

Study of Oil Soluble Polymers as Drag Reducers

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This investigation was undertaken to find the most effective material which would reduce the friction coefficient in turbulent flow when added in small quantities to oil pipelines. For this purpose, a series of oil-soluble polymers, namely homopolymers and copolymers of alkyl methacrylates, alkyl acrylates, and alkyl styrenes were synthesized. Emulsion polymerization techniques were used. Commercially available alkyl methacrylate and alkyl acrylate monomers were used in the synthesis. Monomeric alkyl styrenes were synthesized and structures established prior to polymerization. Intrinsic viscosities were measured and viscosity average molecular weights were calculated for several of the homopolymers synthesized in this study. Reduction of frictional drag and resistance to shear degradation were measured by pumping a solution of the polymer in a hydrocarbon solvent through a pipe and recording the pressure drop across the pipe. Drag-reducing properties of several of the polymers were correlated in terms of their viscosity average molecular weights. Drag reduction of poly(isodecyl methacrylate) was studied in various hydrocarbon solvents. Drag-reducing behavior of polymers prepared in this study exhibited a strong dependence on molecular weight; increasing the molecular weight increased the drag reduction for a given polymer concentration and pipe size. Several of these polymers were found to be superior to commercially available polyisobutylene as drag reducers, especially in terms of shear stability.

INTRODUCTION

In the process of transferring a Newtonian fluid through a conduit, considerable energy may be expended to overcome friction encountered in movement of the liquid. When a liquid is pumped under pressure, friction pressure is apparent as a pressure drop along the conduit. Such pressure drops are particularly noticeable under conditions where the velocity of liquid has surpassed the critical limit for laminar flow. To compensate for the loss of energy due to friction pressure, additional energy must be consumed. Consequently, a decrease in friction loss would allow lower energy consumption or alternatively an increased flow rate under the original pumping conditions. Thus, a method whereby friction loss in the flow of liquids can be appreciably reduced is desirable. Also, it is economically profitable to industrial organizations engaged in movement of large volumes of liquid at high flow rates for considerable distance as in hydraulic fracturing of oil and gas wells.

A survey of published data indicates that considerable efforts have gone into searching for methods to reduce friction losses in turbulent fluid flow (1-3). Although polymers for use as friction reducing agents in water-based systems are widely known and have been extensively explored, a lack of comparable adducts for

hydrocarbon-based fluids has existed for some time. A few polymers, homopolymers of isobutylene (4), isoprene (5) (hydrogenated) and α -olefins with C_6 to C_{20} aliphatic chain (6) have been used as drag reducing additives in crude oil, both in laboratory tests and large-scale field trials. However, polyisobutylene is the only polymer that has received a certain degree of acceptance (7).

This paper summarizes the drag reduction properties of a series of homo- and copolymers of alkyl styrenes, acrylates, and methacrylates in hydrocarbon solvents. The effect of molecular weight of polymers on drag reduction is also reported. This study also shows solvent and shear effects on drag reduction properties of polymers.

EXPERIMENTAL

The parasubstituted alkyl styrenes were prepared by acylation and reduction of the corresponding alkyl benzenes to yield carbinols which were dehydrated with fused potassium hydrogen sulfate to the alkyl styrenes. Gas liquid partition chromatographic analysis showed the alkyl styrenes (8) to be greater than 99 percent pure. Structures of the prepared products were confirmed by infrared and nmr spectroscopy.

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Rohm and Haas Company supplied the following monomers: 2-ethylhexyl acrylate, isobutyl acrylate, isobutyl methacrylate, lauryl methacrylate and isodecyl methacrylate. Their purities were established by glpc while their structures were confirmed by spectroscopic methods.

Homo- and copolymers of alkyl styrenes, acrylates and methacrylates were prepared by emulsion polymerization (9). A standard procedure for emulsion polymerization is described below. Into a round bottom flask, fitted with a mechanical stirrer, a thermometer, a gas inlet tube, and a Liebig condenser equipped with a gas outlet tube, was placed triple-distilled water and the flask was flushed with nitrogen for 30 min. The flask was then charged with sodium lauryl sulfate, potassium persulfate, sodium bisulfite, and freshly distilled monomer. Polymerizations were carried out in a nitrogen atmosphere for a period of 3 to 6 h at 60°C. At the end of this period, the coagulated polymer was recovered by filtration and dried under vacuum.

Drag reduction properties of the polymers were evaluated by a friction reduction meter (10). The FR meter is a small, closed-loop pipeline apparatus designed for one point pressure sensing. A four-gallon volume of fluid is circulated through the loop at a mean velocity of approximately 18 ft/s at a flow rate of about 12 gal/min by a Robbins and Myers progressing cavity type pump powered by a 1/3 horsepower motor through a six foot length of 3/8-in. nominal diameter Schedule 40 stainless steel pipe. The pressure drop across the pipe is transmitted to a differential pressure transducer which converts the pressure change to a continuously variable output recorded by an x-y electronic recorder as a percent drag reduction. The base fluid is circulated through the loop and the recorder is adjusted to zero drag reduction. While static, i.e., no flow, the recorder is adjusted to 100 percent drag reduction. A solution of the polymer is then added to the loop reservoir while fluid is circulated and percent drag reduction is recorded. The solution is subjected to additional shear by introducing a mechanical shearing device operating at 20,000 rpm. In addition, measurements of the drag reducing properties of iDMA were made at various flow rates in a pipeline described by Melton and Malone (11) using a 3/4-in. nominal diameter test section. These data were scaled up to a 2.875 inch oil field pipe with a 2.441 in. I.D. using the procedure of Lord, *et al.* (12).

Approximate average molecular weights were calculated from the well-known Mark-Houwink-Sakurada equation. Solution viscosity measurements were made at constant temperature using Cannon-Ubbelohde Semi-Micro Dilution viscometers. Solvent efflux times were kept longer than 80 s by proper selection of viscometer size. It was assumed that for efflux times of this magnitude the effect of shear rate would be minimal; consequently, no shear corrections were applied to the data. Intrinsic viscosities were determined using the standard procedure of extrapolating viscosity numbers to infinite dilution. For the general class of poly alkyl styrenes, it was assumed that the presence and nature of the alkyl group had no effect on the molecular weight-

intrinsic viscosity relation. Therefore, it was possible to use the relation $(\eta) = 1.34 \times 10^{-4} M_v^{.71}$ which has been shown to be valid for polystyrene in toluene at 25°C (13). Chinai and Guzzi (14) have determined the relationship between intrinsic viscosity and molecular weight for poly (lauryl methacrylate) to be $(\eta) = 8.64 \times 10^{-5} M_v^{.64}$ in butyl acetate at 23°C. For our work, it was assumed that this equation was valid for polymers of the methacrylate and acrylate class under the same conditions of solvent and temperature.

RESULTS AND DISCUSSION

Often times hydraulic fracturing is used to stimulate oil and gas wells where a hydrocarbon fluid is used as the fracturing fluid. It is necessary that these fluids be pumped at high rates, under high shear conditions, with minimum pumping pressure loss to fracture hydrocarbon bearing rock formations. Drag reducers for hydrocarbon fluids have been used for years to meet these requirements; however, they were often less effective than desired. For example, the most commonly used additive was polyisobutylene which has a high degree of instability to mechanical shear. This investigation was undertaken to develop an effective drag reducer for hydrocarbon fracturing fluids.

Homo- and copolymers which were synthesized are listed along with their corresponding abbreviations in Table 1.

Drag reducing properties of several alkyl styrene polymers are shown in Table 2. A limited amount of these polymers were synthesized and no attempt was made to repeat the polymer synthesis in order to optimize molecular weight and drag reducing properties. Drag reducing properties of iBS were found to be much superior to the other alkyl styrene polymers listed. Intrinsic viscosity data indicated that this sample of iBS had an approximate molecular weight in excess of several million.

During this investigation tBS was the only commercially available alkyl styrene monomer; therefore, it re-

Table 1. Polymers Synthesized

Poly(n-propyl styrene)	nPS
Poly(isopropyl styrene)	iPS
Poly(n-butyl styrene)	nBS
Poly(isobutyl styrene)	iBS
Poly(sec-butyl styrene)	sBS
Poly(tertiary-butyl styrene)	tBS
Poly(isobutyl acrylate)	iBA
Poly(2-ethylhexyl acrylate)	2EHA
Poly(isobutyl methacrylate)	iBMA
Poly(isodecyl methacrylate)	iDMA
Poly(lauryl methacrylate)	LMA
Poly(tertiary-butyl styrene-co-styrene)	tBS-S
Poly(isodecyl methacrylate-co-lauryl methacrylate)	iDMA-LMA
Poly(2-ethylhexyl acrylate-co-isobutyl acrylate)	2EHA-iBA
Poly(2-ethylhexyl acrylate-co-isobutyl methacrylate)	2EHA-iBMA
Poly(2-ethylhexyl acrylate-co-isodecyl methacrylate)	2EHA-iDMA
Poly(isodecyl methacrylate-co-styrene)	iDMA-S

Table 2. Drag Reducing Properties of Alkyl Styrene Polymers in Kerosene

Polymer (0.06 wt percent)	Percent drag reduction	Intrinsic viscosity* (dl/g)
nPS	32	—
iPS	16	—
nBS	16	—
sBS	8	—
iBS	70	7.1

*At 25°C in toluene.

ceived the major emphasis. Poly (tertiarybutyl styrene) was synthesized under varying conditions of concentrations and temperatures to obtain polymers with differing average molecular weights as shown in Table 3. Increased molecular weight was shown to enhance its drag reducing properties. Table 4 shows data for this polymer at four different concentrations, the highest concentration gave the highest percent drag reduction. It is possible that for this polymer sample, the maximum drag reduction could have been obtained at a concentration between 0.04 and 0.15 weight percent. Shear stability properties of tBS and iBS were found to be much superior to polyisobutylene. This may be seen in Table 5 by comparing their initial and final percent drag reduction. The difference between the two values gives a relative comparison of their shear stability.

As shown above, the alkyl polymers in particular tBS and iBS, are effective drag reducing materials. It is believed that improvement in the polymerization techniques could have further improved their properties. However, it was decided to synthesize and investigate another class of polymers, the alkyl acrylates and methacrylates shown in Table 1.

Table 6 lists the drag reduction properties compared to approximate molecular weights for LMA, iDMA and 2EHA. The homopolymers of iBA and iBMA are not listed since they were found to have poor solubility properties in kerosene and therefore showed little drag reducing capabilities. As with tBS, increasing the molecular weight of LMA, iDMA and 2EHA improved their performance. However, the LMA sample with an approximate molecular weight of 14 million gave a higher percent drag reduction than the sample of 2EHA with an approximate molecular weight of 15 million. Also, the iDMA sample which had an approximate molecular weight of 20 million performed better than the sample of 2EHA with an approximate molecular

Table 4. Drag Reduction Properties of tBS vs Concentration in Kerosene

Concentration (wt percent)	Percent drag reduction
0.15	64
0.04	63
0.02	61
0.01	56

weight of 23 million. It is believed that since LMA and iDMA have larger oleophilic branches, they are more soluble in kerosene which contributed to their enhanced drag reduction. It can be seen from the data that each polymer was substantially more effective at the higher concentration, with the exception of the higher molecular weight sample of iDMA. This sample performed exceptionally well with a minimum concentration effect. This indicated to the authors that this sample of iDMA was close to the optimum molecular weight for maximum performance.

A series of copolymers was synthesized at various monomer feed levels, Table 7. No attempt was made to analyze the composition of the products. The copolymer of iDMA and LMA was the best performer and showed the least concentration dependence. However, this copolymer reduced drag only slightly better than the higher molecular weight sample of iDMA shown in the previous table. It was concluded this difference was not significant enough to warrant further evaluation of the more complex copolymer. Therefore, the homopolymer of iDMA was thought to be the most potentially useful drag reducer and was selected for further study. The concentration dependence of an optimum sample of iDMA was evaluated. These data shown in Table 8 indicate a decrease in percent drag reduction with increasing concentration, which is thought to be due primarily to viscosity effects.

Drag reduction and shear stability properties of polyisobutylene and iDMA were compared in four different solvents. In the crude oils, as well as the refined oils, iDMA was substantially more effective, especially in terms of shear stability as shown in Table 9. Solvent effects of iDMA were further evaluated in Table 10. These data indicate that iDMA performed better in the aromatic and chlorinated hydrocarbon solvents than in kerosene.

All data presented above were obtained at a constant flow rate on the small test loop described earlier. Drag reducing properties of iDMA were evaluated at several flow rates using the large scale test equipment referenced earlier. These data were scaled up to 2.441 in. I. D. pipe using the procedure described in Ref. (12) and

Table 3. Drag Reduction Properties of tBS vs Molecular Weight at a Concentration of 0.06 Wt Percent in Kerosene

$\bar{M}_n \times 10^{-6}$	Percent drag reduction	Intrinsic viscosity* (dl/g)
0.5	14	1.6
0.8	15	2.1
0.9	25	2.3
2.0	46	4.0
2.1	56	4.2
2.5	56	4.7
2.9	57	5.1
5.5	72	8.2

*At 25°C in toluene.

Table 5. Shear Stability of tBS and iBS Compared to Polyisobutylene in Kerosene

Polymer (0.06 wt percent)	Percent drag reduction		
	Initial	Final	Difference
Polyisobutylene	75	37	38
tBS	72	53	19
iBS	68	57	11

Table 6. Drag Reduction Properties vs Molecular Weight of Various Polymers in Kerosene

Polymer	Percent drag reduction		$\bar{M}_v \times 10^{-6}$	Intrinsic viscosity* (dl/g)
	0.03 wt percent	0.06 wt percent		
LMA	43	53	10.0	2.6
LMA	58	68	14.0	3.2
iDMA	67	72	20.0	4.1
iDMA	76	77	26.0	4.9
2EHA	44	56	15.0	3.4
2EHA	55	64	23.0	4.5

*At 23°C in butyl acetate.

Table 7. Drag Reduction Properties of Various Copolymers in Kerosene

Copolymer	Percent drag reduction	
	0.03 wt percent	0.06 wt percent
2EHA (50%)-iBA (50%)	48	59
2EHA (75%)-iBA (25%)	37	49
2EHA (25%)-iBA (75%)	37	47
2EHA (50%)-iBMA (50%)	51	61
2EHA (50%)-iDMA (50%)	58	67
iDMA (50%)-S (50%)	44	52
iDMA (66%)-LMA (34%)	79	80
tBS (50%)-S (50%)	64	68

are shown in Table 11. The friction pressure drop for kerosene was reduced more effectively by iDMA as the flow rate increased.

SUMMARY

Several alkyl styrenes, alkyl acrylates and alkyl methacrylates have been homopolymerized and copolymerized to high molecular weight polymers. These polymers were shown to reduce frictional pressure drop in hydrocarbon fluids while flowing through circular conduits. The percent drag reduction was found to be dependent upon polymer composition, molecular weight and concentration, as well as the solvent and its flow rate.

Several polymers investigated in this study, in particular, poly(isodecyl methacrylate) were found to be appreciably less sensitive to shear and more efficient in reducing frictional pressure losses of hydrocarbon fluids flowing in pipe than polyisobutylene. This has resulted

in the commercialization of poly(isodecyl methacrylate) as a drag reducing agent for hydrocarbon fluids in hydraulic fracturing operations.

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Table 9. Drag Reduction and Shear Stability Properties of iDMA Compared with Polyisobutylene

Polymer (0.06 wt percent)	Solvent	Percent drag reduction		
		Initial	Final	Difference
iDMA*	Kerosene	79	64	15
Polyisobutylene	Kerosene	75	37	38
iDMA*	QC-1156**	78	64	14
Polyisobutylene	QC-1156	76	31	45
iDMA*	Cardium***	69	55	14
Polyisobutylene	Cardium	67	34	33
iDMA*	Ellenberger***	71	50	21
Polyisobutylene	Ellenberger	69	29	40

*Intrinsic viscosity of 5.5 dl/g at 23°C in butyl acetate.

**QC-1156 is primarily an aromatic hydrocarbon with an API gravity of 22.5° and a boiling point in the range of 395-500°F.

***Crude oils.

Table 10. Drag Reduction Properties of iDMA (0.06 wt percent) in Various Solvents

Solvent	Percent drag reduction
Kerosene	70
Benzene	78
Toluene	76
1,1,1-Trichloroethane	78

Table 8. Effect of Increasing iDMA Concentration on Drag Reduction Properties and Solution Viscosity

Polymer concentration (wt percent)	Percent drag reduction	Viscosity* (centistokes)
0.0	0.0	1.53
0.03	80.0	1.80
0.06	78.0	2.03
0.12	74.0	2.67
0.24	70.0	4.07
0.36	66.0	4.33
0.48	62.0	9.59
0.60	58.0	13.64
0.72	55.0	18.54
0.84	52.0	24.96
0.96	48.0	33.04

*At 100°F.

Table 11. Drag Reduction Properties of iDMA at Various Flow Rates

Flow rate* bbl/min	v ft/s	N_{Re} general $\times 10^{-5}$	Friction pressure psi/100 ft		Percent drag reduction
			Polymer solution**	Kerosene	
8	23.0	1.9	8.3	30.0	72
10	28.8	2.3	11.9	45.0	74
20	57.6	4.7	36.0	160.0	78
40	115.0	9.4	109.0	575.0	81
50	144.0	12.0	155.0	870.0	82

*In 2.441 in. I.D. pipe.

**iDMA at 0.06 wt percent in kerosene.

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