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Mechanical degradation of dilute polymer solutions under turbulent flow

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Abstract

The degradation of high molecular weight polystyrene under turbulent flow was investigated using a rotating disk apparatus for three different solvent systems at a maximum polymer concentration of 150 ppm by weight. The drag reduction efficiency decreases with time due to the mechanical degradation of the polymer molecules, and the extent of the degradation was found to be a function of the solubility parameter of the solvents. A theoretical model for molecular degradation provides excellent agreement with our experimental data. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Mechanical shear degradation hampers the practical usage of polymers for turbulent drag reduction (DR) application. Mechanical degradation refers to the chemical process in which the activation energy of polymer chain scission is exceeded by the mechanical action on the polymer chain, and bond rupture occurs. There have been numerous investigations on the mechanical degradation of both dilute and concentrated polymer solutions, which show conflicting results depending on the experimental conditions, such as laminar and turbulent flow, polymer concentration range, and solvent nature effect [1–9]. Patterson et al. [1] observed that the breakdown of small amounts of the high molecular weight fraction causes a decrease in the first normal stress difference and DR for polyisobutylene (PIB) in the two different solvents. Nakano and Minoura [2,3] observed that the rate of scission of polymer chains becomes greater in a good solvent than in a poor solvent at a low concentration by noting that the interaction between polymer molecules weakens at low concentrations (a decrease in concentration favorably affects the scission of chains). This fact suggests that the "stretching" and "entanglements" of polymeric chains affect the mechanical degradation [4]. It has also been found that chain scission occurs around the chain midpoint indicating that the macromolecules are highly extended when they break [4–7].

Mechanical shear degradation has been encountered in various practical situations such as the use of polymers for turbulent DR and as viscosity enhancers in motor oils [4]. Since polymeric drag reducers have been successfully applied in the Trans-Alaskan Pipeline [10], they have spread worldwide for crude oil pipeline transportation and are of great potential benefit to many industrial processes [11] including long-distance transportation of liquids, oil well operations [12], fire fighting [13], transport of suspensions and slurries [14], biomedical applications [15]. However, industrial application has been complicated due to polymer degradation. Therefore, polymeric degradation has become one of the critical issues in applications dealing with polymer-induced turbulent DR.

Many mechanical shear degradation experiments have been performed under turbulent flow conditions. Zakin and Hunston [16] monitored DR efficiency in a capillary tube, which is very sensitive to changes in polymer molecular weight at extremely low concentrations. On the other hand, Culter et al. [17] pointed out that much of the mechanical degradation in turbulent flows through capillary tubes occurs at the entrance. To reduce the entrance effect, Horn and Merrill [8] installed a conical funnel at the entrance of the tube from the feed solution reservoir.

We have been working on polymer-induced turbulent DR with various polymeric additives using a rotating disk apparatus (RDA) [18–21], which is designed to investigate

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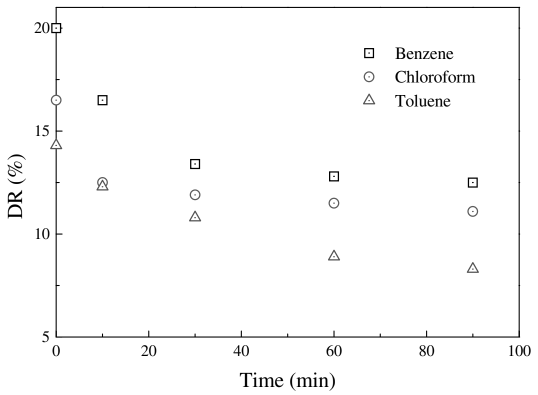

Fig. 1. Percent DR vs. time for PS in three different solvents (150 ppm).

external flow problems. One normally studies typical frictional drag using an internal flow set-up, whereas total drag (friction plus form drag) is typically studied using an external flow set-up. For a homologous series of PIB with three different solvents, we recently reported the effect of solvent on universal DR characteristics in a RDA. We found that the differences in DR of the PIB in three different solvents systems were linked to differences in solubility parameters [20,21].

In this study, we investigated the effect of solvent on both the mechanical degradation and DR using the RDA and high molecular weight polystyrene (PS) at turbulent flow regime.

2. Experimental

The RDA was used not only to study the rupture of the polymeric chains in a turbulent flow but also to observe the DR efficiency of PS. The specifications of the RDA have been previously reported [18,19]. The RDA consists of a stainless steel disk whose dimensions are 14.5 cm (diameter) by 0.32 cm (thickness) and is enclosed in a cylindrical, thermostatically controlled container. A transducer was used to monitor the torque on the disk, which was rotated at 1800 rpm. The temperature of the system was maintained at (25 ± 0.5)°C. The torque required to rotate the disk, for solvents alone, at a given speed was measured first. The percent DR was then calculated by measuring the corresponding torque required at the same rotational speed for a dilute polymer solution:

$$\mathrm{DR}(\%) = \frac{T_\mathrm{S} - T_\mathrm{P}}{T_\mathrm{S}} \times 100, \tag{1}$$

where T_S is the torque measured for a pure solvent system, and T_P is the measured torque for a polymer solution.

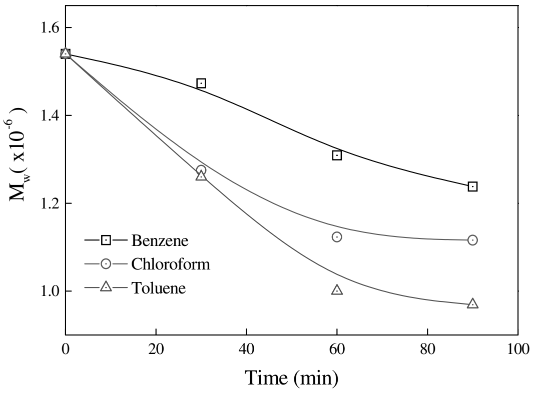

Fig. 2. Solvent effect on the mechanical degradation of PS.

Anionically polymerized PS standard was obtained from Polyscience Inc. The weight average molecular weight ($\bar{M}_\mathrm{W}$) was 1.54×10^6 and the polydispersity index (PI $\equiv \bar{M}_\mathrm{W}/\bar{M}_\mathrm{n}$) was 1.05. Here, $\bar{M}_\mathrm{n}$ is the number average molecular weight. The solvents for PS were first grade chloroform, benzene, and toluene.

For the DR measurement, 1 w/w% stock solutions of PS for each solvent were initially prepared by mildly stirring the sample for one week with a magnetic stirrer. DR measurements were then made by injecting carefully measured quantities of stock solution directly into the turbulent flow field generated by the RDA. The percent DR was then obtained as a function of time.

Size exclusion chromatography (SEC) was used to determine $\bar{M}_\mathrm{W}$ and the PI of the polymer in the solution before and after being exposed to the turbulent flow field. The SEC used in the present study consists of four Waters Ultra-Styragel Columns (HR 1, 2, 4, and linear columns), a Waters Rheodyne injector, a 510 HLPC pump, and a Waters R410 refractive index detector. Tetrahydrofuran was chosen as the solvent, and the flow rate was maintained at 1.0 ml/min. In order to obtain good resolution, the experiments were performed at 40°C. Before testing the samples, a calibration curve was constructed using a PS standard calibration kit (Polyscience Inc.). The calibration curve was utilized to obtain molecular weight distribution or PI curves for the injected PS samples.

3. Results and discussion

The mechanical degradation of PS was investigated in this paper using a RDA. The RDA measures changes in DR as a function of time and the stability of polymers in a strong turbulent flow. Fig. 1 depicts the DR as a function of time for three different PS–solvent systems at a rotational speed of 1800 rpm and indicates that the DR decreases with time due to the degradation of the polymer molecules under turbulent flow. The different values of percent DR efficiency are due to the difference in polymer–solvent interaction. The solubility parameters (δ) of PS, benzene, chloroform, and toluene are 18.72, 18.8, 19.0, and 18.2 MPa$^{1/2}$, respectively [22], and because benzene is a good solvent for PS base on the solubility parameter, the coil dimensions of the PS in benzene will be the largest out of the three solvents. In a previous study [23], it was observed that the DR ability of polymer–solvents decreased as the solvent approached the

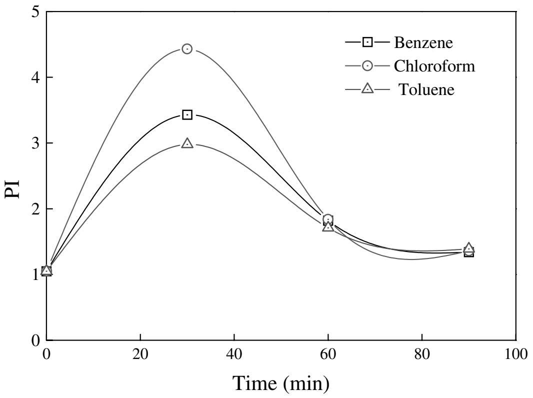

Fig. 3. Evolution of the PI for PS in three different solvents.

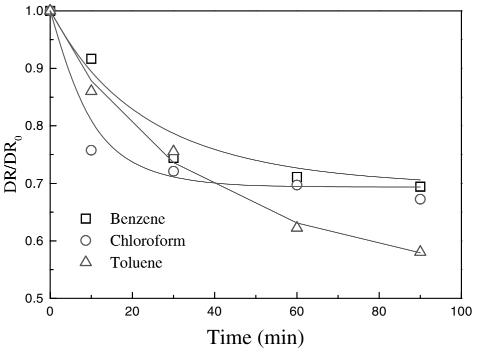

Fig. 4. Time dependence of the relative DR, DR(t)/DR$_0$ or $M(t)/M_0$, for PS. The symbols represent the experimental values; lines are derived from Eq. (5).

theta condition. Thus, at equal concentrations, the more expanded polymer conformations result in more effective DR [23]. Putting these facts together, it is expected that PS molecules in benzene will provide the most effective DR; this is confirmed from Fig. 1.

Each polymer solution was sampled using a syringe during the DR experiments to determine the molecular weight change of the polymer. Fig. 2 demonstrates that DR decreases due to chain scission.

Fig. 3 shows the changes in PI for PS in the three different solvents during the DR experiments. As shown in the plot, the PIs go through a maximum at 30 min regardless of the solvent. For the degradation of monodisperse PS, high molecular weight molecules are preferentially broken [4]. Therefore, the initial degradation of the monodisperse PS broadens the molecular weight distribution (becomes more polydisperse), and further degradation of polydisperse PS solutions narrows the molecular weight distribution principally through the break up of polymer molecules as time progresses. Yu et al. [4] observed that the maximum polydispersity is less than two, and the conflict of this result with Fig. 3 may be due to the strength and uniformity of the shear flow field. Contrary to their degradation experiments in laminar flow field, which has uniform shear rate and shear stress, our DR were performed in turbulent flow with non-uniform shear rates and very high shear stresses. The PI reaches 1.5 at the end of experiment regardless of solvent quality, which implies that degradation occurs at near the center of the chain backbone. Thus, polymer degradation may not be a random process with its preference near the center of the chain [4,8]. If we take into account only the polymer–solvent interaction to describe the degradation phenomenon, we expect the PI of the PS molecules in benzene will have the largest value among these at 30 min of exposed time [2,3]. However, the PI of the PS molecules in chloroform exhibits the maximum value. DR efficiency generally increases with increased turbulence intensity, which is described by the Reynolds number, $\mathrm{Re} \equiv \omega r^2/\nu$ (ω, a angular velocity; r, radius of the disk; and ν, the fluid kinematic viscosity). Because ω is held fixed at 1800 rpm in our experiments, the Re of the PS–organic solvents pairs, which dependent on the solvents' kinematic viscosities, are 2.58×10^6, 1.36×10^6 and 1.47×10^6 in chloroform, benzene and toluene solutions, respectively. Since PS molecules in chloroform are exposed to a stronger turbulence intensity solvent than the other two solvents (based on the Re), the polymer molecules in the chloroform environment experience more severe degradation than in the other environments. This results in the largest PI for chloroform as shown in Fig. 3. In the case of benzene and toluene, the Re for toluene (1.47×10^6) is a little larger than that of benzene, thereby the PS–toluene system may have a larger PI value at 30 min than the PS–benzene (1.36×10^6) system. However, since benzene is a good solvent for PS, the two effects (Re dependence and solvent quality) will be balanced.

There exist several correlations between DR efficiency and mechanical degradation. Brostow and his coworkers [7,24,25] have developed a model from a statistical mechanical approach [24] and have recently investigated the validity of their model based on computer simulations. The DR efficiency and mechanical degradation are related to macromolecular conformation in solution, and the DR efficiency is proportional to the molecular weight of the polymers. The DR efficiency ratio is expressed as:

$$\frac{\mathrm{DR}(t)}{\mathrm{DR}_0} = \frac{M(t)}{M_0}, \tag{2}$$

where DR(t) and DR$_0$ are the percent DR at times t and $t = 0$. $M(t)$ and M_0 are the effective number-average molecular mass at times t and $t = 0$. More mechanical degradation was observed in a poor solvent than in good solvents under the same flow conditions [7]. A limiting molecular weight M_∞ can be defined by: $M_\infty \equiv \lim_{t\to\infty} M(t)$. M_∞ becomes smaller in the poor solvent than in good solvents for a given polymer, as illustrated in Fig. 2. Brostow et al. [7,24] noted that the points on the chain where changes of direction occur are more vulnerable to chain scission. Depending on their specific location, some of them might be protected from degradation by their surroundings, while others will undergo

Table 1
Comparison of the degradation rates ($DR(t)/DR_0$) for PS

	Solvents	Time exposed to turbulence (min)				
		0	10	30	60	90
Theoretical model, Eq. (5)	Benzene	1	0.879	0.772	0.721	0.706
	Chloroform	1	0.762	0.699	0.694	0.693
	Toluene	1	0.878	0.736	0.631	0.580
GPC Measurement	Benzene	1		0.956	0.850	0.804
	Chloroform	1		0.827	0.729	0.725
	Toluene	1		0.818	0.649	0.629

scission during flow. The average number of points per chain of the latter kind are denoted by *W*, and:

$$M_\infty = \frac{M_0}{1 + W}. \tag{3}$$

Here, *W* is proportional to the number of the breakable sequences having two different orientations and changing extended-to-compact or compact-to-extended conformations. For a polymeric drag-reducing agent, *W* can also be related to the drag reducer concentration *C*, the energy $U_d(t)$ originating from turbulence intensity that produces degradation, and the energy ϵ necessary to break one bond [24]:

$$W = \frac{M_0 U_d(\infty)}{C N_A \epsilon}. \tag{4}$$

Here N_A is Avogadro's number. By introducing the single exponential model (with *h* as the decay constant), Brostow et al. [24] obtained:

$$\frac{DR(t)}{DR_0} = \frac{1}{1 + W(1 - e^{-ht})}. \tag{5}$$

A larger value of *h* indicates fast degradation, and a larger value of *W* implies a low shear-stability. To study the shear stability or mechanical degradation of polymer chains in a turbulent flow for our experimental data, we used Eq. (5). Fig. 4 represents the relative DRs as a function of time for PS in three different solvents. As time elapses, the DR efficiency ratio approaches a constant limiting value. The solid lines are obtained from Eq. (5). Fig. 4 shows that both the calculated and the measured values of DR efficiency ratio coincide within the limits of experimental accuracy. From this plot, we obtained W for PS in benzene, chloroform, and toluene, and they are: 0.43, 0.44 and 0.96, respectively. Since higher *W* values yield lower mechanical stability, the PS in toluene is the most shear degradable substance. In addition, in turbulent flow, polymer molecules degraded faster in a poor solvent at low Re, whereas an opposite effect was observed at high Re [26]. We compared the degradation rate obtained from Eq. (5) with that obtained from the gel permeation chromatopraphy (GPC) measurement, which is summarized in Table 1. The relative DR ($DR(t)/DR_0$) obtained from the Eq. (5) have lower values than that from the GPC measurement and differences between these two values decrease with time. Also, we see that the decreasing rate of the $DR(t)/DR_0$ is initially steep.

4. Conclusion

We presented the combined effects of both turbulent flow and solvent quality on the polymer degradation in solutions. DR reduces with time due to molecular degradation. The limiting value of the PI becomes 1.5, as time progresses under an exposed turbulent flow, and this suggests that polymer scission appears to be a nonrandom process. Degradation of monodisperse PS results first in a broadening of and then a narrowing of the molecular weight distribution. We adopted the theoretical model for molecular degradation in turbulent flow proposed by Brostow et al. [24] to our experimental data and obtained an excellent fit.

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