

Thermo-responsive polymers for drag reduction in turbulent Taylor–Couette flow

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ABSTRACT: The addition of a small amount of high molecular weight polymer to a solvent can substantially decrease friction losses by approximately 80%. This phenomenon known as drag reduction (DR) is used extensively in oil recovery during hydraulic fracturing and in many other applications to reduce the pumping costs. However, because of long chain length, these polymers get adsorbed on the surface of reservoir, diminishing the effectiveness of fracking. In the current study, a thermo-responsive polymer, i.e., poly(N-isopropylacrylamide) (PNIPAM) is investigated as a drag reducing agent (DRA), which collapses reversibly above 33 °C known as lower critical solution temperature (LCST), thereby preventing it from getting adsorbed beyond this temperature. Free radical polymerization was used to synthesize the PNIPAM and a Taylor–Couette (TC) setup with a rotating inner cylinder was utilized for measuring the DR. The effect of concentration, Reynolds number (Re), and temperature on DR were studied and a maximum of 50% DR was observed at 400 PPM concentration. PNIPAM demonstrated significant decrease in DR beyond LCST, validating its thermo-responsive nature that could be beneficial for DR in oil recovery or in providing a control modality to DR technologies. DR versus temperature for PNIPAM solution (500 PPM) at $Re = 100,000$ demonstrating responsive behavior with temperature © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44191.

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INTRODUCTION

Drag reduction (DR) in turbulent flow using high molecular weight polymers, known as drag reducing agent (DRA), has been a field of intensive research.^{1–3} Utilization of these long-chain polymers at a very low concentration as additives can significantly reduce the pressure drop, leading to substantial cost and energy savings.⁴ Because of these benefits, DRA has gained wide attention in fluid transportation pipelines and has enhanced oil recovery such as in hydraulic fracturing.⁵ Polyacrylamide (PAM) is the most commonly used DRA for this purpose and has been studied extensively in the past.^{6,7} Pipe diameter (d), $Re (=ud/\nu)$; where u is the fluid velocity and ν is the fluid kinematic viscosity), DRA concentration and DRA molecular weight have been reported to be the significant parameters affecting DR in a pipe flow.^{8–10} Several theories have been postulated in the last few decades to explain the mechanism of DR by polymers.⁷ All these theories revolve around a major idea that the long-chain polymers are extended in high shear rate zones, leading to enhanced elongational viscosity in this extended state, which interacts with the microvortices in

turbulent flow and diminishes the energy required to grow.^{8,11} Although the mechanism behind DR is not completely understood yet, it is well acknowledged that considerably high molecular weight or long chain length of the polymer is one of the key requirements for DR.^{12,13}

Because of the low permeability of the shale gas reservoirs, hydraulic fracturing is a commonly used well-stimulation technique (to achieve improved recovery rate) in which a fracking fluid is injected at high pressure into wellbore.¹⁴ This fracking liquid consists of sand, proppants, and high molecular weight polymers as DRA. However, the conventional long-chain polymers used as DRA in fracturing gets adsorbed on the surface, reducing the permeability of reservoirs and requires cleanup procedures with the help of oxidizers to break the adsorbed polymers.^{15,16} Using a polymer that gets degraded into a short chain length with some trigger could be a potential solution to decrease the adsorption of these polymers.

Kot *et al.*¹⁶ introduced some weak links in the polymer chain which degrades with increase in temperature, narrowing the chain length. However, the degradation was irreversible, making

the polymer cost ineffective. Responsive polymers that could collapse reversibly with a trigger such as pH or temperature could be a potential solution to overcome this limitation. Thermo-responsive polymers exhibit reversible shrinkage of polymer chains with change in temperature. These polymers drastically transits from its hydrophilic nature to hydrophobic nature at a temperature, known as lower critical solution temperature (LCST). Poly(N-isopropylacrylamide) (PNIPAM) is a widely known thermo-responsive polymer with an LCST of 32 °C.¹⁷ The thermo-responsive nature in PNIPAM arises from the balance between entropy and enthalpy term in Gibbs free energy. The polar groups in PNIPAM form hydrogen bonding with the water molecules, which leads to negative ΔH (enthalpy) in free energy (ΔG).

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

This requires reorientation of PNIPAM molecules, thereby decreasing the entropy of mixing (ΔS) making the second term positive. For the polymer to be soluble, Gibbs free energy in eq. (1) needs to be negative. Below LCST, because of small temperature, the first term dominates and because of negative ΔG , the polymer is soluble in water. However, with an increase in temperature, the second term starts dominating, leading to positive ΔG above the LCST, and in turn precipitation of the polymer.¹⁸ Further, this change in polymer solubility is reversible, that is, cooling the solution back below 32 °C will lead to solubility of PNIPAM in water again.

Since high chain length is an important criterion for a polymer to show DR, PNIPAM can be easily synthesized using free radical polymerization to achieve longer chain length, qualifying them as a potential DR candidate.¹⁹ Murnick *et al.*²⁰ studied PNIPAM in a laminar flow and reported maximum DR of 30%. However, this study was not extended to a turbulent regime.

Pipe/Channel flow is the commonly used platform for testing the drag reducing additives.²¹ However, synthesizing polymers at a lab scale is challenging as a large amount of polymer is required to test for DR properties in a channel flow. Taylor–Couette Flow (TC) setup can overcome this constraint because of its requirement of less fluid volume and has been identified as a reliable platform for measuring DR.^{22,23} Hence, in the present investigation, a TC setup consisting of two concentric cylinders was utilized to measure the DR. High Re TC flow is a turbulent fluid motion in an annular gap because of rotation of either one or both of the concentric cylinders. Considerably high Re ($\sim 400,000$) can be easily achieved by simply rotating either of the cylinders at high speed.²⁴ Drag can be inferred from the torque acting on either inner or outer cylinder using a torque sensor or load cells. Torque in this setup can be nondimensionalized using the following expression²⁵:

$$G = \frac{T}{\rho v^2 L} \quad (2)$$

where G is the nondimensional torque, ρ is the fluid density, v is the kinematic viscosity, and L is the length of inner cylinder. Drag reduction (DR %) is then calculated from the difference between skin friction coefficient (c_f) of pure solvent and DRA solution by the following equations:

$$c_f = \frac{G}{Re^2} \quad (3)$$

$$DR\% = \frac{c_{f,w} - c_{f,s}}{c_{f,w}} \times 100 \quad (4)$$

Here, $c_{f,w}$ is the skin friction coefficient of water and $c_{f,s}$ is the skin friction coefficient of DRA solution.

Although significant research has been conducted on DR in past 60 years, thermo-responsive polymers have not been looked into as a DRA in turbulent flow. Employment of responsive polymer as a DRA leads to tailored DR, which could be easily controlled by an external stimulus, such as temperature. The current investigation studies the effect of PNIPAM on DR in a turbulent TC Flow. The effect of Re , temperature, and polymer concentration is investigated. Further, the reversible nature of these responsive polymers on DR is also verified.

EXPERIMENTAL

Materials

All the chemicals were purchased from Sigma-Aldrich Chemicals (Oakville, ON, Canada). *N*-isopropylacrylamide (NIPAM) was purified in benzene and recrystallized in hexane prior to use. Ammonium persulfate (APS) and tetramethylethylenediamine (TEMED) were used as such.

Polymer Synthesis and Characterization

Conventional free-radical polymerization using redox initiation was used to synthesize the PNIPAM in an aqueous media in an inert environment at 20 °C. APS [(NH₄)₂S₂O₈] was used as an initiator, whereas TEMED was used as an accelerator. In a round bottom flask, 0.45M solution of NIPAM in DI water was prepared by stirring for 10 min. About 0.2 mol % (% of NIPAM) APS was separately dissolved in 2 mL of DI water and then added to the monomer solution. In the final step, 10–15 μ L of TEMED was added, followed by immediate sealing of the flask. After degassing the flask by purging with N₂ for 30 min, the solution polymerization reaction was maintained by stirring it for 24 h. The polymer solution was then purified by dialysis, using membrane tubing with a molecular weight cutoff of 6000 to 8000 g/mol to remove the unreacted monomers and initiator. After 48 h of dialysis, the solution was then freeze dried for 3 days.

Gel Permeation chromatography was used to determine the molecular weight of PNIPAM. LCST of the PNIPAM was determined using a UV-vis spectrometer by measuring transmittance of 400 PPM aqueous solution of PNIPAM at 500 nm. Transmittance was continuously recorded by the spectrometer at a heating rate of 0.5 °C/min with temperature range from 20 to 40 °C. The viscosity of PNIPAM solution at desired concentrations was measured using a Rheometer (*Anton Paar, RheolabQC*) by varying the shear rate from 1 to 1000 s⁻¹ at different studied temperatures. Two repeat viscosity measurements were conducted for each sample and there was no deviation observed in the acquired readings (viscosity measured up to two significant digits).

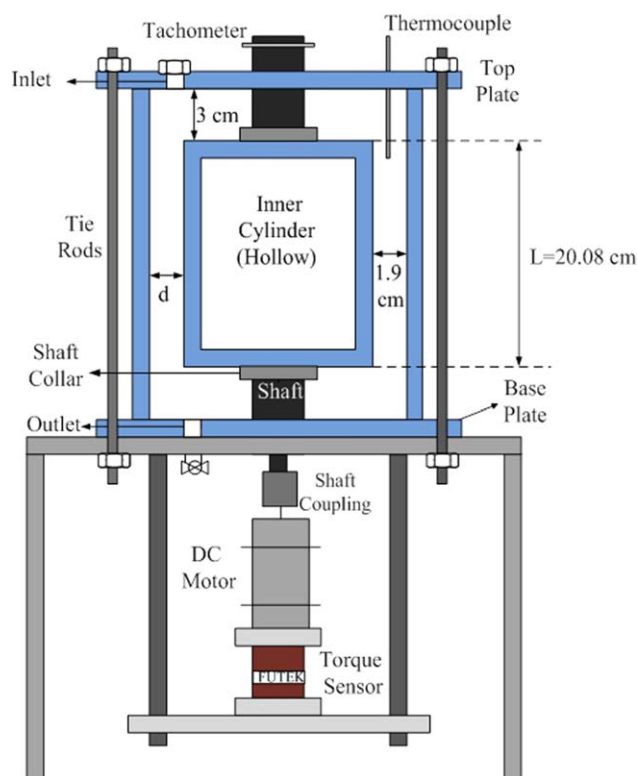


Figure 1. Schematics for Taylor-Couette setup for measuring drag reduction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Measurement of DR

DR was measured using a TC setup with a stationary outer cylinder and a rotating inner cylinder, both the cylinders fabricated from acrylic (Figure 1). The following parameters describe the system utilized in this study:

Annular gap ($d = r_o - r_i$) = 1.9 cm

Radius ratio ($\eta = r_i/r_o$) = 0.76

Inner cylinder length (L) = 20.08 cm

Aspect ratio ($\Gamma = L/d$) = 10.56

Reynolds number ($Re = \frac{\Omega_i r_i (r_o - r_i)}{\nu}$)

Here r_i is the inner cylinder radius, r_o is outer cylinder radius, Ω_i is the angular velocity of the inner cylinder, and ν is the fluid kinematic viscosity. The inner cylinder is mounted on a shaft (using shaft collar) which is then connected to a speed control motor using a shaft coupling. The motor is a 120 V AC, NEMA 34, 1/3 hp DC Motor (Amatek) having a speed range of 300–3450 RPM. The torque acting on the inner cylinder is measured using a reaction torque sensor (TFF425, Futek Advanced Sensor Technology) which is mounted at the base of the motor. The torque sensor has a capacity of 7 N m and provides 2 mV/V of rated output (RO). It was precalibrated by Futek Advanced Sensor Technology and showed an error of 0.02% of RO in the clockwise direction and -0.03% of RO in the anti-clockwise direction. A USB 220 kit was used to digitize the output signals of the sensor which were then recorded using SENSIT Test and

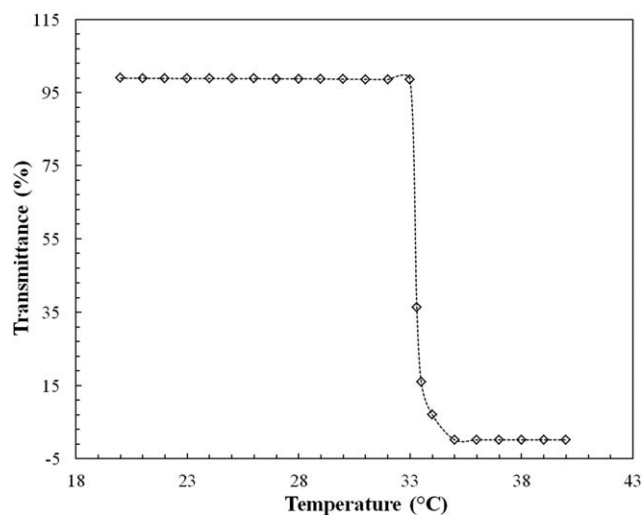


Figure 2. Transmittance of 400 PPM aqueous PNIPAM solution at different temperatures.

Measurement software. The inner cylinder angular velocity was measured using an optical tachometer. The temperature of the fluid in annular gap was assessed using a K-type thermocouple that was mounted at the top plate of TC setup.

This system was utilized for testing DR using commercial DRAs in our previous study and was verified as a powerful tool for assessing DR.²⁶ DRA solution was prepared by stirring the desired amount of PNIPAM in water for 2 h at 200 RPM on a magnetic stirrer. Six different concentrations ranging from 100 to 600 PPM were studied with Re varying from 40,000 to 250,000 and for each measurement five repeat measurements were conducted. The standard deviation in all the measurements was less than 0.05 DR %. DR was measured at 20 and 40 °C in order to check the difference in DR below and above LCST. In order to verify the reversible nature of these polymers, the heated solution was cooled back again to 20 °C and the corresponding DR was measured. For 500 PPM solution, DR was measured at six different temperatures varying from 15 to 40 °C in order to determine the effect of temperature (apart from LCST) on DR.

RESULTS AND DISCUSSION

Polymer Synthesis and Characterization

Figure 2 shows the transmittance of 400 PPM aqueous PNIPAM solution at different temperatures varying from 20 °C to 40 °C. Polymer is completely transparent in water below 33 °C signifying

Table I. Viscosity of PNIPAM Solutions at 20 and 40 °C

Concentration (PPM)	Viscosity at 20 °C (Pa s)	Viscosity at 40 °C (Pa s)
100	1.1×10^{-3}	0.9×10^{-3}
200	1.2×10^{-3}	0.9×10^{-3}
300	1.3×10^{-3}	0.9×10^{-3}
400	1.6×10^{-3}	0.9×10^{-3}
500	2.1×10^{-3}	0.9×10^{-3}
600	2.1×10^{-3}	0.9×10^{-3}

Table II. Viscosity of 500 PPM PNIPAM Solution at Different Temperatures

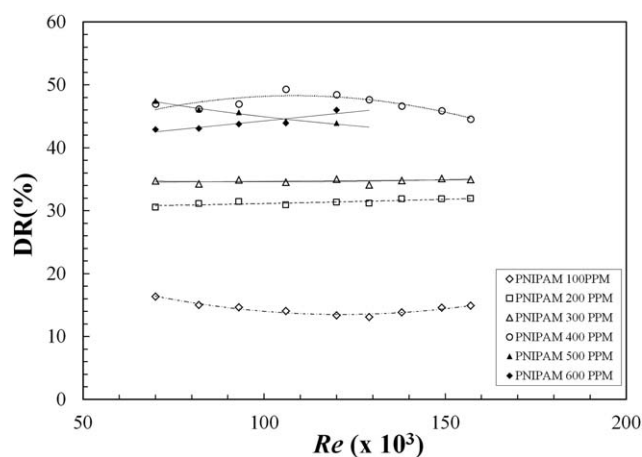
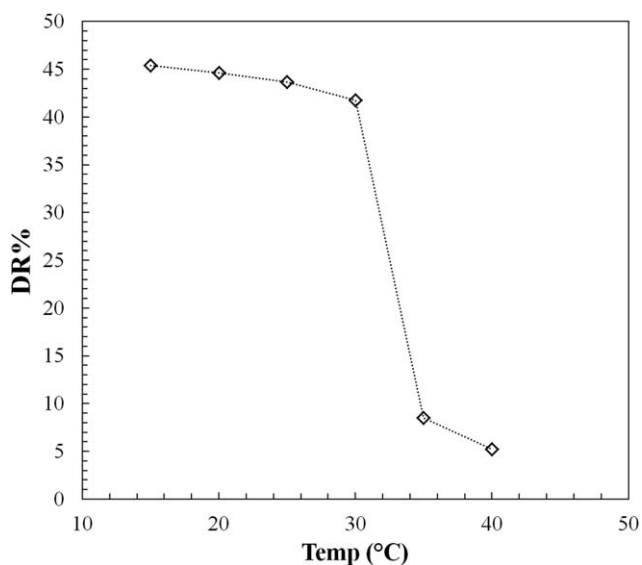
Temperature (°C)	Viscosity (Pa s)
15	2.4×10^{-3}
20	2.1×10^{-3}
25	1.7×10^{-3}
30	1.4×10^{-3}
35	1.0×10^{-3}
40	0.9×10^{-3}

good solubility. LCST of the polymer is observed at 33°C where transmittance is dropped from 99% to 0.15% indicating precipitation of PNIPAM beyond 33°C. Insolubility of the polymer after 33°C verifies the thermo-responsive nature of the polymer.

Weight-average molecular weight of the polymer was observed to be 254,000 Da (with polydispersity of 9.5) signifying a sufficiently long polymer chain length, which can exhibit enhanced elongational viscosity required for DR. Rheological measurement provided stress versus strain curves for the PNIPAM solutions and power law model was used to measure the solution viscosity. Because of very low concentration, all the solutions exhibited Newtonian behavior. Table I summarizes the viscosity of PNIPAM solutions at 20 and 40°C. Table II provides viscosity of 500 PPM PNIPAM solution at different temperatures ranging from 15 to 40°C.

Drag Reduction

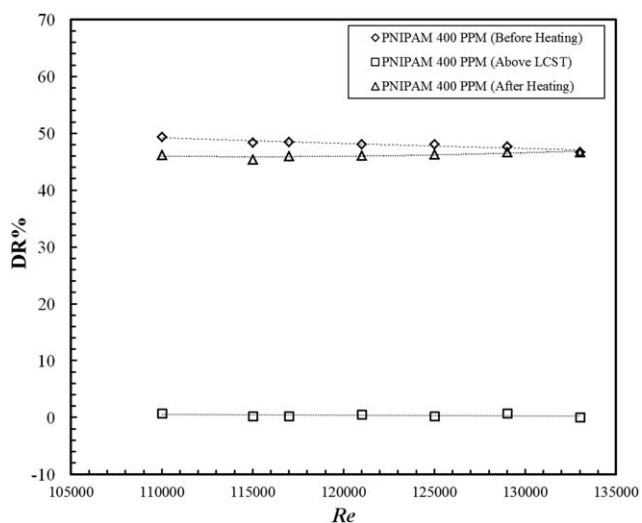
Figure 3 shows the DR versus Re for different concentrations of PNIPAM ranging from 100 to 600 PPM at 20°C (Below LCST). Since all the measurements were conducted at fairly high Re , the effect of Re cannot be seen on DR. However, there is significant effect of PNIPAM concentration on DR indicating maxima at 400 PPM. As indicated in previous studies on conventional DRA such as polyacrylamide,⁹ there is a maximum concentration beyond which there is a decrease in DR with increasing concentration. This increase in DR with increase in concentration is because of higher interaction of polymer chains with turbulent micro-vortices leading to larger dissipation of turbulent

**Figure 3.** Drag reduction (DR) versus Re for different concentrations of PNIPAM solution at 20°C.**Figure 4.** DR versus temperature for 500 PPM solution at $Re = 100,000$.

energy.²⁷ On the other hand, decrease in DR beyond 400 PPM could be attributed to enhanced entanglements of these long-chain molecules among themselves, leading to reduced mobility of the polymer chains.

The previous study conducted on this setup, while using commercial polyacrylamide (Magnafloc, BASF) as DRA, exhibited Maximum DR of 60% at 160 PPM solution concentration.²⁶ Maximum DR obtained in this study ($\sim 50\%$) is in good range with MDR of commercial polymer. Commercial polymer required less concentration to achieve the same drag reduction, owing to the fact they have significantly high molecular weight ($M_w \sim 2,000,000$ Da in comparison 254,000 Da for PNIPAM).

Figure 4 summarizes the effect of temperature on DR for 500 PPM concentration at $Re = 1 \times 10^5$. Temperature does not alter the DR below the LCST, that is, 33°C; however DR drastically reduces to 5% above the LCST. Above the LCST, the thermo-responsive polymers become hydrophobic in nature and act as

**Figure 5.** DR versus Re for 400 PPM solution below and above LCST.

collapsed particles which easily go along with the fluid flow without interacting with the turbulence and without getting adsorbed to the surface. This plot is similar to Figure 2, which shows transmittance of PNIPAM solution with a change in temperature.

Figure 5 compares the DR for 400 PPM at two different temperatures, that is, 20 °C (Below LCST) and 40 °C (Above LCST). The third plot with legend PNIPAM 400 PPM (after heating) indicates the DR of the solution at 20 °C after it was cooled down from 40 °C in order to verify the reversible nature of these polymers. PNIPAM, above its LCST at 40 °C, shows negligible DR because of precipitation of molecules, validating its thermo-responsive nature. Further, after cooling back the solution to 20 °C, DR properties of the polymer are retrieved back, verifying the reversible nature of the polymer. Similar behavior was observed for other concentrations where polymer exhibited drastic decrease in DR above LCST and showed reversible DR after cooling back.

CONCLUSIONS

In this study, a thermo-responsive polymer, that is, PNIPAM was investigated for the first time as a DRA in a turbulent TC flow with water as solvent. Conventional free-radical polymerization using a redox pair, i.e. ammonium persulfate and TEMED, in an inert environment was used to synthesize the PNIPAM in aqueous solution. A high molecular weight of 254,000 Da (weight average molecular weight) was confirmed using gel permeation chromatography. The effect of *Re*, concentration, and temperature was studied on DR, and maximum DR was observed to be 50% at 400 PPM concentration. The polymer exhibited a prominent responsive nature at its LCST (33 °C), and precipitated in the solution at this temperature. It did not exhibit any DR beyond 33 °C, making it a suitable candidate for DR in enhanced oil recovery, where temperature can be used as a trigger to prevent these polymers from getting adsorbed at reservoir surfaces. Further, on cooling back to 20 °C, the DR properties of the polymer could be retrieved back to their original value, making them cost-effective additives for tailored and controlled DR in other applications. The study validates PNIPAM as a potential DRA, which will not affect the permeability of shale reservoirs and has a capability to be triggered for DR for other applications.

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