NOTES

Effects of Solvent Nature on the Mechanical Degradation of High Polymer Solutions

Recent reports by Nakano and Minoura[1,2] have claimed that the mechanical degradation of high polymers in solution at low concentrations is enhanced if the polymer is dissolved in a thermodynamically "good" solvent. The minimum concentration used in their study ($c \approx 0.04\%$) gave solutions in which the nominal pervaded volume fraction of polymer,[3] $c[\eta]$, was in the range 0.03–0.14. In contrast, several earlier reports[4-7] have indicated that the mechanical degradation of polymers in "poor" solvents was more rapid than in good solvents. All of the latter results, however, were obtained at higher concentrations where the values of $c[\eta]$ exceeded 0.6 for the fresh good solvent solutions and 0.1 for the fresh poor solvent solutions.

In an effort to clarify this situation, we have degraded very dilute solutions of polystyrene in good solvents (benzene and toluene) and in a mixed (58% toluene–42% isooctane) solvent which at 25°C is close to theta conditions. The polystyrene samples, which were obtained from Duke Standards, were prepared through anionic polymerization and have very narrow molecular weight distributions.[8] Moreover, the viscosities for all three solvents are similar: benzene, 0.599 cp; toluene, 0.556 cp; and mixed solvent, 0.475 cp. These two factors help simplify the interpretation of results.

The properties of the solutions studied in the degradation experiments are listed in Table I. At low concentrations it is difficult to make the molecular weight measurements necessary to follow the degradation process. We have solved this problem, however, by monitoring drag reduction effectiveness, which is very sensitive to changes in polymer molecular weight[9] and can be measured at extremely low concentrations.[10] The drag reduction was measured in a capillary tube (0.158 cm in diameter) using an automated turbulent flow apparatus.[11] This device records the wall shear stress τ_w as a function of flow rate, and thus the percent drag reduction at a fixed flow rate is 100(1 − τ_{wp}/τ_{ws}), where τ_{wp} and τ_{ws} are the values of τ_w in solution and solvent, respectively. These measurements[10] can be made at concentrations as low as a few parts per million by weight (ppm) and can detect small changes in molecular weight that are difficult to monitor by other techniques such as viscometry.[9]

Mechanical degradation was accomplished in two ways: turbulent flow through a capillary tube and high-speed stirring. The first set of experiments employed a polystyrene sample (designated 7M) with a molecular weight of 7.1×10^6 and $M_w/M_n \approx 1.1$. A 150-ppm solution of this sample in benzene was passed through the 0.158-cm-diameter capillary tube[11] in turbulent flow, and the drag-reducing effectiveness of the solution was observed as a function of the number of passes (Fig. 1). After 40 passes no significant change in drag-reducing effectiveness and hence in molecular weight was noted. A similar result was obtained with a 5-ppm polystyrene solution in benzene although it gave only 28% drag reduction. This suggests that, for the polystyrene–benzene system in this

TABLE I
Polymer Solution Properties

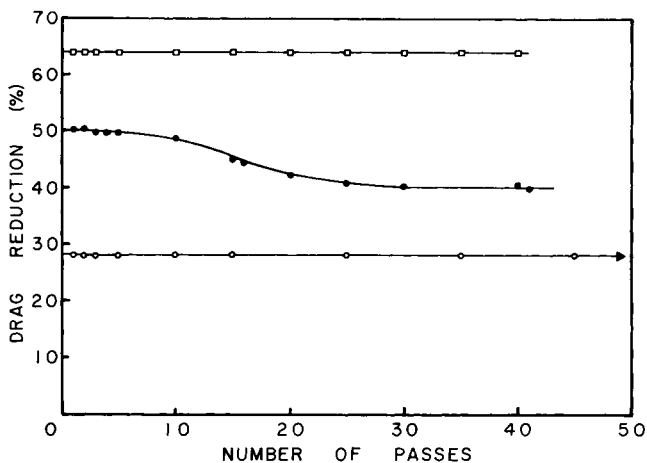| Polystyrene sample	Solvent	Weight-average molecular weight	M_w/M_n	$[\eta]$, dl/g	c, ppm	$c[\eta]$
7M	benzene	7.1×10^6	1.1	10.9	150	0.14
7M	benzene	7.1×10^6	1.1	10.9	5	0.005
7M	58% toluene 42% isooctane	7.1×10^6	1.1	2.5	150	0.029
4M	toluene	4.1×10^6	1.1	7.4	150	0.096
4M	58% toluene 42% isooctane	4.1×10^6	1.1	1.8	150	0.021
4M	58% toluene 42% isooctane	4.1×10^6	1.1	1.8	600	0.086

Fig. 1. Capillary degradation curves for 7M polystyrene. The 150-ppm mixed solvent solution (●) shows evidence of degradation while the 150 ppm (□) and 5 ppm (○) benzene solutions do not degrade. The 5-ppm solution remained unchanged even after 60 passes.

apparatus, 7.1×10^6 is less than the critical molecular weight for degradation, i.e., the molecular weight below which no degradation is observed for a given set of flow conditions. In this case the flow conditions corresponded to a maximum wall shear stress $\tau_{wp,\max}$ of 865 dynes/cm^2 (5 ppm solution).

In contrast, Figure 1 also shows the results for polystyrene 7M in the (poor) mixed solvent, and the presence of degradation is apparent. The shape of the degradation curve can be explained as follows. Since the 7M polymer is a very effective drag-reducing agent,[10] 150 ppm is a very high concentration. Consequently, some degradation is required before the drag reduction is affected. This degradation proceeds until the molecular weight of each molecule is below the critical molecular weight for degradation in this solvent under the prevailing flow conditions. For this particular case the results indicate that the degradation approaches a limiting value after about 30 passes. This solution, however, still gives a drag reduction of 40%. Based on molecular weight-versus-drag reduction data that will be published in a subsequent paper, this would suggest an apparent critical molecular weight of about 5.5×10^6. Since the maximum flow rate is the same for all of these experiments, $\tau_{wp,\max}$ depends on the viscosity and per cent drag reduction. In the mixed solvent experiments, $\tau_{wp,\max}$ reached a value of 625 dynes/cm^2 at 40% drag reduction.

A recent report by Culter et al.[12] indicates that much of the degradation in turbulent flows of polymer solutions through capillary tubes occurs at the entrance. While their results are for a tube with a diameter about one third that for the capillary used here, the present data may also reflect significant entrance degradation. Since the maximum shear stress in the entrance region is related to the maximum wall shear stress, comparisons of $\tau_{wp,\max}$ are at least qualitatively valid even though the significance of the absolute values may be questionable.

In a second series of tests, experiments were performed using a polystyrene sample (designated 4M) having a molecular weight of 4.1×10^6 and $M_w/M_n \approx 1.1$. After preparing two 150-ppm solutions, one in toluene and one in the mixed solvent, each was degraded under very severe shear stresses using a Virtis homogenizer at 3,000 rpm. At selected time intervals during the degradation, samples were extracted and measured in the drag reduction apparatus. In Figure 2, the ratio of the drag reduction at time t to the drag reduction of the fresh solution (both measured at the same flow conditions) is plotted as a function of t. In this case both solutions show degradation, but it is clear that the rate of molecular scission in dilute polymer solutions is less rapid in good solvents than in poor solvents when both are subjected to the same degradation conditions. At long degradation times the drag reduction goes to 0% with both solvents. This means that the limiting molecular weights for degradation in this system are less than ~1 million since this is the minimum molecular weight necessary to observe drag reduction in the apparatus employed.[9]

For the comparison above, both solutions contained the same weight concentration of polymer. An alternate procedure is to test solutions with equal pervaded volume fraction of polymer. Such an experiment was performed by measuring a 600-ppm solution of polystyrene 4M in the mixed
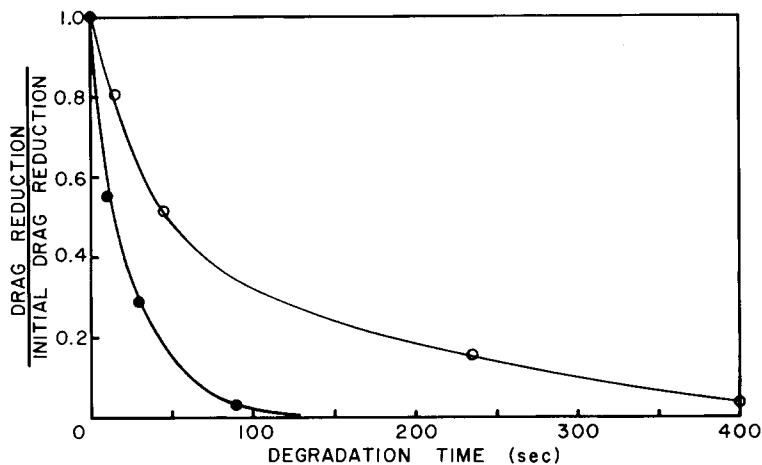
Fig. 2. Homogenizer degradation curves for 150-ppm solutions of 4M polystyrene. The rate of degradation is larger in the mixed solvent solution (●) than in the toluene solution (O). Data points for a 600-ppm solution in mixed solvent are very close to those for the 150-ppm mixed solvent solution.

solvent (Table I). Here again, the degradation was monitored by measuring drag-reducing efficiency (samples were diluted to 150 ppm for these measurements). These results indicate that the increased concentration had little effect on the rate of degradation, and thus the data were almost identical to those obtained for the 150-ppm polystyrene 4M in mixed solvent. Consequently, whether the comparisons are made at equal weight percent or at equal pervaded volume fractions, molecular weight loss due to mechanical degradation is greater for poor solvents than for good solvents. This result contradicts the observations of Nakano and Ninoura.[1,2] Their tests were performed at very high stirring rates (30,000 rpm), and this may have been a factor in their unusual results. It is clear, however, that the use of very low concentrations is not sufficient in itself to reverse the normal solvent effect.

In summary, then, these experiments suggest three important conclusions:

(1) Mechanical degradation was observed in a poor solvent at very low concentrations under fixed flow conditions and not in a good solvent under the same flow conditions. This indicates that the threshold molecular weight for mechanical degradation is lower in the poor solvent.

(2) When shear conditions were increased to the point where both good and poor solvent solutions degraded, the polymer in the poor solvent degraded more rapidly. This may be related to a lower threshold molecular weight in the poor solvent and/or to conditions in the poor solvent which promote mechanical degradation.

(3) In the poor solvent the rate of degradation was relatively independent of concentration in dilute solutions.

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