationship and Flory's equivalent sphere model.[48]

Drag reduction measurements were performed in the rotating disk and tube flow testing systems described previously,[8] in the solvents specified. Solution preparation and data analysis were performed as in the previous study. Friction factors and Reynolds numbers were calculated from equations developed for rotating disk and tube flow.[40,41]

Results and Discussion

Copolymer Models and Solution Properties. Synthetic copolymer models with specific structural and molecular weight variations were employed to examine the effects of molecular parameters and solvent changes on hydrodynamic volume (HDV) and on drag reduction performance. Of particular interest were copolymers with clearly observed changes in HDV with addition of sodium chloride or urea. Structures of the polymers studied, along with brief descriptions of their solution properties, are shown in Table I. The number following the acronym in a sample name describes the feed composition during synthesis; experimentally determined mole percentages of the monomers in the final copolymer are shown in brackets. Table I lists values for zero shear intrinsic viscosity, $[\eta]$, obtained from low shear rheometry, weight-average molecular weight (M_w) and second virial coefficient (A_2) from classical low angle laser light scattering, and translational diffusion coefficient (D_0) and hydrodynamic diameter (d_0) from quasielastic light scattering for each sample.[8] Intrinsic viscosity data and light scattering data in deionized water and 0.514 M NaCl solutions are given for comparative copolymers. Associative polymer viscosities are given in urea solutions as well.

Two uncharged, hydrophilic homopolymers, poly(ethylene oxide) (PEO) and polyacrylamide (PAM), were included in the study for comparison with the copolymers. PEO samples of three different molecular weights ranging from 1.7 to 5.3 × 10^6 were obtained from Union Carbide. Acrylamide monomer was polymerized under controlled reaction conditions to provide homopolymers of 6.0 and 24.0 × 10^6 weight-average molecular weights, respectively. Both PEO and PAM show minimal change in HDV with added electrolytes.

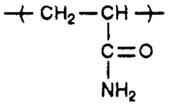
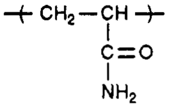
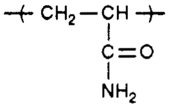
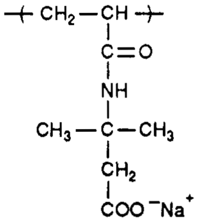
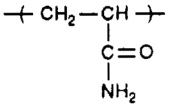
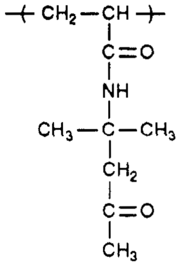
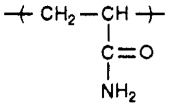
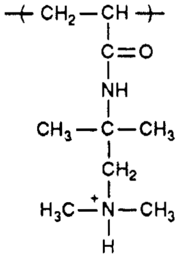
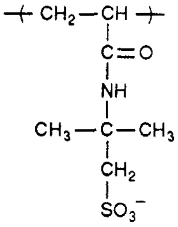
Two series of NaAMB copolyelectrolytes were synthesized with equal copolymer compositions but different molecular weights.[36,37] Comparative intrinsic viscosities for the low and high molecular weight series are shown in Table I. Conventional polyelectrolytes such as partially hydrolyzed acrylamide show decreased viscosity in saline in comparison to aqueous solution. The NaAMB copolyelectrolytes also exhibit this trend, but to a much smaller extent.[42]

The polyampholytes, ADASAM and ADAS series, studied were of somewhat lower molecular weight than the NaAMB polyelectrolytes (Table I).[38,39] Polyampholyte solution behavior is dictated by the presence of intra- and interpolymer ionic interactions. If there is a large excess of one charged species over the oppositely charged comonomer in a copolymer, the molecule behaves predominantly as a classical polyelectrolyte. At approximately equimolar ratios of positively and negatively charged moieties, however, the polymer exhibits behavior opposite that of a polyelectrolyte. As demonstrated in Table I, polyampholytes display greater viscosity in saline than in aqueous solution. In deionized water, the chain is collapsed due to strong intramolecular ionic bonding. When salt is added, the charges on the polymer chain are partially shielded by electrolyte by-ions and the chain expands. Both low charge density (ADASAM) and high charge density (ADAS) polyampholytes were studied. As shown in Table I, the low charge density polyampholytes are more expanded and exhibit larger hydrodynamic volumes than the high charge density polyampholytes.

The hydrophobically modified diacetone acrylamide (DAAM) copolymers were also of lower molecular weight than the PAM-4 or NaAMB copolymers. Copolymers of DAAM with AM have been shown to form reversible intermolecular associations that yield aggregates of greater hydrodynamic volume in saline solution than in deionized water.[43] The associations are thought to be due to hydrophobic or other cooperative interactions between DAAM moieties on different polymer molecules. Intramolecular associations, which result in decreased coil volume, also are present in DAAM copolymers of certain compositions. The extent and nature of these associations are dependent on solvent type.

Table I lists intrinsic viscosities for the DAAM copolymers obtained in aqueous, 0.514 M NaCl and 1 M urea solutions. Urea is known to be a water structure break-

Table I

sample	repeating units [mol %^{a}]			intrinsic viscosity [η], (dL/g)			light scattering^h			
				H_2O	0.514 M NaCl	1 M urea	$10^{-6}M_w$, g/mol^b	10^4A_2, (mol cm^3/g^2)^c	10^8D_0, cm^2/s^d	d_0, Å^e
WSR-301	$-\!\!\!+O-CH_2-CH_2+\!\!\!-$	[100]			16.0		5.3^f			
WSR-N-60K	$-\!\!\!+O-CH_2-CH_2+\!\!\!-$	[100]			13.0		4.0^f			
WSR-N-12K	$-\!\!\!+O-CH_2-CH_2+\!\!\!-$	[100]			6.4		1.7^f			
PAM-4	 $-\!\!\!+CH_2-\begin{array}[t]{c}CH\\\vert\\C{=}O\\\vert\\NH_2\end{array}+\!\!\!-$	[100]		35.0	34.0		24.0	3.0	1.3	3300
PAM-MC	 $-\!\!\!+CH_2-\begin{array}[t]{c}CH\\\vert\\C{=}O\\\vert\\NH_2\end{array}+\!\!\!-$	[100]		9.6	9.3		6.0	3.0	4.2	1600
	 $-\!\!\!+CH_2-\begin{array}[t]{c}CH\\\vert\\C{=}O\\\vert\\NH_2\end{array}+\!\!\!-$	 $-\!\!\!+CH_2-\begin{array}[t]{c}CH\\\vert\\C{=}O\\\vert\\NH\\\vert\\CH_3-C-CH_3\\\vert\\CH_2\\\vert\\COO^-Na^+\end{array}+\!\!\!-$								
NaAMB 5	[95]	[5]			22.0		24.0	2.4	1.9	2900
NaAMB 10	[90]	[10]			47.0		28.0	3.2	1.4	3300
NaAMB 10*	[90]	[10]			1.8					
NaAMB 25	[78]	[22]			52.0		25.0	3.9	2.5	2200
NaAMB 25*	[76]	[24]			6.3					
NaAMB 40	[66]	[34]			40.0		22.0	3.8	2.7	2000
NaAMB 40*	[64]	[36]			9.0					
NaAMB 100	[0]	[100]			8.4		3.6	4.5	2.9	1600
	 $-\!\!\!+CH_2-\begin{array}[t]{c}CH\\\vert\\C{=}O\\\vert\\NH_2\end{array}+\!\!\!-$	 $-\!\!\!+CH_2-\begin{array}[t]{c}CH\\\vert\\C{=}O\\\vert\\NH\\\vert\\CH_3-C-CH_3\\\vert\\CH_2\\\vert\\C{=}O\\\vert\\CH_3\end{array}+\!\!\!-$								
DAAM 15	[83]	[17]		15.0	18.0	13.0	7.5 (3.5)	1.3 (3.0)	1.2 (2.9)	3800 (1700)
DAAM 20	[80]	[20]		11.0	16.0	14.0	6.9 (4.3)	1.7 (2.6)	1.8 (3.1)	2600 (1600)
DAAM 25	[74]	[26]		7.0	8.4	8.5	3.9 (2.6)	2.1 (2.1)	2.9 (4.4)	1700 (1200)
DAAM 30	[71]	[29]		6.2	8.0		6.1 (5.9)	1.7 (3.0)	2.8 (3.3)	1700 (1500)
DAAM 35	[65]	[35]		3.1	3.4	15.0	3.6 (3.4)	4.0 (2.7)	3.3 (4.1)	1400 (1200)
	 $-\!\!\!+CH_2-\begin{array}[t]{c}CH\\\vert\\C{=}O\\\vert\\NH_2\end{array}+\!\!\!-$	 $-\!\!\!+CH_2-\begin{array}[t]{c}CH\\\vert\\C{=}O\\\vert\\NH\\\vert\\CH_3-C-CH_3\\\vert\\CH_2\\\vert\\H_3C-\overset{+}{N}-CH_3\\\vert\\H\end{array}+\!\!\!-$	 $-\!\!\!+CH_2-\begin{array}[t]{c}CH\\\vert\\C{=}O\\\vert\\NH\\\vert\\CH_3-C-CH_3\\\vert\\CH_2\\\vert\\SO_3^-\end{array}+\!\!\!-$							
ADASAM 2.5-2.5	[91.2]	[5.4]	[3.4]	4.5	14.0		7.4	2.9	1.7	2800
ADASAM 5-5	[85.6]	[8.2]	[6.2]	4.0	17.0		8.8	9.3	1.7	2700
ADASAM 5-10	[81.7]	[8.3]	[10.0]	24.0^g	20.0		10.0	2.4	1.1	4200
ADAS 10	[0]	[27.0]	[73.0]	20.0^g	8.0		9.5	1.6	2.5	2000
ADAS 50	[0]	[47.0]	[53.0]	4.0	9.0		2.7	4.5	4.0	1000

[a] Mole % in copolymer. [b] Weight-average molecular weight. [c] Second virial coefficient. [d] Translational diffusion coefficient. [e] Hydrodynamic diameter calculated from diffusional coefficient. [f] Viscosity average molecular weight. [g] Approximate values (polyelectrolyte effect). [h] Data for *b*, *c*, *d*, and *e* were determined in 0.514 M NaCl. Values in parentheses are for deionized water.

er[44,45] and thus interferes with hydrophobic bonding. In general, apparent intrinsic viscosities are greater in saline than in aqueous solution, indicating that addition of electrolytes promotes intermolecular association. However, relative viscosities in urea solutions vary with copolymer composition. For DAAM 15 (low hydrophobic content), [η] is lower in urea than in deionized water solution, indicating that intermolecular associations present in deionized water are likely eliminated in urea solution. For the copolymer containing the greatest amount of hydrophobe (DAAM 35), however, [η] is 5 times greater in urea than in deionized water solution. These findings indicate that intramolecular interactions are prevalent in aqueous solutions of the DAAM 35 copolymer. Urea interferes with the intrapolymer bonds and allows the coil to expand to yield a final [η] which is very similar to that of DAAM 15.

It is important to note that the association behavior described for the DAAM copolymers has been based on static or low shear solution measurements. In the high-shear, turbulent conditions under which drag reduction performance is measured, aggregation state and the dependence of association on copolymer composition may be very different. Shear-induced association or dissociation may occur which would greatly change hydrodynamic volume and drag reduction effectiveness. Studies of the solution behavior of the DAAM copolymers as a function of shear rate are presently underway in our laboratories.

Drag Reduction Studies. Effects of Changes in Molecular Structure. In order to examine individually the effects of molecular structure on drag reduction performance, percent drag reduction (% DR) data were normalized for polymer volume fraction, [η]C. Drag reduction efficiencies were thus determined for a number of copolymer types shown in Table I. Key features are summarized below; efficiency plots and details of the structural aspects are given in the previous paper in this series.[8] The most effective samples in those studies were those exhibiting the largest values of reduced DR at the lowest values of [η]C.

Efficiency plots show that incorporation of small mole percentages of charged comonomers in the polyelectrolyte (NaAMB 10) or polyampholyte (ADASAM 5-5) samples results in an increase in drag reduction efficiency in comparison to homopolyacrylamide (PAM-4), while incorporation of large mole percentages of charged groups serves to decrease DR efficiency (NaAMB 100 and ADAS 50). For the charged systems, relative DR efficiency increases with increasing hydrodynamic volume as exhibited by [η] and d_0 measured in saline solution (Table I).

The DAAM copolymers showed increasing DR efficiency with increasing incorporation of comonomer. This trend parallels the hydrophobicity of the copolymers and not hydrodynamic volume (Table I), indicating that intermolecular associations and polymer/solvent interactions exert a large influence on the DR properties of the DAAM copolymers. The importance of inter- and intrapolymer interactions is further illustrated by comparing the relative drag reduction efficiencies of the associating DAAM copolymers and the intramolecularly associating high charge density polyampholytes with the nonassociating polyacrylamide sample. The DAAM copolymers show enhanced DR efficiency in comparison to homopolyacrylamide (PAM-4), while the high charge density polyampholyte (ADAS 50) exhibits decreased DR efficiency.

Effects of Changes in Molecular Weight with Constant Structure. The effect of molecular weight on drag reduction behavior was studied by using polymer samples with identical chemical structures but different molecular weights. Figure 1a is a plot of friction factor vs Reynolds number for 3 ppm solutions of the three PEO samples measured in the rotating disk apparatus. As expected, when polymer concentration is held constant, friction reduction increases with increasing molecular weight. That is, measured friction factors are lowest for the high MW WSR-301 sample and highest for the low MW WSR-N-12K. In Figure 1b, polymer concentration was adjusted to yield an equal value of polymer volume fraction for solutions of the three PEO samples. At a constant polymer volume fraction, the three samples yield similar DR effectiveness curves regardless of molecular weight. Figure 1c shows a plot of DR efficiency for the polymers where % DR normalized for polymer volume fraction is plotted against [η]C. Again, similar DR efficiency curves are obtained for the different MW samples.

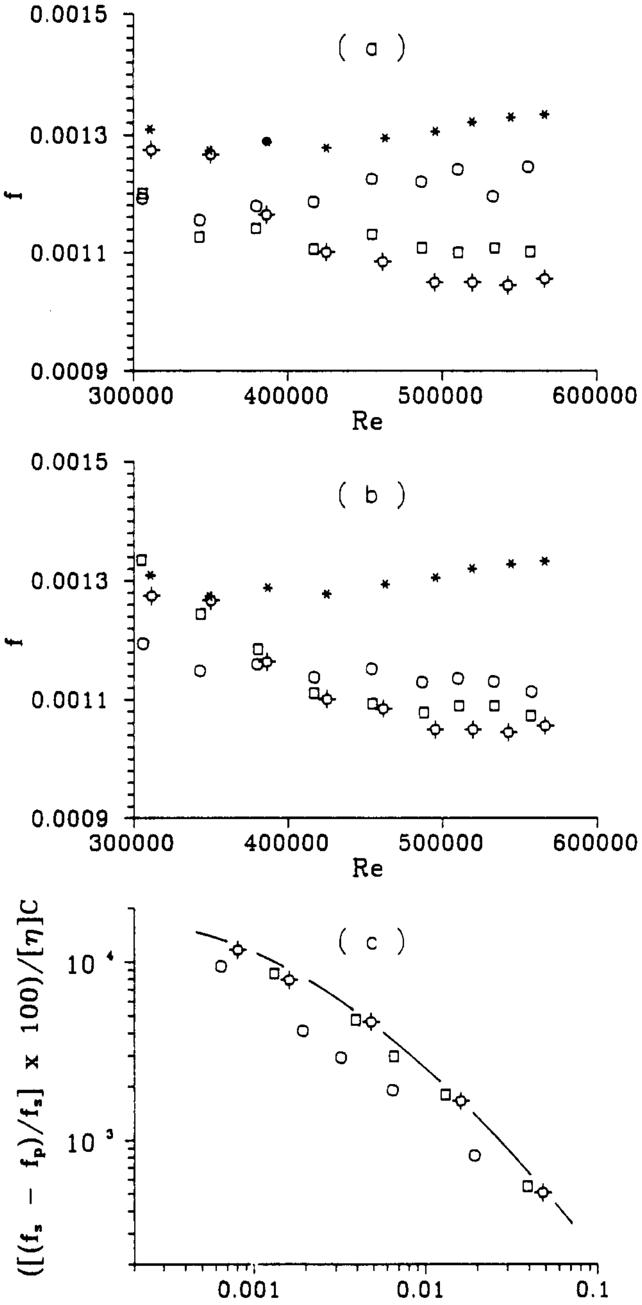


Figure 1. Drag reduction behavior of PEO polymers in 0.514 M NaCl tested by rotating disk: solvent (*); WSR-N-12K, MW = 1.7 × 10^6 (○); WSR-N-60K, MW = 4.0 × 10^6 (□); WSR-301, MW = 5.3 × 10^6 (-◇-). (a) Friction factor versus Reynolds number for 3 ppm PEO solutions. (b) Friction factor versus Reynolds number at constant polymer volume fraction, [η]C = 0.007. (c) Drag reduction efficiency measured at Re = 520 000 versus PEO polymer volume fraction.

The plots in parts b and c of Figure 1 show that the low molecular weight WSR-N-12K sample is slightly less effective than the two higher MW PEO samples, even at constant volume fraction. These findings indicate that there may be a low molecular weight limit for volume fraction correlations. Polymers with molecular weights

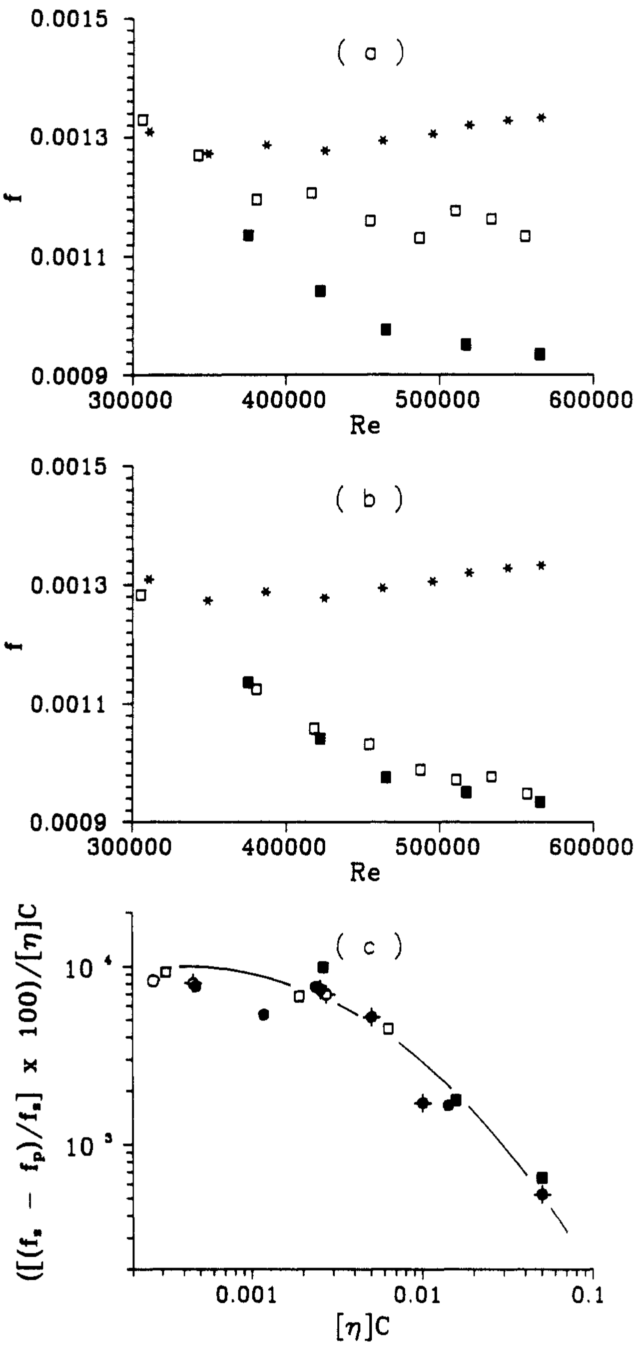


Figure 2. Drag reduction behavior of NaAMB copolymers in 0.514 M NaCl tested by rotating disk: solvent (*); NaAMB 10, $[\eta]$ = 1.8 dL/g (○); NaAMB 10, $[\eta]$ = 47 dL/g (●); NaAMB 25, $[\eta]$ = 6.3 dL/g (□); NaAMB 25, $[\eta]$ = 52 dL/g (■); NaAMB 40, $[\eta]$ = 9.0 dL/g (◇); NaAMB 40, $[\eta]$ = 50 dL/g (◆). (a) Friction factor versus Reynolds number for 3 ppm NaAMB 25 solutions. (b) Friction factor versus Reynolds number for NaAMB 25 solutions at constant copolymer volume fraction, $[\eta]C$ = 0.010. (c) Drag reduction efficiency measured at Re = 520 000 versus NaAMB copolymer volume fraction.

well below those in our experiments may not be effective in drag reduction. Molecular weight distribution, which is not addressed in this study, may also play an important role in these relationships.

The NaAMB copolymers with like compositions but different molecular weights exhibit trends similar to those displayed by the PEO samples. In parts a and b of Figure 2, f vs Re plots of low and high molecular weight NaAMB 25 samples are shown. In the first plot, polymer concentration is held constant and friction reduction increases with increasing molecular weight. In Figure 2b, polymer volume fraction is held constant and a single curve results. Plots for the other molecular weight NaAMB samples also show separate curves at constant polymer concentration but a single curve at constant polymer volume fraction. A drag reduction efficiency plot for the NaAMB copolymers with different molecular weights yields a single curve (Figure 2c).

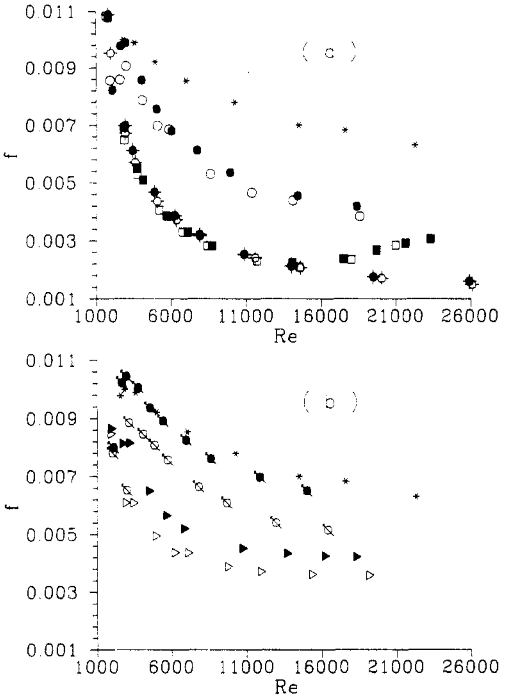


Figure 3. Friction factor versus Reynolds number for polymer solutions using deionized water (filled symbols) and 0.514 M NaCl (open symbols) solvents tested in tube flow. (a) Deionized water (*), 10 ppm PAM-MC solutions (●, ○), 3 ppm NaAMB 10 solutions (■, □), 10 ppm NaAMB 10 solutions (◆, ◇). (b) Deionized water (*), 5 ppm ADAS solutions (◣, ◺), 5 ppm ADASAM 2.5-2.5 solutions (▶, ▷).

The results of these studies indicate that for polymers with similar chemical structures, DR performance correlates well with polymer volume fraction even when polymer MW is varied. The fact that single efficiency curves are obtained for polymers of varying molecular weights when % DR is reduced for $[\eta]C$ (Figures 1c and 2c) indicates that normalizing for volume fraction also results in normalization for molecular weight effects. The relationships observed here are for polydisperse, high molecular weight copolymers ($M_w \geq 1 \times 10^6$). Further study of the effects of molecular weight distribution and of polymers of lower molecular weight should provide a better understanding of these correlations.

Effects of Changing Polymer Hydrodynamic Volume While Molecular Structure and MW Are Held Constant. The relationship between polymer hydrodynamic volume and drag reduction performance was further examined in a study of the DR behavior of copolymer models in solvents of varying ionic strength. In these studies coil volume was altered by changing solvent nature, while polymer molecular weight remained unchanged.

Figure 3a is a plot of f vs Re for 10 ppm solutions of a homopolyacrylamide sample (PAM-MC, $M_w = 6 \times 10^6$) in deionized water and 0.514 M NaCl measured in tube flow. The friction factor curves are virtually identical in aqueous and saline solutions. This is the expected result because the intrinsic viscosity of these uncharged homopolymers is very similar in the two solvents (Table I).

Figure 3a also shows the frictional reduction behavior of NaAMB 10 solutions in deionized water and 0.514 M

NaCl measured in tube flow. Unexpectedly, the curves are identical in aqueous and saline solutions. This is contrary to the behavior observed by others for traditional polyelectrolytes, in which it was found that the amount of drag reduction at a given Reynolds number and the shape of the friction factor curve varied with solution ionic strength.[4,6,7] Evidently, the relative insensitivity of these solutions to added salts[42] due to the chain-stiffening, intrapolymer interactions is manifested under test conditions.

The polyampholyte models, however, exhibit changes in DR performance when solvent ionic strength is changed. Plots of *f* vs Re of 5 ppm solutions in tube flow of the ADAS 50 (high charge density) copolyampholyte and the ADASAM 2.5-2.5 (low charge density) terpolymer in the presence and absence of added salt are shown in Figure 3b. In both cases, the polyampholytes show increased frictional reduction in saline solution. This is the trend expected for these polymers since the coil expands with increasing solvent ionic strength (Table I).

At equal concentrations, the reduction in friction exhibited by the low charge density polyampholyte is greater than that obtained with the high charge density polymer. Plots of DR normalized for polymer volume fraction (Figure 4c) show that drag reduction efficiency for the low charge density ADASAM polyampholytes is also greater than that obtained for the ADAS copolymers. Thus, relative drag reduction effectiveness of these copolymers correlates with polymer coil volume as evidenced by hydrodynamic diameters measured by quasielastic light scattering. As indicated by the data in Table I, the low charge density terpolymers are in general more expanded in saline solution than the high charge density copolymers.

For polyampholytes of a single structure, DR behavior in different solvents can be normalized by adjusting polymer volume fraction. Figure 4a is a plot of *f* vs Re obtained in the rotating disk apparatus for the low charge density polyampholyte, ADASAM 5-5, in deionized water and 0.514 M NaCl at different concentrations but constant volume fraction. Similar curves are obtained in both solvents. Figure 4b is a constant volume fraction plot for ADAS 50, a high charge density polyampholyte. Again, a single curve is obtained in both solvents when concentration is adjusted to give equal volume fractions. Results of the polyampholyte studies suggest that coil volume expansion due to polymer/solvent interactions and the presence of intra- and intermolecular associations are directly related to drag reduction effectiveness.

Effect of Associations and Solvent Nature. The effects of interpolymer associations and solvent nature were examined in studies of the DR performance of the hydrophobic PAM-*co*-DAAM copolymers in different solvents. In these studies, equal concentrations of copolymers of a single composition were dissolved in solvents that promoted varying degrees of association. In general, the drag reduction behavior of the DAAM copolymers in different solvents parallels aggregation behavior. Figure 5 shows *f* vs Re plots for DAAM copolymers tested in the rotating disk apparatus. Figure 5a is a plot of 3 ppm DAAM 15 solutions in deionized water, 1 M urea, and 0.514 M NaCl, respectively. Friction reduction is greatest in the saline solution in which associative bonding would be expected to be enhanced and least in the urea solution were hydrophobic association should be limited; thus, DR behavior does not correlate with the [η] values as it does with the other nonionic or polyelectrolyte models. Identical trends are seen in Figure 5b, in which data for 15 ppm DAAM 35 copolymer solutions are plotted.

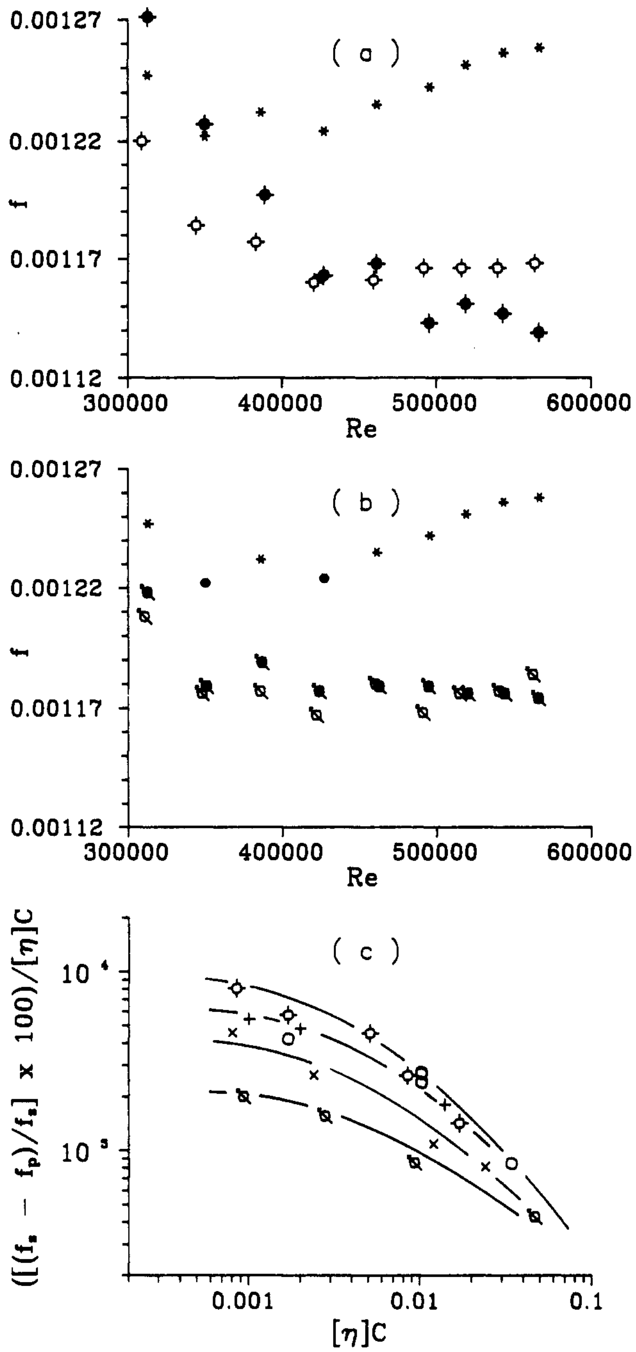


Figure 4. Drag reduction behavior of polyampholyte copolymer solutions using deionized water (filled symbols) and 0.514 M NaCl (open symbols) solvents tested by rotating disk. (a) Friction factor versus Reynolds number for ADASAM 5-5 solutions (◆, ◇) at constant copolymer volume fraction, $[\eta]C = 0.0015$. (b) Friction factor versus Reynolds number for ADAS 50 solutions (▲, △) at constant copolymer volume fraction, $[\eta]C = 0.009$. (c) Drag reduction efficiency measured at Re = 520 000 versus polymer volume fraction for low and high charge density polyampholytes in 0.514 M NaCl: PAM-4 (○); ADAS 10 (×); ADAS 50 (△); ADASAM 5-5 (◇); ADASAM 5-10 (+).

Results of these studies indicate that both polymer/polymer and polymer/solvent interactions are important factors in the DR behavior of hydrophobically modified polymers. Enhanced DR occurs in dilute solution when molecular associations are present. We suggest that at low shear, DAAM 35 and DAAM 15 exist as coils with a high degree of intramolecular association and water structuring. In turbulent flow, water structure changes as does polymer conformation. As clearly seen in Figure 5, addi-

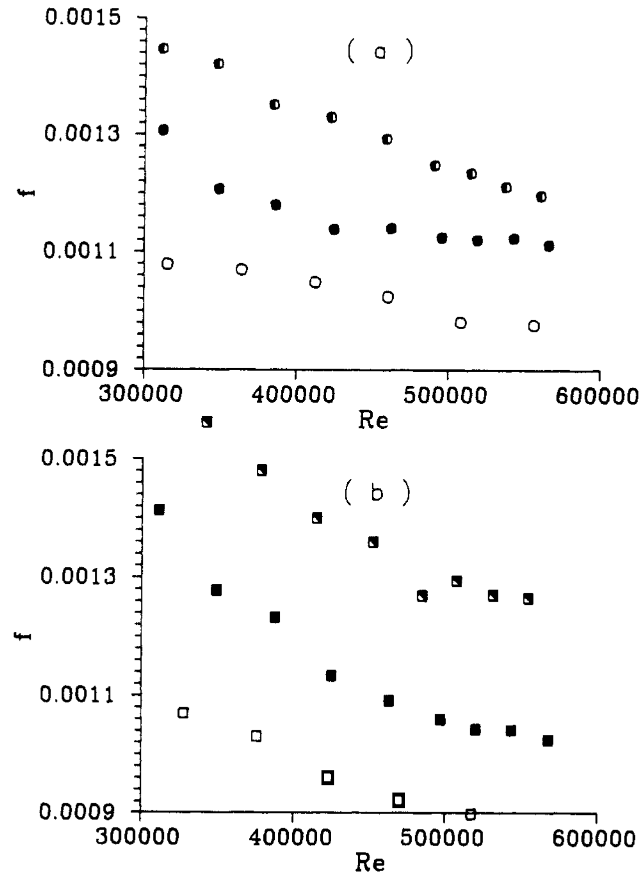


Figure 5. Friction factor versus Reynolds number for DAAM copolymers using various solvents tested by rotating disk: (a) 3 ppm DAAM 15 in 1 M urea (◐), in deionized water (●), in 0.514 M NaCl (○); (b) 15 ppm DAAM 35 in 1 M urea (◧), in deionized water (■), in 0.514 M NaCl (□).

tion of urea, a "water structure breaker," greatly decreases drag reduction performance; addition of NaCl which encourages hydrophobic bonding increases drag reduction. These findings, combined with the fact that hydrophobic groups incorporated into water-soluble polymers are known to elicit "icelike" structures in water in the vicinity of the polymer chain,^{33,34} indicate that solvent ordering or changes in solvent/polymer association in turbulent flow may be integrally involved in the drag reduction mechanism.

Conclusions

The results of these studies have demonstrated the importance of polymer chemical composition and structure in the DR phenomenon, especially in terms of polymer/polymer and polymer/solvent interactions. In general, increases in polymer hydrodynamic volume result in enhanced DR performance. However, DR enhancement is also observed with associating DAAM copolymers likely due to polymer/solvent interactions. The effects of solvent changes on DR performance vary with polymer chemical composition, structure, molecular weight, concentration, and flow rate. The degree to which solvent affects DR behavior depends on the strength of the polymer/solvent interaction. Changes in solvent that drastically change polymer hydrodynamic volume and solution viscosity likewise alter DR performance. If polymer hydrodynamic volume is similar in two different solvents, then DR behavior is also similar in the two solvents. Chain stiffening interactions, which may vary in different solvents, enhance DR effectiveness.

Results of these studies further demonstrate the complexity of the drag reduction phenomenon. DR effectiveness trends for different copolymer types as a function of molecular weight, coil volume, or solvent nature vary widely. Simple, normalization methods based solely on polymer coil dimensions for copolymers of different structures cannot accurately predict drag reduction behavior. Further experiments studying solvent structure, shear-induced phenomena, and polymer association behavior in relation to drag reduction performance are necessary to provide a better understanding of these effects.

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Registry No. (NaAMB)(PAM) (copolymer), 100047-18-5; NaAMB 100 (homopolymer), 40404-89-5; DAAM (copolymer), 25231-54-3; ADASAM (copolymer), 125847-98-5; ADAS (copolymer), 125847-99-6.

High-Resolution Solid-State Carbon-13 Nuclear Magnetic Resonance Study of Polybenzimidazole/Polyimide Blends

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ABSTRACT: Miscible blends of polybenzimidazole with an aromatic polyimide and a polyetherimide have been studied by high-resolution ^{13}C CPMAS NMR in the solid state. The observed resonance signals in the spectra of individual components of the blends have been assigned, and these assignments have been supported by interrupted decoupling experiments. The blending of PBI with polyimide induces a broadening and a downfield shift of the aromatic polyimide phthalimide carbonyl resonance with respect to that of the pure material. This difference between the spectra of the blends and those of the respective mechanical mixtures has been interpreted to be the result of the formation of specific hydrogen bonds between the PBI imidazole amine function and the polyimide phthalimide carbonyl function. Miscibility in the blend of PBI with the aromatic polyimide has also been confirmed by a study of the proton rotating frame spin-lattice relaxation behavior.

Introduction

A new class of high-performance, miscible binary blends of polybenzimidazoles (PBI) with several aromatic polyimides (PI) has recently been described.[1] Miscibility in these blends over a wide range of compositions has been demonstrated by differential scanning calorimetry as well as by dynamic mechanical analysis.[1,2] Infrared spectroscopic studies of these PBI/PI systems have indicated that misicibility in these polymers is related to a specific interaction involving the phthalimide carbonyl groups of polyimide and imidazolic amine groups of PBI.[3,4]

The aim of the present work has been to obtain evidence for misicibility and interchain interaction in PBI/PI binary blends by means of high-resolution solid-state ^{13}C CPMAS NMR.[5] A strong interaction between blend components such as hydrogen bonding should cause changes in the ^{13}C chemical shifts of those resonances involved in the interaction, in this case the phthalimide carbonyl with the bibenzimidazole amine. We report here composition dependent changes in the ^{13}C CPMAS line shape of the phthalimide carbonyl in blends with PBI and show that these changes are consistent with hydrogen bonding between the blend constituents. In addition, ^{13}C CPMAS NMR has been used to study proton spin diffusion in these blends,[6-10] and evidence for misicibility was obtained from an equality of the values of the proton rotating frame spin-lattice relaxation time $T_{1\rho}{}^{H}$ for the two blend components.

Experimental Section

The following polymers were used in the study: poly(2,2′-(*m*-phenylene)-5,5′-bibenzimidazole) [PBI, Celanese Corp. (T_g = 420 °C)], poly[2,2′-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane-*m*-phenylenediimine] [Ultem 1000, General Electric Co. (T_g = 220 °C)], and the condensation product of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride and 5(6)-amino-1-(4′-aminophenyl)-1,3,3′-trimethylindan [XU 218, Ciba-Geigy Corp. (T_g = 320 °C)]. Chart I lists the structures. These polymers

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