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## Entrance Effects On Capillary Degradation Of Dilute Polystyrene Solutions

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## Entrance Effects on Capillary Degradation of Dilute Polystyrene Solutions

### INTRODUCTION

In recent years there has been increasing interest in the degradation of dilute polymer solutions by mechanical shear. Application of the drag reduction phenomenon observed in dilute polymer solutions has been limited because of the problems of polymer degradation. For these dilute solutions there are still uncertainties about such questions as: (1) the effect of polymer molecular weight on degradation; (2) the existence of a minimum molecular weight below which no degradation occurs in a particular shear field or the existence of a minimum force on individual molecules below which no degradation occurs.

This work was aimed at trying to answer these questions by degradation experiments on dilute, narrow molecular weight distribution ( $M_w/M_n < 1.20$ ) polystyrene solutions in laminar flow in capillary tubes.

### EXPERIMENTAL

#### Materials

In all cases the solvent was spectrometric-grade toluene at 25.0°C, the polymer concentration was 0.1 wt-%, and the shear stress at the wall was in the range of 800–1750 dynes/cm<sup>2</sup>. The extent of degradation was determined by measuring the intrinsic viscosity  $[\eta]$  of the polystyrene samples before and after flow through capillary tubes having a wide range of length-to-diameter ( $L/D$ ) ratios. The polystyrene samples are described in Table I.

#### Apparatus

The capillary-tube flow system is shown in Figure 1. Three glass capillary tubes having a diameter of 0.0100 in. and three tubes having a diameter of 0.0067 in., and all having a 0.0080-in. brass orifice, were used in this investigation. Length-to-diameter ratios ( $L/D$ ) are listed in Table III. Several attempts were made to fabricate orifices having diameters the same as the glass tubes. The smallest round orifice obtained was that made from brass with a diameter of 0.0080 in. (by scanning electron microscopy).

#### Procedure

**Solution Preparation.** All solutions were made up to contain  $0.100 \pm 0.003$  g polymer per  $100.0 \pm 0.2$  ml toluene solution at 25°C in a 100-ml volumetric flask. The solutions

TABLE I  
Polymer Characteristics

Polymer <sup>a</sup>	$M_w \times 10^{-4}$	$M_w/M_n$	$[\eta]$
PS-1	180	<1.20	3.25
PS-2	86	1.10	2.09
PS-3	63.3	1.08	1.72
PS-4	41.1	1.06	1.28
PS-5	16	1.06	0.666
PS-6	2	1.06	0.144

<sup>a</sup> These samples and characterizations were furnished by the Mellon Institute, Pittsburgh, Pa., and Pressure Chemical Co., Pittsburgh, Pa.;  $M_w$  was obtained by light scattering and  $M_n$  by membrane osmometry.

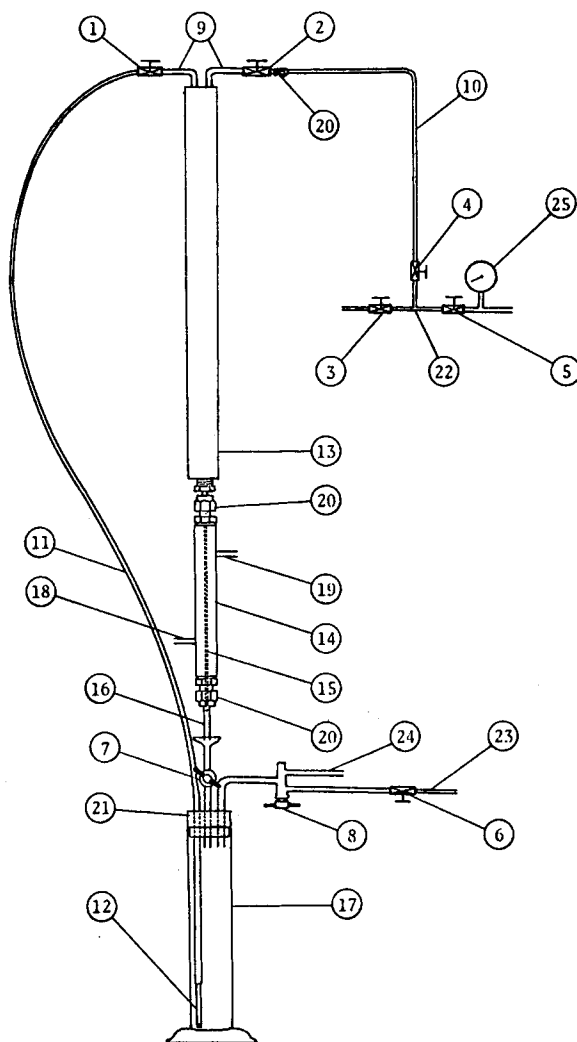


Fig. 1. Schematic diagram of degradation test system: (1-6) valves; (7) Pyrex glass stopcock with adapter and Teflon plug; (8) three-way Pyrex glass stopcock with Teflon plug; (9)  $\frac{1}{4}$ -in. O.D. stainless steel tube; (10)  $\frac{1}{8}$ -in. O.D. stainless steel tube; (11)  $\frac{1}{4}$ -in. O.D. Teflon tube; (12)  $\frac{1}{4}$ -in. O.D. glass tube with sintered glass filter at lower end; (13) reservoir: 1-in. O.D. stainless steel pipe; (14) aluminum jacket; (15) capillary tube; (16)  $\frac{1}{4}$ -in. O.D. brass tube; (17) graduate glass cylinder of 200 ml; (18) inlet water line from bath:  $\frac{1}{4}$ -in. O.D. brass tube; (19) outlet water line to pump and bath:  $\frac{1}{4}$ -in. O.D. brass tube; (20) brass connector: Swagelok fitting; (21) Teflon cover with three straight bores; (22) brass tee; (23) inlet from nitrogen gas cylinder; (24) pressure-discharge line; (25) high-pressure gauge (500 psi maximum).

were allowed to stand overnight in a dark cabinet after apparent dissolution. Angular dissymmetry measurements showed the polymers to be dissolved.

**Capillary Tube Flow Degradation.** Referring to Figure 1, the following procedure was used in all of the tests. The polymer solution was forced through the filter and into the reservoir from the graduated glass cylinder by nitrogen pressure. The solution was then

forced through the capillary tube by means of nitrogen pressure back into the glass cylinder. This procedure was repeated at a given pressure and at 25°C until the solution was subjected to the desired number of passes. Different shear rates could be obtained by varying the pressure for a given capillary. All of the tests reported here were at a Reynolds number of approximately 1800. Fresh polymer solutions were subjected to the filtering operation and checked for degradation. No significant changes in  $[\eta]$  were observed.

**Calibration of Tubes.** Distilled toluene at 25°C was used as the calibration fluid in this work. Since the fluid was discharged from the capillary tube at atmospheric pressure, the pressure drop was measured by an accurate pressure gauge on the inlet side of the capillary tube. The diameter of the tube was calculated by means of the Hagen-Poiseuille equation for a number of pressures for the long tubes, and the average value was taken as the diameter. Because of the high  $L/D$ , entrance corrections were small. Calculated values for  $D$  varied by less than  $\pm 0.5\%$ . The lower  $L/D$  tubes were from the same stock as the larger  $L/D$  tubes.

**Recovery of Polymer.** After completion of the flow tests, the polymer solution was transferred to a freeze-drying flask, cooled to liquid nitrogen temperatures, and allowed to freeze dry to a constant weight. The dried polymer was stored in clean, dry glass bottles pending intrinsic viscosity determination. Several polymer samples were repeatedly freeze dried with no significant change in  $[\eta]$ , demonstrating that this method of recovery did not degrade the sample.

**Intrinsic Viscosity Determination.** Intrinsic viscosity determinations were made in the freeze-dried samples utilizing a #50 Cannon-Ubbelohde dilution viscometer. Kinetic energy effects were negligible. Standard viscosity dilution procedures were followed in making the determinations. The initial concentrations were such that before dilution, the relative viscosities were approximately 2.0.

## RESULTS AND DISCUSSION

Data for the 0.0100-in. ( $L/D = 444$ ) and 0.0067-in. ( $L/D = 800$ ) glass tubes are shown in Table II. They confirm trends observed by other investigators on broader-distribution samples at higher polymer concentrations.

TABLE II  
Polymer Degradation in 0.0100-in. and 0.0067-in. Tubes

Sample	No. of passes	0.0100-in. Tube <sup>a</sup>		0.0067-in. Tube <sup>b</sup>	
		$[\eta]$ , dl/g	$\frac{[\eta]_0 - [\eta]}{[\eta]_0}$	$[\eta]$ , dl/g	$\frac{[\eta]_0 - [\eta]}{[\eta]_0}$
PS-1 ( $[\eta]_0 = 3.515$ )	1	3.180	.09	3.105	.12
	20	3.050	.13	2.830	.17
PS-2 ( $[\eta]_0 = 2.090$ )	1	1.960	.06	1.930	.08
	20	1.910	.09	1.860	.11
PS-3 ( $[\eta]_0 = 1.71$ )	1	1.630	.05	1.610	.06
	20	1.570	.08	1.540	.10
PS-4 ( $[\eta]_0 = 1.28$ )	1	1.175	.08	1.160	.09
	20	1.140	.11	1.110	.13
PS-5 ( $[\eta]_0 = 0.666$ )	1	0.588	.12	0.581	.13
	20	0.586	.12	0.580	.13
PS-6 ( $[\eta]_0 = 0.144$ )	1	0.144	0	0.144	0
	20	0.144	0	0.144	0

<sup>a</sup>  $\tau = 800$  dynes/cm<sup>2</sup>;  $L/D = 444$ .

<sup>b</sup>  $\tau = 1750$  dynes/cm<sup>2</sup>;  $L/D = 800$ .

The intrinsic viscosity decreases relatively quickly during the first pass and then more slowly in succeeding passes. Similar results were reported by Harrington and Zimm<sup>1</sup> in capillary flow (with a tapered entrance region) of 0.05% polystyrene in toluene solutions. For an equal number of passes, the relative degradation,  $[\eta]_0 - [\eta]/[\eta]_0$ , is more or less constant for polymers other than PS-6 ( $MW = 2 \times 10^4$ ). This is in agreement with the results of Porter and Johnson who sheared polyisobutylene solutions between concentric cylinders.<sup>2</sup> Also the relative degradation was more severe for an equal number of passes in the small tube where wall shear stresses were higher than in the large tube. Porter and Johnson<sup>2</sup> also observed that relative degradation increased with stress.

The critical molecular weight below which no degradation occurs appears to be between  $2 \times 10^4$  and  $1.6 \times 10^5$  for these shear stresses. This is in agreement with the results of Cereas and Watson<sup>3</sup> based on mastication of 26% polystyrene in toluene solutions. They found a critical  $[\eta]$  of 0.2 dl/g. Thus, the narrow-distribution polymers in dilute solution show degradation behavior similar to that of more concentrated polydisperse systems previously studied.

The most surprising results are the extents of degradation as a function of  $L/D$ . Table III shows the intrinsic viscosities of sample PS-2 ( $[\eta]_0 = 2.09$  dl/g) under various shearing conditions after one and 20 passes for different  $L/D$  ratios. The tube length has no significant effect on degradation for any of the measurements in this region. That is, the extent of degradation at shear stresses of 800–1750 dynes/cm<sup>2</sup> is independent of the  $L/D$  ratio. If the shearing in the fully developed flow region of the tube were effective, the degradation should increase with tube length for a given number of passes. Therefore, these measurements suggest that under these flow conditions it is the relatively high shear stresses at the entrance of the capillary that cause most of the polymer degradation. The shear stresses at the entrance are not easily determined but are probably related to average wall shear stress. Wall shear stresses in the smaller tube were greater than in the larger tube, and degradation is more severe in the smaller-diameter tube.

TABLE III  
Degradation of Polymer Sample PS-2,  $[\eta]_0 = 2.09$  dl/g

Wall shear stress, dynes/ cm <sup>2</sup>	Wall shear rate, (sec <sup>-1</sup> ) $\times 10^{-5}$	$[\eta]$ , dl/g		Diameter, in.	Length, in.	$L/D$
		1 Pass	20 Passes			
800	1.2	1.96	1.91	0.0100	4.44	444.
800	1.2	1.97	1.90	0.0100	1.00	100.00
800	1.2	1.96	1.91	0.0100	0.25	25.00
1750	2.6	1.93	1.86	0.0067	5.36	800.00
1750	2.6	1.94	1.86	0.0067	0.67	100.00
1750	2.6	1.96	1.91	0.0067	0.25	37.50
1200	1.8	1.98	1.92	0.0080	0.014	1.75

(orifice)

The entrance geometry affects the magnitude of the stresses at the tube entrance. In this investigation, a square-edged capillary entrance was used. As the fluid enters the capillary, the bulk of the fluid is flowing at the same velocity, with only a minor portion being sheared near the wall. In this entrance region, boundary layer theory can be used to determine the velocity profile. Local shear rates near the wall are related to the ratio of centerline velocity to the boundary layer thickness.<sup>4</sup> Since the boundary layer thickness varies from zero at the entrance to larger values, the shear

rates decrease from infinity to the usual value of  $8V/D$ . Thus, extremely large stresses are imposed on a small portion of the fluid in the entrance region. There are also large stresses in the region just before the tube entrance.

The fact that degradation did not occur in the fully developed region in the tubes may be explained by a comparison of the present results with those of Harrington and Zimm.<sup>1</sup> From their data they reported that the critical minimum force for degradation of polystyrene molecules in toluene was  $3.5 \times 10^{-8}$  dynes. They calculated the average force per molecule for Newtonian polymer solutions from

$$\langle f \rangle_{av} = \frac{\eta_{sp}\eta_0 M}{cNz} \left( \frac{4Q}{\pi R^3} \right)$$

where  $\langle f \rangle_{av}$  = average force per molecule,  $\eta_{sp}$  = specific viscosity,  $\eta_0$  = solvent viscosity,  $M$  = average molecular weight,  $c$  = concentration (mass/volume),  $N$  = Avogadro's number,  $z$  = projected length perpendicular to flow (taken as  $r/\sqrt{3}$ ),  $r$  = root mean square end-to-end distance of polymer coil in solution at zero shear rate,  $Q$  = volume flow rate, and  $R$  = tube radius. The highest force produced on PS-2 was  $7 \times 10^{-8}$  dynes at the wall in the smaller tube. Since no PS-2 was subjected to a force above the critical value in the fully developed laminar flow region even in the smallest tube, degradation under these conditions should be insensitive to tube length.

In closing, it should be noted that care must be taken in interpreting capillary degradation results on polymer solutions. The relative effects of degradation due to entrance effects and degradation due to steady laminar shear must be determined or the former must be kept negligible.

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