Enhancing the Shear Stability in Drag-Reducing Polymers through Molecular Associations[†]

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ABSTRACT: The presence of ionic interactions in polymers has been utilized to stabilize macromolecular assemblies in dilute solutions. The ionic aggregates display unique solution properties. Molecular associations in such polymers lead to higher viscoelasticity compared to that in the nonionic polymeric precursor. Such ionic aggregates are shown to lead to oil-soluble drag reducers with improved shear stability. In this study, we found that the drag reduction levels in the ionomer can be about twice as much as those in the nonionic polymeric precursor. On the other hand, a study of the shear stability indicates that the decay of the drag reduction activity for the nonionic polymer is more than twice that of its derived ionic polymer. Interestingly, the solution characteristics of ionic aggregates improve with increasing temperature, as manifested by enhanced drag reduction levels due to such a polymer, whereas for the nonionic polymer the reverse trend is observed. The findings of this work may have a significant bearing on the design of new generation drag reducers.

Introduction

The extent of drag reduction and shear stability are the two important factors deciding the efficacy of a polymer used for reducing the frictional losses under turbulent flow conditions. The extent of drag reduction increases as the molecular weight of the polymeric additive increases.[1] Poor shear stability has been a major drawback for the commercial application of the phenomenon of drag reduction. Therefore, there is a continuous search for innovative solutions to this problem of achieving higher levels of drag reduction without sacrificing the shear stability. Polymers based on α-olefins have been used extensively as drag reducers,[2] but their poor shear stability is a problem in the application of such polymers.[3] Several homo- and copolymers based on alkylstyrenes, alkyl acrylates, and methacrylates are also known to be effective drag reducers in dilute solutions.[4] Poor shear stability and high treatment levels are the inhibitive factors against the use of such polymers. Surfactants can also be used as the drag-reducing additives.[5] These are known to impart high drag reduction levels and are known to be shear stable as the associating type of superstructures of surfactants can break reversibly at high wall-shear stresses. However, such systems have found no commercial applications so far. Such additives suffer from the limitation that they are effective drag reducers in large concentrations and their drag reduction efficacy is sensitive to several other factors like the critical shear rates, the presence of ions, and temperature. Kowalik et al.[6] have demonstrated that polymers forming molecular complexes not only enhance drag reduction levels but also impart a higher resistance to degradation. However, they demonstrated this concept only for the pure solvents like xylene, which has little commercial relevance.

In this paper, we examine the potential of an ionomeric drag reducer in hydrocarbon solvent. The potential use of such drag reducers in commercial applications has been demonstrated by us recently,[7] where we have achieved 76% drag reduction at 20 ppm polymer concentration. Basically, the strategy adopted is to introduce ionic functionalities onto the backbone of a low molecular weight polymer which is highly soluble in commercial solvents like kerosene. Ionic clustering causes a considerable chain expansion around the overlap concentration, C^*, which increases the apparent molecular weight and hence the drag reduction effectiveness. The secondary interactions in such polymers are responsible for enhancing shear stability by breaking reversibly under the induced stresses, which would have caused scission of the backbone. Although, the ionic content, concentration, and solvent dependency on the dilute-solution behavior of ionomers has been studied extensively,[8] their potential as drag reducers has not been examined before, presumably because they display limited solubility in the hydrocarbon solvents of practical importance. In this study, we specifically examine a copolymer of an acrylic ester and sodium methacrylate. Since ionic associations play a key role in the performance of these drag reducers, it is studied in detail by light scattering, spectroscopy, and dilute-solution viscometry. We will also compare the drag reduction effectiveness and shear stability of the ionomer with those of a corresponding nonionic polymeric precursor.

Experimental Section

A copolymer of dodecyl acrylate and methacrylate acid was synthesized. A total of 97 parts by weight of dodecyl acrylate was copolymerized with 3 parts by weight of methacrylic acid by means of a standard emulsion polymerization method. The polymer from the emulsion was isolated by precipitation in cold methanol. The isolated polymer was dried under vacuum at 60 °C. The dried polymer was dissolved in toluene and was used as a nonionic drag reducer.

The sodium ionomer was prepared by neutralizing a 1% (w/v) solution of the polymer in tetrahydrofuran with sodium hydroxide. Phenolphthalein was used as an indicator for the complete neutralization of methacrylic acid. The total amount of sodium hydroxide required for the complete neutralization was 1.35 g/100 g of solid polymer. The ionomer thus formed was isolated by precipitation in cold methanol and dried under vacuum at 45 °C. The dried polymer was dissolved in toluene by swelling it in the solvent for 2 weeks. The solution was used as an ionomeric drag reducer.

Hydrodynamic radii were measured by dynamic light scattering. The light scattering measurements were carried by a BI 2030AT Model of Brookhaven Instruments.

FT IR measurements of ionic (IP) and nonionic (NIP) polymers were carried on a Perkin-Elmer 1600 series FT IR spectrometer. Spectra were scanned with a resolution of 4 cm^{-1}. An average of 16 scans was taken.

Viscosity measurements of the ionomer and its nonionic precursor were carried out in a Cannon–Ubbelohde dilution

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viscometer. Temperatures of the measurements were controlled within ±0.05 °C.

Drag reduction studies were carried out in a capillary flow apparatus, using kerosene as the carrier fluid. The apparatus is a cylindrical, jacketed vessel, fitted with a pressure gauge, an addition funnel, an air inlet, and an outlet in the form of a 30-cm-long capillary tube of 3.0 mm inside diameter. The test fluid could be pressurized up to a pressure of 3.5 kg cm^2 by means of a compressed gas.

Drag reduction was evaluated in terms of throughput increase by measuring the volumetric flow rate of kerosene and that of the polymer solution in kerosene at a given pressure. The percent throughput increase (TI) was calculated using the following equation:

$$\%\ \mathrm{TI} = 100(Q_2 - Q_1)/Q_1$$

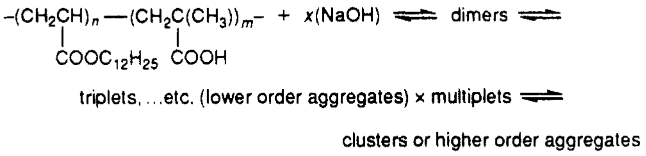
Here TI is the throughput increase and Q_1 and Q_2 are the volumetric flow rates of kerosene and the polymer solution in kerosene, respectively.

Polymer solutions were characterized for shear stability by determining the ratio of the throughput increase at a particular pass number to the initial throughput increase, at a wall-shear rate of around 16 000 s^{-1}. The solutions were rested for about 15 min after each pass.

The phenomenon of the breakage and formation of molecular associations in the IP was studied by shearing a 1% (w/v) solution of the polymer in methylene chloride by means of a magnetic stirrer, operating at the maximum shear rate of around 100 s^{-1}. The polymer was isolated at different intervals by reducing the temperature to about 5 °C and dipping a sodium chloride window in the solution. Solvent was evaporated by keeping the window in a draft of warm air. A thin layer of the polymer was formed on the sodium chloride window as soon as it was removed from the solution. FT IR spectra of the sheared polymer film were recorded.

Results and Discussion

Studies on Ionic Associations. Electrostatic interactions arising from sodium methacrylate can give rise to the multiplets or higher order aggregates of polymer chains. The various states of aggregations exist in equilibrium as shown below:



$$-(\mathrm{CH_2}\underset{\mathrm{COOC_{12}H_{25}}}{\underset{|}{\mathrm{C}}}\mathrm{H})_n-(\mathrm{CH_2}\underset{\mathrm{COOH}}{\underset{|}{\mathrm{C}}}(\mathrm{CH_3}))_m- + x(\mathrm{NaOH}) \rightleftharpoons \text{dimers} \rightleftharpoons \text{triplets, ...etc. (lower order aggregates)} \times \text{multiplets} \rightleftharpoons \text{clusters or higher order aggregates}$$

Depending on the number of ionic groups, their relative distribution on the backbone, and other thermodynamical factors governing the cooperativity between the interacting chains, the particular aggregation state in the above equation predominates. Accordingly, the resulting ionomer in solution can have a "gel type" structure for lower order aggregates of chains or a "compact" structure for higher order aggregates of associating chains. If the difference between the solubility parameters of the solvent and the ionic complex is large enough, the ionic complex with compact structure can be phase separated from the solution.[9] Therefore, for most of the solution properties, formation of a gel type complex is desirable. The degree of association is an important parameter that decides the structure of the complex. For instance, formation of higher order aggregates of associating chains in an ionic polymer with a high ionic content is more probable than that of lower order aggregates. The intrinsic poor solubility of the polymers with higher ionic contents may further deteriorate due to nonsolvation of the ionic associations by a nonpolar solvent.

The composition of our ionic copolymer was fixed by considering its solubility in hydrocarbon solvents and its performance as a drag reducer. Polymers synthesized with higher contents of sodium methacrylate could not be properly solubilized in solvents used in our study, and the polymers with lower sodium methacrylate contents were not found to be specifically effective as drag reducers. In this polymer, formation of lower order aggregates of ionic chains is likely to be more favorable than that of higher order aggregates, as the bulky dodecyl groups provide a large steric hindrance for the required "degree of fit" to be achieved for the large number of chains to associate. As described above, a low degree of association is likely to favor the formation of a gel type complex. The ionic interactions even among fewer chains are strong enough to influence the dilute-solution behavior of such polymers, as we will discuss in the following sections.

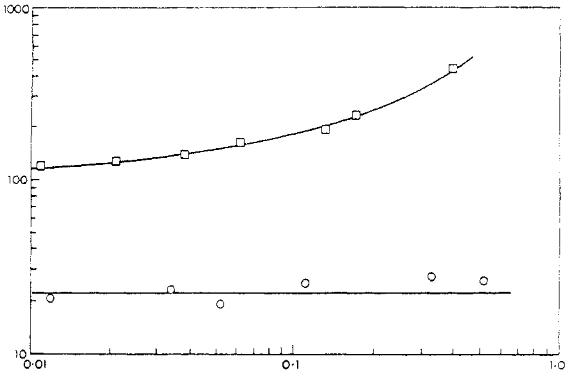


Figure 1. Comparison of hydrodynamic radii of the ionic polymer (□) and its nonionic precursor (○).

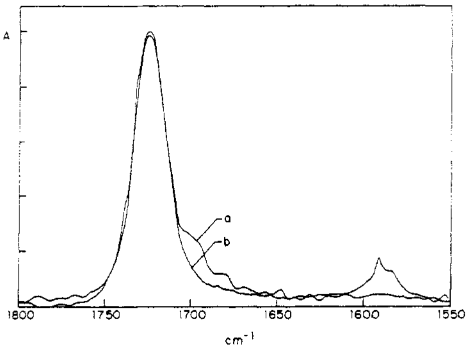


Figure 2. FT IR spectra of (a) poly(dodecyl acrylate–methacrylic acid) (NIP) and (b) the derived ionic polymer (IP).

The formation of clusters due to ion-pair interactions in dilute toluene solutions has been confirmed by dynamic light scattering data. As can be seen from Figure 1, the values of hydrodynamic radii for the ionic polymer are an order of magnitude higher than those for its parent nonionic polymer. The size of molecular aggregates or clusters for IP increases as more ionic contacts are established as the polymer concentration increases. In contrast to most of the theoretical predictions and experimental findings on the dilute-solution behavior of ionomers, IP appears to associate at polymer concentrations less than the overlap concentration: $C^* = 0.66$ g/dL for the NIP and 0.37 g/dL for the IP. Here with the usual convention C^* is expected to be on the order of the reciprocal of the intrinsic viscosity $[\eta] = 1.51$ for the NIP and 2.7 for the IP. This observation can be attributed to the residual ion pairs which are not solvated in the course of dilution. It is important to mention here that, at identical concentrations, the drag reduction levels due to the IP are higher than those due to the NIP even below the overlap concentrations.

Figure 2 presents the FT IR spectra of the ionic polymer and the nonionic polymer. Absence of the absorption band at 1699 cm^{-1} due to the C=O stretching frequency of

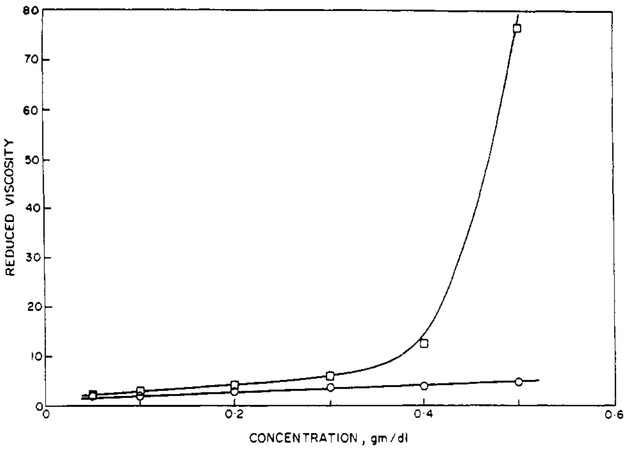


Figure 3. Reduced viscosity vs concentration for IP (□) and NIP (○).

methacrylic acid in NIP indicates the complete neutralization of carboxylic groups of NIP. In the spectra of IP, absorption bands at 1578 and 1584 cm^{-1} are due to the C=O stretching frequency of sodium methacrylate. The higher intensity of the absorption band at 1584 cm^{-1} compared to the band at lower wavenumber (1578 cm^{-1}) suggests the formation of multiplets of associating chains. The increased intensity of the absorption band at higher wavenumber can be explained on the basis of the increased force constant of the ionic bonds as the various chains associate.[10] Such ion pairs are not likely to be solvated in a hydrocarbon solvent of low dielectric constant like toluene and kerosene.

Figure 3 compares the reduced viscosity of the ionic polymer with the nonionic polymer (NIP) at various concentrations. It is evident from the results that the reduced viscosity–concentration relationship is linear for NIP, whereas, for IP, the reduced viscosity increases nonlinearly with concentration and, particularly at higher concentrations, the rise in reduced viscosity is rather rapid. The abrupt increase in the reduced viscosity at higher concentrations for IP is due to the formation of ionic aggregates. In dilute solutions, however, the ionic aggregates are likely to be smaller in size due to the lower probability of chain collisions or contacts compared to those in concentrated solutions.

Drag Reduction Studies. Throughput increase is a direct measure of drag reduction. Therefore the term drag reduction will refer to throughput increase in the course of this discussion. TI was measured at various concentrations ranging from 50 to 1500 ppm at a constant temperature, at a fixed solvent Reynolds number of 10 800. Effect of the variation of polymer concentration on drag reduction was studied (Figure 4). The experimental results shown in Figure 4 indicate that the extent of drag reduction increases with the increase in polymer concentration initially but then this increase levels out at polymer concentrations higher than 750 ppm.

A comparative study of drag reduction produced by IP and NIP reveals that TI observed due to IP is higher than that due to NIP at various polymer concentrations. The onset polymer concentration for drag reduction in the case of IP is 50 ppm compared to 250 ppm for NIP at a Reynolds number of 4850. This arises due to the higher apparent molecular weight of IP compared to NIP, as explained earlier.

The variation of drag reduction with Reynolds number is shown in Figure 5. With an increasing Reynolds number, there is an increase in the extent of drag reduction. Once again, IP shows a substantially higher throughput increase in comparison to NIP. The qualitative trend is in line with the accepted trends and qualitative models of drag reduction under turbulent conditions.[11]

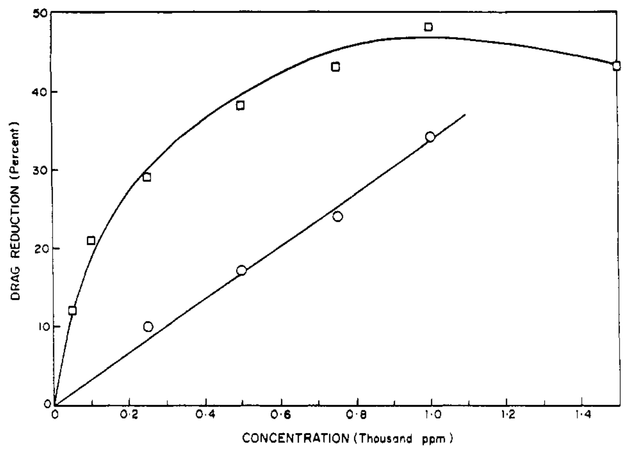


Figure 4. Variation of percent throughput increase with polymer concentration for ionic (□) and nonionic (○) polymers.

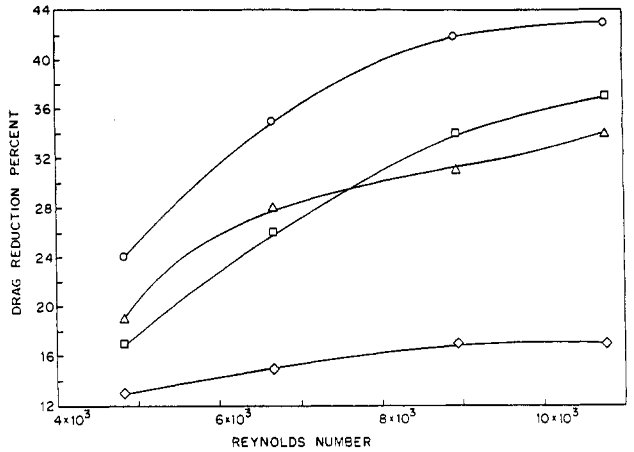


Figure 5. Variation of percent throughput increase with Reynolds number for ionic and nonionic polymers at various concentrations: (○) IP, 1000 ppm; (□) IP, 500 ppm; (△) NIP, 1000 ppm; (◇) NIP, 500 ppm.

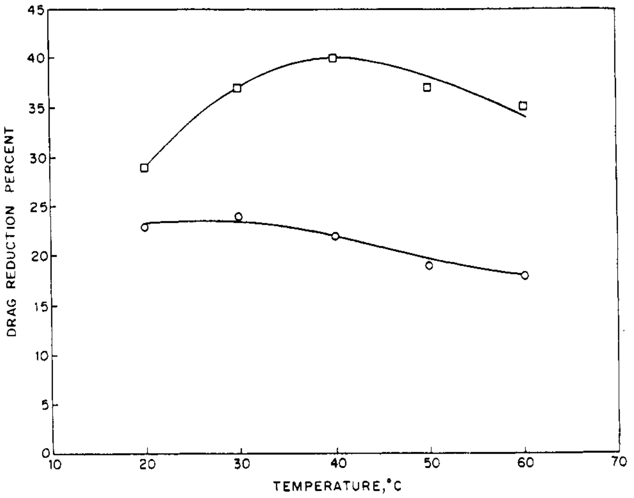


Figure 6. Variation of percent throughput increase with temperature for IP (□) and NIP (○) at 500 ppm polymer concentration.

For IP, the extent of drag reduction increases with an increase in temperature (Figure 6) up to a temperature of 40 °C, and beyond this temperature there is drop in drag reduction levels. On the contrary, for NIP, drag reduction improves only marginally when the temperature is increased from 20 to 30 °C, and at higher temperatures, a drop in drag reduction levels is observed. These observations on the effect of temperature are interesting per se,

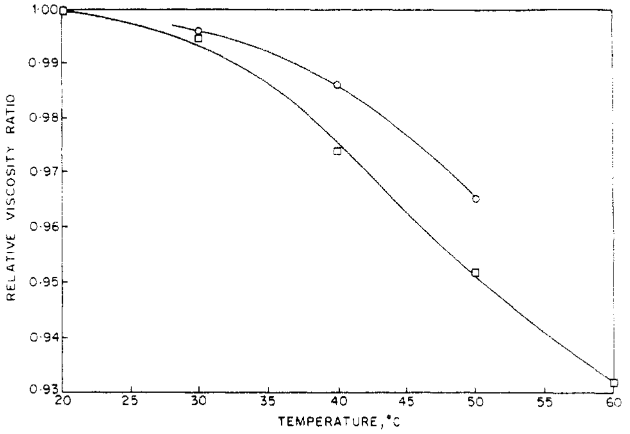


Figure 7. Decay of the relative viscosity with temperature for the ionic polymer in (□) toluene and (○) a toluene/kerosene mixture.

Table I
Differences in the Relative Viscosities between Toluene and a Toluene/Kerosene Mixture for IP and NIP at Various Temperatures

polymer	temp (°C)	differences in rel viscosities ($\eta_{\mathrm{rel,tol}} - \eta_{\mathrm{rel,tol/ker}}$)
IP	20	0.363
IP	30	0.349
NIP	20	0.090
NIP	30	0.097

since the majority of the studies on the temperature–drag reduction relationship[12] show that the extent of drag reduction reduces continuously with temperature.

This difference in the drag reduction behavior between the two polymers could be ascribed to their different solution properties. The relative viscosity of a polymer in a particular solvent is considered as the criterion for determining its solubility in that particular solvent system.[13] Kerosene or a kerosene/toluene mixture (1:1) constitutes a poor solvent for both the polymeric system and more so for IP at ambient temperature. This observation is supported by the larger differences in the relative viscosities between toluene and a toluene/kerosene mixture for IP than those for NIP (see Table I) at a particular temperature and concentration.

The polymer–solvent interaction improves with an increase in the temperature as the chains uncoil in a poor solvent. The phenomenon is manifested either by increasing the solution viscosity or by offsetting the decay in solution viscosity, which would have been observed in the case of a polymer dissolved in a good solvent.

These observations can be further substantiated by the results in Figure 7, which indicate a higher decay in the relative viscosity with temperature in toluene (good solvent) than in a toluene/kerosene mixture (poor solvent) for IP. Moreover, NIP, in comparison with IP, shows larger decays in a toluene/kerosene mixture. However, the decay of the relative viscosity in NIP in the two solvent systems is not significantly different, as can be seen in Figure 8. It should be noted that the drop in the relative viscosity for IP at higher temperatures could be due to the elimination of ionic associations also.

The decay in viscosity of the solution of a drag-reducing polymer in fluids and thus the drop in the drag reduction due to high temperatures could be offset by manipulating the solution characteristics of the drag reducer in the particular fluid.

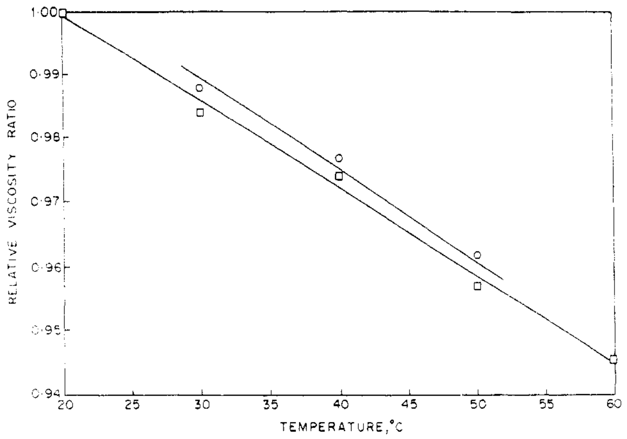


Figure 8. Decay of the relative viscosity with temperature for the nonionic polymer in (□) toluene and (○) a toluene/kerosene mixture.

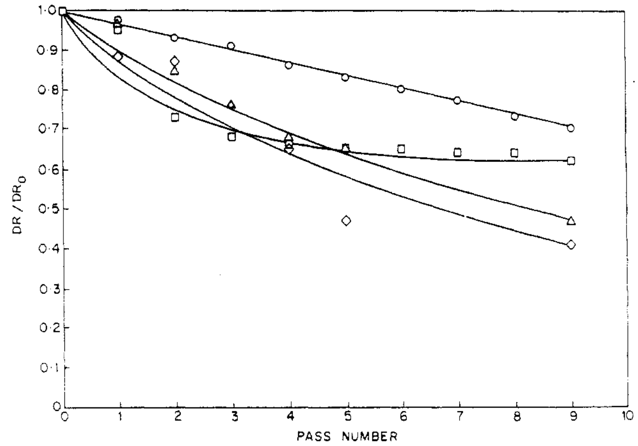


Figure 9. Shear stability of IP and NIP at a shear rate of 16 000 s^{-1}: (○) IP, 1000 ppm; (□) IP, 500 ppm; (△) NIP, 1000 ppm; (◇) NIP, 500 ppm.

Shear Stability. Degradation of long-chain molecules occurs under turbulent flow conditions due to high shear stresses present in such fields. Although there is some description of the factors that cause such a degradation in the literature,[14] there is no quantitative basis as yet for estimating the extent of degradation even in well-characterized monodisperse polymers, let alone for the complex associating polymers, as studied in this work.

The shear stabilities of IP and NIP are evaluated by determining the ratio of throughput increase at a particular pass number to the original throughput increase at polymer concentrations of 500 and 1000 ppm in kerosene, while the solutions are rested for about 15 min after each pass. The results are shown in Figure 9. IP retains about 70% of its initial value of TI at a polymer concentration of 1000 ppm as compared to 47% by NIP at the same polymer concentration after 10 passes at a wall-shear rate of around 16 000 s^{-1}.

The rate of decay of drag reduction effectiveness with respect to pass number can be represented by a simple empirical equation, which is commonly used in literature.[15]

$$\mathrm{TI}/\mathrm{TI}_0 = e^{-RN}$$

Here TI is the throughput increase at pass number N, and TI_0 is the initial throughput increase.

The results in Table II indicate that the retention of drag reduction effectiveness increases with an increase in the polymer concentration for either of the polymers. The higher shear stability at higher concentrations for either of the polymer systems could be due to the inhibition of chain stretching at higher polymer chain concentrations[16] and due to enhanced molecular associations in the case of IP.

The value of the decay coefficient (R) at a polymer concentration of 500 ppm is found to be half the value for

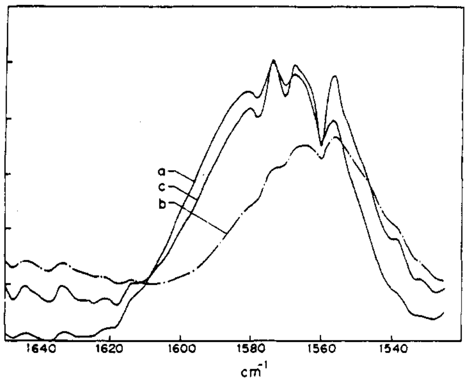


Figure 10. FT IR spectra for IP: (a) before shearing; (b) sheared; (c) rested after shearing.

Table II
Values of Decay Coefficient (*R*) and Initial Throughput Increase (TI_0) for IP and NIP at 500 and 1000 ppm

polymer	conc	R	% TI_0
IP	500	0.0532	37
IP	1000	0.0399	43
NIP	500	0.112	17
NIP	1000	0.0971	34

NIP (Table II), indicating a greater shear stability of IP than that of NIP (Table II). To explain the higher shear stability of the IP, we propose that the ionic clusters disintegrate in the process of shearing. However, these aggregates are formed again while the solution of the IP is rested after each pass. In other words, we can say that the intensity of forces responsible for chain degradation gets reduced in breaking the weaker associations which would have caused the scission of the backbone. A similar explanation has been offered in the case of the sodium salt of acrylic acid.[17] We substantiate these results by our FT IR study.

Figure 10 shows the FT IR spectra of the sheared IP and that of the sample rested after shearing. Before discussing these results, it is important to point out that rapid evaporation of a low-boiling solvent like methylene chloride would freeze the various molecular aggregates, as the chain mobilities are likely to reduce substantially. The various C=O stretching, absorption frequencies between 1580 and 1556 cm^{-1} could be attributed to the different sizes of the ionic aggregates. As mentioned earlier, the bands at higher wavenumbers are due to higher order aggregates than the bands at lower wavenumbers. As shown in the Figure 10, the intensities of the absorption bands for the sheared sample of IP, at the higher wavenumbers, 1580 and 1574 cm^{-1}, are relatively weaker than the intensities of the absorption bands at lower wavenumbers, especially when compared with the intensities and the widths of the absorption bands at the corresponding wavenumbers for the unsheared sample. This is obviously related to the breaking of ionic interactions and the formation of lower order aggregates in the process of shearing. The breaking of the ionic associations appears to be reversible, as the spectra of the sample rested after shearing appears to be similar to the one before shearing.

Specific comments need to be made about the observation on the reversibility of ionic structures in the magnetic stirrer experiments and on the irreversible loss in the drag reduction activity made in the capillary flow apparatus. The magnitude of shear rates in a magnetic stirrer experiment (calculated approximately by the procedure given by Holland and Chapman[18]) is about 100 s^{-1}, whereas the shear rates in the turbulent flow capillary apparatus are an order of magnitude higher, i.e., 16 000 s^{-1}. Thus, although the shear rates associated with the magnetic stirrer are not high enough to cause any polymer chain scission, these results could be correlated with the higher shear stability of the ionic polymer in terms of the recovery of the structure of the ionic aggregates. Thus, the reversible breaking of ionic aggregates under the induced stresses explains the higher shear stability of the IP. Nevertheless, at high shear rates, the irreversible breaking of carbon–carbon covalent bonds in the polymer backbone explains the irreversible loss in the drag reduction for the IP and the NIP at different pass numbers.

At this stage, a quantitative evaluation of degradation is difficult. Efforts are underway to study the exact mechanism of degradation of the ionic polymer under well-defined flow conditions. For now, it can be concluded that ionic interactions do play a strong role in reducing the extent of degradation, although not completely eliminating it.

Conclusions

Due to strong intermolecular associations, it is possible to get a higher drag reduction in polymers which associate than in their nonassociating counterparts. We have demonstrated this by using an ionic copolymer and its nonionic counterpart. Drag reduction levels improve with increasing polymer concentration, but at higher concentrations the extent of drag reduction levels out. The extent of drag reduction brought about by IP, at a particular concentration and Reynolds number, improves with an increase in the temperature. However, at temperatures above 40 °C, the extent of drag reduction reduces. The ionic polymer retains its drag reduction effectiveness for a longer time than the nonionic polymer. The retention of drag reduction activity improves as the polymer concentration increases. The conclusions of this work may have a significant bearing on developing the new generation, shear stable drag-reducing polymers.

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