

A New Drag-Reducing Polymer with Improved Shear Stability for Nonaqueous Systems

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Synopsis

Tri-*n*-butylstannyl fluoride exhibited 75% drag reduction in a capillary rheometer at 25,000 Reynolds number in hexane at 0.1% concentration. There was no loss of drag reduction from shear degradation after 300 cycles at 17,000 Reynolds number. Tri-*n*-butylstannyl chloride showed no drag reduction under these same conditions. Polyisobutylene, similarly examined, gave 72% and 69% drag reduction at 0.01 and 0.1% concentrations, respectively; but after 300 cycles at 17,000 Reynolds number, the drag reduction fell to 45% for the 0.1% solution and to 40% after only 100 cycles for the 0.01% solution. The effectiveness of tri-*n*-butylstannyl fluoride is explained by the formation of a linear polymer $\text{Sn}-\text{F}-\text{Sn}-\text{F}$ in which pentacoordinate tin is linked through fluorine bridges. The relative viscosity of tri-*n*-butylstannyl fluoride in hexane increased more rapidly with increased concentration and decreased more rapidly with increased temperature than similar solutions of polyisobutylene. This result is probably due to a shift in the average molecular weight of tri-*n*-butylstannyl fluoride.

INTRODUCTION

Toms¹ found that an abnormally low coefficient of friction was observed when small quantities of poly(methyl methacrylate) were added to chlorobenzene. Recently, Hoyt² reviewed the application of polymeric additives to fluid friction reduction with emphasis on aqueous applications. Other investigators³⁻⁵ have attempted unsuccessfully to apply friction-reducing polymers to nonaqueous systems. Crowley³ and Elata⁴ found that polymer degradation by shearing forces in pumps and pipelines prohibited practical application to operating systems. Little⁵ found that association colloids were sensitive to moisture and catalyzed degradation of petroleum-base hydraulic fluids.

Recently, Dunn and Oldfield⁶ observed that tri-*n*-butylstannyl fluoride, when dissolved in organic solvents of zero dipole moment, produced very viscous solutions. They theorized that dipole-dipole interactions due to the electronegativity difference between tin and fluorine rehybridize the tin atom to the pentacoordinate state with the tin atoms linked through fluorine bridges to produce a linear polymer of the type $\text{Sn}-\text{F}-\text{Sn}-\text{F}$. It was reasonable to believe that such a polymer, if of sufficiently high molecular weight, might exhibit friction reduction. Furthermore, although high shear stress might rupture the coordination polymer, it should re-form as soon as the stress is relieved.

This note describes initial work with trisubstituted stannyl fluorides and compares the results with those obtained using polyisobutylene, a polymer known to exhibit the phenomenon of drag reduction.

EXPERIMENTAL

The solubility of candidate compounds in nonpolar organic solvents was first determined by agitating sufficient compound with the solvent for 24 hr at room temperature to produce 0.2% (2000 wppm) solution. If solid remained, the solution was filtered and the solubility was calculated. If no precipitate remained, the solution was diluted to the desired concentration for viscosity and drag reduction measurements. Fresh solutions for shear stability were similarly prepared. The relative viscosities of the solutions were calculated from kinematic viscosities obtained using Cannon-Fenske viscosity tubes. These tubes operate at very low shear rates. The procedure followed was the American Society for Testing Materials (ASTM) Method D445. The relative viscosities of solutions were calculated because of the possible correlation with drag reduction.⁷

Drag reduction was obtained on a rheometer⁸ using Truebore precision glass capillaries 2 ft (60.96 cm) long with diameters in the range of 0.1 cm known to an accuracy of 0.001 cm. Pressure to ± 0.1 psi was read on pre-calibrated gauges. Flow time was measured to ± 0.01 sec and volumes were measured to ± 1 ml. A mercury switch attached to a flow-diverting elbow, placed at the exit end of the capillary, started and stopped the time and the volume measurements simultaneously. A 1-gallon solution reservoir tank, pressurized through diaphragm valves, was connected to the entrance end of the capillary through a ball valve. Shear stability was measured in a rheometer modified to recirculate the solution through the capillaries described above. Raw data were calculated to friction factor and Reynolds number by standard equations.⁹ Drag reduction was calculated from the friction factors:

$$\% \text{ D.R.} = 100 \times \left(1 - \frac{f_{\text{solution}}}{f_{\text{solvent}}} \right)$$

where f_{solution} = friction factor of the solution and f_{solvent} = friction factor of the solvent.

The stannyl halides were obtained commercially, and because their melting or boiling points were within $\pm 1^\circ\text{C}$ of literature values, they were used as received. The polyisobutylene was obtained from BASF Wyandotte Corporation under the trade name Oppanol 200. The manufacturer cites a viscosity-average molecular weight of 4.7×10^6 . All solvents were ACS grade.

RESULTS

The solubility data shown in Table I limited further interest to only tri-*n*-butylstannyl fluoride (TBuSnF) in pentane, hexane, heptane, methy-

TABLE I
Solubility Data^a

Solvent	Solubility, wppm		
	Tributyl- stannyl fluoride (TBuSnF)	Tricyclohexyl- stannyl fluoride (TChSnF)	Triphenyl- stannyl fluoride (TPhSnF)
Acyclic			
Pentane	>2000	—	—
Hexane	>2000	<100	<100
Heptane	1183	—	—
Octane	488	—	—
Isocyclic, Satd.			
Methylcyclopentane	>2000	—	—
Cyclohexane	>2000	<100	<100
Decalin	375	<100	424
Isocyclic, Unsatd.			
Cyclohexene	>2000	—	—
Tetralin	709	922	374
Aromatic			
Benzene	685	412	<100

^a Tri-*n*-propylstannyl fluoride (TPrSnF) was insoluble (<100 ppm), and polyisobutylene (PIB) was soluble (>1000 ppm) in hexane.

cyclopentane, cyclohexane, and cyclohexene. Therefore, the relative viscosities (Table II) and drag reductions (Table III) were obtained in only these solvents. The solubility parameter δ is used to predict and interpret solubility data in a semiquantitative manner. Generally, a substance is soluble in solvents over a range of 2δ . It is defined as follows:

$$\delta = (-E/V)^{1/2}$$

where E is the energy of vaporization and V is the modal volume of the solvent.

The relationship between two dimensionless parameters, the friction factor (f) and the Reynolds number (Re) may be used to describe one-dimensional steady-state flow of an incompressible fluid in a circular tube of constant diameter.¹⁰

In the region of laminar flow ($Re \leq$ ca. 2000), the relationship between these two dimensionless parameters is

$$f = 16/Re.$$

In the region of turbulent flow ($Re \geq$ ca. 3000), the relationship approximates the Blasius equation

$$f = 0.0791 Re^{-1/4}.$$

Virk proposed the relationship

$$f = 0.42 Re^{-0.55}$$

TABLE II
Relative Viscosities (η_{rel}) of TBuSnF and PIB Solutions
and Solubility Parameter of Solvents^a

Solvent	Polymer	Temp., °C	η_{rel}	Solubility parameter δ (25°C) ^b
Pentane	TBuSnF	30	6.32	7.05
Hexane	TBuSnF	30	3.36	7.30
Hexane	TBuSnF	37.8	2.18	
Hexane	TBuSnF	37.8	1.07 ^c	
Hexane	TBuSnF	37.8	1.007 ^d	
Hexane	PIB	30	1.70	
Hexane	PIB	37.8	1.63	
Hexane	PIB	37.8	1.064 ^e	
Heptane	TBuSnF	30	3.56	7.45
Methylcyclopentane	TBuSnF	30	2.02	8.4 ^f
Methylcyclopentane	TBuSnF	37.8	1.76	
Cyclohexane	TBuSnF	30	2.76	8.20
Cyclohexene	TBuSnF	30	1.16	—
Cyclohexene	TBuSnF	37.8	1.05	

^a Unless otherwise noted, polymer concentration was 1000 ppm.

^b Unless otherwise noted, data are taken from J. H. Hildebrand and R. L. Scott, *Solubility of Non-Electrolytes*, Reinhold Publishing Co., New York, 1950.

^c 750 ppm polymer.

^d 500 ppm polymer.

^e 100 ppm polymer.

^f Calculated from heat of vaporization, *Handbook of Chemistry and Physics*, 51st ed., and molal volume.

TABLE III
Drag Reduction^a

Solute	Solvent	Drag Reduction, %
TBuSnF	pentane	68
TBuSnF	hexane	65 ^b
TBuSnF	hexane	75
TBuSnF	hexane	76 ^c
TBuSnF	cyclohexane	68
TBuSnF	cyclohexene	29
TBuSnF	methylcyclopentane	73
TBuSnF	heptane	73
TBuSnF + TPrSnF	hexane	70 ^d
PIB	hexane	72 ^e
PIB	hexane	69

^a Unless otherwise noted, data are given for 20,000 Reynolds number, 1000 ppm solute concentration, and capillary diameter 0.1026 cm.

^b 750 ppm.

^c Capillary diameter, 0.0788 cm.

^d 500 ppm TBuSnF + 435 ppm TPrSnF (1:1 mole ratio).

^e 100 ppm.

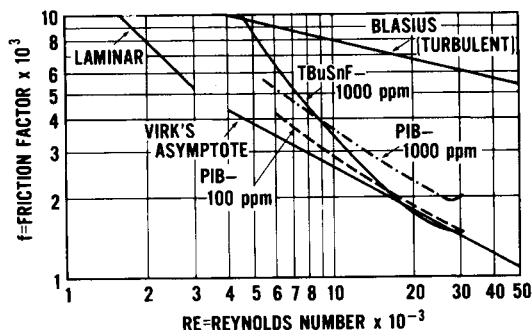


Fig. 1. Friction factor vs. Reynolds number.

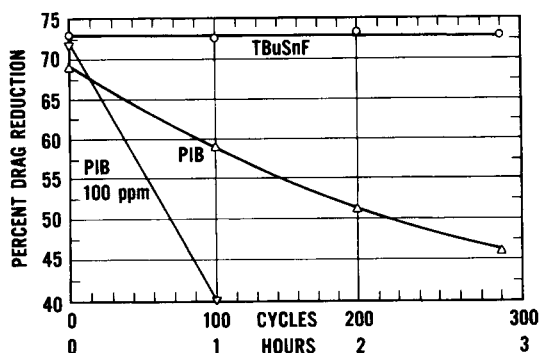


Fig. 2. Shear stability: $Re = 17,000$: 1000 ppm in hexane.

as the limit for the lowering of the friction factor by drag-reducing materials. A typical graph of friction factor versus Reynolds number for TBuSnF and PIB in hexane is shown in Figure 1, together with lines for laminar flow, turbulent flow, and the Virk asymptote for reference.

Drag reduction may be calculated at either a constant wall shear stress (which is proportional to pressure drop) or at a constant Reynolds number, but the result is of necessity not the same. In this note, drag reduction is calculated at constant Reynolds number. For solutions, the Reynolds number was calculated using the *solvent* viscosity.

A comparison of the shear stability of TBuSnF and polyisobutylene (PIB) is shown in Figure 2.

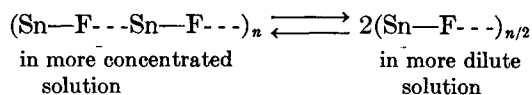
Friction factor measurements also were made on two solutions not mentioned in Table III. Solutions of tri-*n*-butylstannyl chloride (TBuSnCl) at 1000 ppm and TBuSnF at 500 ppm, both in hexane, gave essentially the same friction factors as the solvent at from 5000 to 30,000 Reynolds numbers.

DISCUSSION

The solubility of TBuSnF followed an expected trend, i.e., it was soluble in pentane and hexane ($\delta = 7.05$ and 7.30), less soluble in heptane ($\delta =$

7.45), and even less soluble in octane ($\delta = 7.55$) than in heptane. It was also insoluble in aromatic and certain isocyclic solvents of high δ value, i.e., in benzene ($\delta = 9.15$), tetralin ($\delta = 9.2$), and decalin (δ cis = 8.2 and δ trans = 7.4). However, TBuSnF was very soluble in methylocyclopentane ($\delta = 8.4$) and cyclohexane ($\delta = 8.20$). Thus, the solubility parameter is apparently not sufficient to predict the solubility of TBuSnF in these solvents.

The relative viscosities of the solutions showed two expected trends. As noted earlier,⁶ the relative viscosity of TBuSnF increased rapidly with an increase in concentration, i.e., from 1.07 to 2.18 at 750 and 1000 ppm, respectively. The relative viscosity of PIB, on the other hand, increased from 1.064 to only 1.63 with a tenfold increase in concentration. The rapid increase noted for TBuSnF may be attributed to an equilibrium of the type:



Some of the dipole-dipole fluorine-to-tin bonds could break, resulting in a lower average molecular weight in more dilute solutions. This effect, of course, cannot be observed with PIB.

The relative viscosities of both TBuSnF and PIB solutions decreased with increasing temperature. However, the relative viscosity of PIB decreased only slightly (from 1.70 to 1.63 at 30° and 37.8°C respectively), whereas TBuSnF decreased from 3.36 to 2.18 at the same concentration and temperatures. This result corroborates the concentration effect discussed above, since an increase in temperature would be expected to shift the equilibrium to the right. The ineffectiveness of TBuSnF at 500 ppm is also probably due to an average molecular weight too low to show drag reduction. However, when an equimolar concentration of TPrSnF was added, the latter dissolved, and frictional drag reduction was slightly higher than with 1000 ppm TBuSnF. This result may be explained by postulating a 1:1 copolymer of the two compounds. The low drag reduction of TBuSnF in cyclohexene may be explained as an interaction between the pi bonds of the solvent and fluorine, resulting in a lower molecular weight of the drag-reducing polymer. The ineffectiveness of TBuSnCl is probably due to the lower electronegativity of chlorine (3.0) compared to that of fluorine (4.0), resulting in fewer, weaker, or even the absence of, dipole-dipole bonds in the TBuSnCl solution.

Figure 1 shows that TBuSnF had a lower friction factor than PIB at Reynolds numbers from 8500 to 30,000. The effectiveness of PIB was improved at a lower concentration, probably because the increased viscosity of the 1000 ppm solution to some extent counteracted its effectiveness in friction factor reduction.

Figure 2 shows the shear stability of TBuSnF compared to the instability of PIB. No degradation of TBuSnF was noted after 300 shear cycles. PIB, on the other hand, degraded rapidly under the same conditions, and

even more rapidly at a lower (100 ppm) concentration. Other investigators¹² have previously reported the shear instability of PIB to mechanical degradation noted here. It is believed, however, that this is the first reported example of a completely shear stable frictional drag-reducing material. It is believed that the polymeric Sn—F—chain, if broken, reforms as soon as the shear stress is relieved.

Further work at higher shear rates is planned.

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