Mechanical Degradation of High Molecular Weight Polymers in Dilute Solution

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Synopsis

The mechanical shear degradation of polydisperse polyisobutene and monodisperse polystyrene in oils of different viscosities in the concentration range of 0.1% to 1% was studied using a high-shear concentric cylinder viscometer under laminar and uniform well-defined shear field conditions. Molecular weight distributions (MWDs) were measured by gel permeation chromatography (GPC). Degradation of polydisperse polyisobutene solutions narrows the distributions principally through the breaking down of large molecules. Degradation of monodisperse polystyrene broadens the distributions at lower shear stresses. At higher shear stresses, the distributions do not broaden as much but are still broader than those of the original polymer. The final M_w/M_n ratios are considerably different from the value of 2 expected for random degradation. Hence, the degradation is likely a nonrandom process. It was found that the extent of degradation has a negative concentration dependence coefficient at relatively high molecular weight and a positive concentration dependence at lower molecular weight. Competing mechanisms of "stretching" and "entanglements" for degradation were postulated to explain the results. The degradation data indicate that the shear stress is the controlling parameter, not the shear rate. The shear degradation is independent of initial molecular weight and viscosity of the solvent.

INTRODUCTION

The mechanical shear degradation of polymer solutions imposes severe limitations on uses where effectiveness is determined by high molecular weight. Mechanical shear degradation has been encountered in such practical cases as the preparation of poly(butene-1 sulfone) film as a positive electron beam resist for lithography and the use of polymers for drag reduction applications and as viscosity index improvers for motor oils. Hence, the need for a better understanding of mechanical shear degradation prompted this research.

There have been a number of papers published on mechanical degradation of dilute polymer solutions in recent years.[1-48] However, most investigators studied degradation in nonuniform and nondefined shear fields such as high-speed mixers, turbulent pipe flows, or laminar capillary flows with entrance effects and attempted to draw conclusions about both degradation kinetics and degradation to equilibrium. While comparative results can be obtained in these experiments, in order to understand the fundamental mechanisms of mechanical shear degradation, it is necessary to perform degradation experiments in a

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laminar and uniform well-defined shear field. Only two groups[23–27] studied degradation in a uniform and defined laminar shear field. Therefore, a high-shear concentric cylinder viscometer was constructed for this study of degradation of polymer solutions.

There are a number of important questions whose answers are uncertain. For example: (1) What is the exact mechanism or mechanisms of mechanical shear degradation? (2) What are the controlling parameters for shear degradation, i.e., what are the effects of initial molecular weight, viscosity of solvent, concentration, and shear stress on shear degradation? This work was aimed at trying to answer these questions.

EXPERIMENTAL

Materials

Dilute solutions of polyisobutene and polystyrene samples were studied. Polymer characteristics and the properties of the solvents used are shown in Tables I and II. Samples with different initial molecular weights were degraded at concentrations of 1%, $\frac{1}{2}$%, $\frac{1}{4}$%, $\frac{1}{8}$%, and $\frac{1}{10}$% by weight in various solvents at 25°C.

In addition to the fact that polyisobutene has high chemical purity and is structurally regular, linear, and nonpolar with no tactic variation,[50,51] polyisobutene has high resistivity toward oxidative degradation. Macroradicals formed after mechanical rupture of bonds are most probably terminated by disproportionation.[52] Therefore, polyisobutene is most suitable for studies of mechanical shear degradation. The polyisobutene samples used are listed in Table I.

TABLE I
Polymer Identification

Polymer	Designation	Source	MW	M_w/M_n
Polyisobutene	PIB L-200	Enjay Corporation	$4.7 \times 10^{6(49)}$ a	—
Polyisobutene	PIB L-140	Enjay Corporation	$1.5 \times 10^{6(49)a}$	—
Polyisobutene	PIB L-80	Enjay Corporation	$8.6 \times 10^{5(49)}$ a	—
Polystyrene	7M	Duke Standards	7.1×10^{6} b	1.1
Polystyrene	4M	Duke Standards	4.1×10^{6} b	1.1
Polystyrene	2M	Pressure Chemical	2.4×10^{6} c	1.2

a Viscosity-average molecular weight.
b Weight-average molecular weight given by manufacturer.
c Analysis by M. R. Seegar, University of Akron.

TABLE II
Properties of Solvents

Name	Viscosity at 25°C, cp	Density at 25°C, g/cm^3	Aniline point, °F	Aromatics, %	Clay gel analysis	
					Saturates, %	Polar compounds, %
Mobilsol 44	13	1.04	less than 30	98	—	—
Shell 131	14	0.86	171	22	77.5	0.2
Shell Vitrea 25	50	0.87	205–208	20	80	0.2
Shell Vitrea 33	110	0.87	216	18	82	0.2

Degrading a monodisperse polymer may give valuable information on the breaking site along the polymer chain. The only polymers readily available with narrow molecular weight distributions are the polystyrenes, and polystyrene standards (Table I) were also used in this work. However, chemical reactions may occur after mechanical degradation of polystyrene.

High-Shear Concentric Cylinder Viscometer

The high-shear concentric cylinder viscometer used in this work is similar to the one used by Barber and co-workers[53] and modified by Porter and Johnson.[54] Other investigators such as Abdel-Alim and co-workers[55] and Reches[56] used similar instruments based on the Porter and Johnson design. The construction of this high-shear viscometer and design considerations have been described by Yu.[48] The bob had a nominal diameter of 1 in. The viscometer was tested with API 10W and 20W oils and Cannon standards S-20, S-60, and S-200. The clearance between the two cylinders was calibrated with these standard oils. The gap so measured was 0.00048 ± 0.00002 in., which agreed with the clearance measured by a micrometer (0.0005 in). The calibrated clearance remained constant within 5% over the months of operation, confirming the reliability of this custom-built high-shear concentric cylinder viscometer. Since the gap was only 0.1% of the radius of the rotor, shear stress across the gap varied by only 0.2%.

The maximum temperature rise in the test fluid increases as the square of the film thickness.[48] With the small gap used here, calculations indicated that the maximum temperature rise in the liquid film in the gap was less than 1°C, and Reynolds number was about unity based on the gap distance at the linear velocity of the inner cylinder wall. No correction was made for this minor temperature effect.

In the range of solution viscosities studied, rotational speeds up to 3600 rpm could be used, corresponding to a shear rate of 380,000 reciprocal seconds. Shear stresses up to 100,000 dynes/cm^2 were measured.

Gel Permeation Chromatography

The molecular weight distributions (MWDs) were measured using a Waters Anaprep gel permeation chromatograph. Four Styragel columns 4 ft long $\times$ $\frac{3}{8}$ in. I.D. of molecular weight ratings 10^7, 3×10^6, 10^5, and 10^4 were used in series. They were operated at a flow rate of 1 ml/min and at a temperature of 30°C using tetrahydrofuran (THF) as the solvent. The columns were calibrated using a series of narrow molecular weight distribution polystyrene standards with molecular weight range from 4.8×10^3 to 7.1×10^6. The concentration of polyisobutene used was 0.1% and that of polystyrene was 0.05%. All test samples were directly diluted with THF to 0.1% or 0.05% and were filtered prior to injection into the columns. In this study the filtration process was determined to have no effect on the MWD. GPC spreading corrections were carried out with the methods presented by Ishige, Lee, and Hamielec.[57] Details of the analysis technique and of the data analysis were given by Yu.[48]

Procedure

Small samples of polyisobutene were freshly cut from the center of one block of polyisobutene, weighed and added to a known weight of solvent in a 1-liter glass bottle which was purged with nitrogen gas. The polyisobutene was dissolved in oil by mild agitation using a magnetic stirrer and heated below 40°C using a heating tape. More than one month was normally required for solutions to become homogeneous. Polyisobutene is notorious for degradation during preparation even under mild conditions. Therefore, the molecular weight distribution of the polyisobutene after solution preparation was considered as that of the original undegraded polyisobutene. The properties of oils used are listed in Table II.

The polystyrene was dissolved in a 13 cp viscosity (25°C) aromatic mineral oil by heating below 40°C in an incubator without agitation. The solutions were gently shaken manually three or four times a day and took approximately two weeks to become homogeneous.

The solutions of polyisobutene and polystyrene did not degrade due to storage in solution. GPC traces on unsheared solution soon after preparation and after the degradation experiments were complete showed no changes in molecular weight distribution (MWD). For polyisobutene in the oil solvents used, storage was six months; for polystyrene storage was three weeks.

The effect of axial motion of the samples was checked by forcing representative samples through the clearance between the two cylinders by applying pressure. The applied pressures were greater than the highest pressures used in the degradation experiments. The extruded sample was examined by GPC analysis. No changes in MWD compared with a nonextruded sample were observed.

Porter and Johnson[24] showed that in their experiments the sheared solutions reached equilibrium conditions at each shearing condition in less than 2 sec. In order to ensure that samples reached the maximum extent of degradation before leaving the clearance, preliminary tests were made to determine the minimum residence time required to reach equilibrium in this study. Degrading polymer solutions with residence times above 2.8 sec showed no further detectable changes in MWD, indicating that equilibrium degradation can be achieved in less than 2.8 sec. In order to avoid any uncertainty about the possibility of degradation of solutions extruded through the cylinders by high pressure and to ensure complete degradation under the experimental conditions, all solutions were degraded with an average residence time of about 20 sec (slow extrusion).

RESULTS AND DISCUSSION

Location of Scission Points

Figure 1 shows the changes in the differential molecular weight distributions with shear intensities for polyisobutylene L-140 in the 50 cp oil. This figure clearly shows that the high molecular weight molecules are preferentially broken and that there is essentially no variation in the minimum molecular weight. The results listed in Table III indicate that the equilibrium M_w/M_n ratio for this solution decreases to approximately 1.5 as degradation proceeds. Similar results are seen for the other solutions listed.

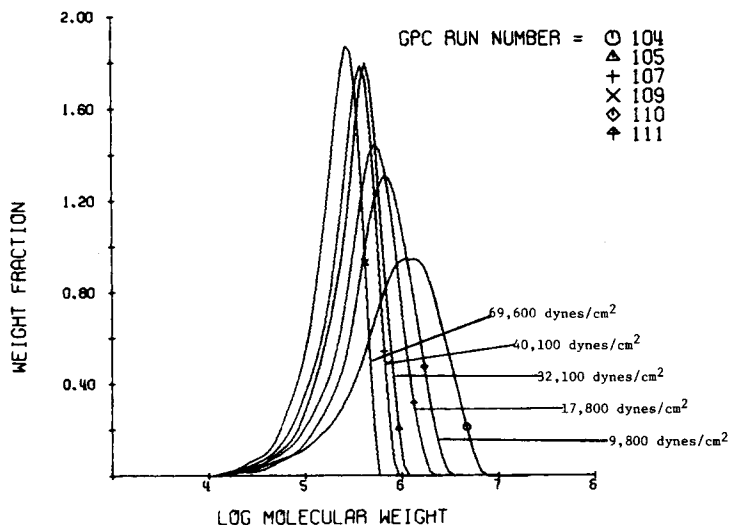Kotliar,[58] using Monte Carlo sampling techniques, found that the M_w/M_n ratio

Fig. 1. Changes in differential MWD with shear stress for 1% by weight of PIB L-140 in 50 cp oil.

should approach the most probable value of 2 if the chain scission is a random process. However, all the results of degrading polyisobutene as shown in Table III and other results reported by Yu[48] indicate that the degradation narrows the M_w/M_n ratio to approximately 1.5. This low ratio is significantly different from the limit of 2 for random degradation. For narrow distributions, the GPC analysis always broadens distributions even after the axial spreading correction is made, so the values shown in Table III are probably high. Since the final M_w/M_n ratio definitely does not approach the most probable value of 2 as predicted by Kotliar, and since it decreases with degradation, which is characteristic of degradation near the center of the chain,[59] it must be nonrandom with sites near the center portion of the chain favored.

Figure 2 shows GPC analyses for polystyrene 4M in 13 cp oil. The GPC analyses for the original polystyrene standards show two peaks.* The relatively low molecular weight peak may be caused by degradation during solution preparation. The molecular weights of the small peaks are 1.8×10^6 for 7M, 2.1×10^6 for 4M, and 1.4×10^6 for 2M. If these small molecular weight peaks are produced from shear degradation, this degradation is consistent with Bueche's midpoint break theory for monodisperse polymers.[59] According to his theory the degraded polymer should have a molecular weight of original molecular weight divided by 2^n, where n is an integer.

As shown in Figure 2, degrading monodisperse polystyrene results in a lower molecular weight end and a broader distribution than expected if the break-in were exclusively at the midpoint of the molecular chain. Generally, the results of degrading monodisperse polystyrene show widening of the distribution initially and then narrowing the distribution at higher shear stresses (for representative

* GPC analyses gave higher values of the M_w/M_n ratio for the unsheared polystyrene standards in solution than shown in Table I. These higher values have also been observed by other investigators.[60] They are probably caused by degradation during the dissolution process and by the skewing phenomena which is usually attributed to the effects of velocity profile and radial dispersion on axial dispersion. Since in this study only relative changes in MWDs are of interest, the effects of skewness on the GPC analysis and breakage during solution preparation are not of major concern.

TABLE III
Ratio of Weight-Average to Number-Average Molecular Weight at Different Levels of Shear
Stress for Polyisobutene at Equilibrium Degradation

Shear rate, $(\text{sec}^{-1}) \times 10^{-4}$	Shear stress, $(\text{dyn/cm}^2) \times 10^{-4}$	M_w/M_n
1% By Weight of PIB L-200 in 14 cp Oil		
0.0	0.0	2.58
0.33	0.29	2.54
1.21	0.71	2.19
3.27	1.26	1.83
6.54	1.88	1.74
10.1	2.50	1.66
13.2	3.12	1.63
19.9	4.20	1.66
1% By Weight of PIB L-140 in 14 cp Oil		
0.0	0.0	2.69
1.31	0.67	2.19
3.27	1.25	1.96
4.91	1.62	2.05
8.18	2.24	1.65
13.1	3.08	1.71
19.6	4.10	1.73
1% By Weight of PIB L-200 in 50 cp Oil		
0.0	0.0	2.70
0.33	0.52	2.25
1.06	1.38	1.98
2.62	2.72	1.80
5.24	4.19	1.59
9.82	7.14	1.53
1% By Weight of PIB L-80 in 50 cp Oil		
0.0	0.00	2.27
1.10	1.29	2.22
5.24	4.15	1.70
10.8	7.67	1.53
½% By Weight of PIB L-200 in 14 cp Oil		
0.0	0.0	2.56
0.80	0.36	2.65
1.64	0.61	2.59
4.91	1.25	1.69
9.82	2.05	1.67
16.4	2.94	1.50
½% By Weight of PIB L-140 in 14 cp Oil		
0.0	0.0	2.33
9.82	2.14	1.57
32.7	4.28	1.50
½% By Weight of PIB L-200 in 50 cp Oil		
0.0	0.0	2.70
0.33	0.45	2.71
0.97	0.94	2.30
2.42	1.87	1.75
5.24	3.39	1.87
9.16	5.35	1.65
16.4	8.92	1.56
½% By Weight of PIB L-140 in 110 cp Oil		
0.0	0.0	2.26
0.26	0.62	2.28
0.52	1.16	1.77

TABLE III. *Continued.*

Shear rate (sec^{-1}) $\times$ 10^{-4}	Shear stress, (dyn/cm^2) $\times$ 10^{-4}	M_w/M_n
1.37	2.45	1.49
3.27	4.33	1.51
3.47	5.17	1.48
6.87	9.30	1.44

TABLE IV

Ratio of Weight-Average to Number-Average Molecular Weight at Different Levels of Shear Stress for Polystyrene at Equilibrium Degradation

Shear rate, (sec^{-1}) $\times$ 10^{-4}	Shear stress, (dyn/cm^2) $\times$ 10^{-4}	M_w/M_n
1% By Weight of 7M in 13 cp Oil		
0.0	0.0	1.17
5.89	1.83	1.68
9.82	2.68	1.60
16.0	3.26	1.60
1% By Weight of 4M in 13 cp Oil		
0.0	0.0	1.18
1.37	0.62	2.03
2.75	1.03	1.91
6.87	2.14	1.73
9.82	2.51	1.79
16.4	3.57	1.56
22.9	4.55	1.56
¼% By Weight 7M in 13 cp Oil		
0.0	0.0	1.17
10.5	1.92	1.99
16.4	2.81	1.65
21.6	3.75	1.61

results see Table IV). At higher shear stresses the distribution, while not as broad as the low shear stress degradation product, is broader than that of the original undegraded polymer. However, degraded polystyrene results in a distribution of M_w/M_n less than a value of 2. Therefore, the midpoint of the molecular chain may be a preferential site for breaking, but not necessarily the only site. The only polystyrene data at different concentrations gave similar results.[48]

Computer simulation was used in this study to attempt to model the process of chain breakage. The strategy for the simulation used here is similar to the one used by Glynn.[39] The probability of choosing a polymer molecule to rupture is assumed to be proportional to the sth power of its molecular weight and the probability of the rupture site is assumed to be a Gaussian distribution about the midpoint with the fraction r of the chain length as standard deviation. This Gaussian distribution is truncated at the ends of the molecules. Thus, two adjustable parameters, s and r, are required to simulate the molecular weight changes caused by chain breakage.

According to Bueche's calculations,[59] at fixed concentration and temperature and an average molecular weight, the probability of choosing a molecule to
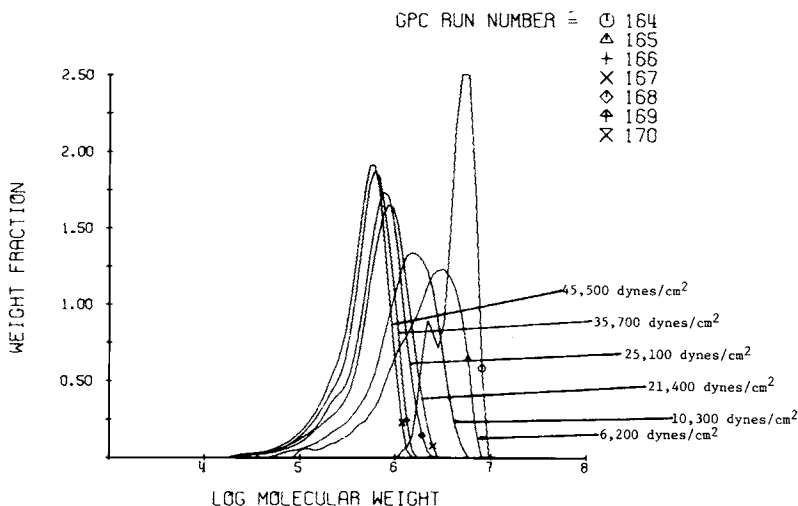
Fig. 2. Changes in differential MWD with shear stress for 1% by weight of polystyrene 4M in 13 cp oil.

rupture at any instant is proportional to exp (MW^2). Bueche also postulated that the ratio of the number of chains which break at the qth link, from the center to the number which break at the center is exp $[-(F_0\delta/KT)(4q^2/Z^2)]$, where F_0 is the tension on the center link of the chain, δ is a distance approximately equal to the distance the bond will stretch before breaking, K is the Boltzmann constant, T is the absolute temperature, and Z is the number of links per molecule. If the probability of the site of rupture is a Gaussian distribution about the central portion of the chain, the standard deviation r is $0.354(KT/F_0\delta)$. Usually, $F_0\delta/KT$ is of the order of 10 to 20. Hence, the standard deviation should be around 0.0178 to 0.0354.

Different sets of values for the parameters r and s have been assumed for simulation. The comparisons between experimental MWD and simulated MWD are not very promising. Any combinations of s with a value of 1.0, 1.4, and 1.6 and r with a value of 0.035, 0.35, and 35.0 may reasonably fit some of the experimental MWD curves. Hence, it is difficult to evaluate the "best" values for a whole set of curves. Generally speaking, s with a value of 1.2 and r with a value of 0.035 fit the experimental MWD curves most reasonably. Obviously, the parameter s is not in agreement with Bueche's prediction. Degradation is a weaker function of molecular weight than he predicted. This disagreement is probably due to the fact that Bueche's prediction is only valid if the polymer is subjected to a low shear stress which gradually increases to its "final" high-shear stress.[59] However, in these studies the polymer was suddenly exposed to a high shear field instead of gradually being brought up to the "final" shear stress, allowing breaks to take place at positions far from the center.

Effect of Initial Molecular Weight and Solvent Viscosity

Three criteria were used to express the extent of degradation. These criteria are M_c, $M_z + 1$, and M_w. M_c is the highest molecular weight existing in the distribution, which is defined as the molecular weight corresponding to the lower

boundary of the highest 0.1% of the total MWD. As discussed previously, the higher molecular weight molecules are more subject to shear-induced degradation. M_c, therefore, is probably the most meaningful molecular weight to consider when studying shear degradation. The higher moments of the molecular weight average are more sensitive to the higher molecular weight fractions in the distribution. Therefore, $M_z + 1$, the $z + 1$ moment of molecular weight average, was chosen as a convenient measure of the molecular weight end. M_w, the weight-average molecular weight, is usually associated with the peak of the molecular weight distribution, and thus M_w is also a suitable criterion for the extent of shear degradation. Equilibrium values of these three molecular weights are shown in Figure 3 as a function of shear stress for 1% by weight solution of
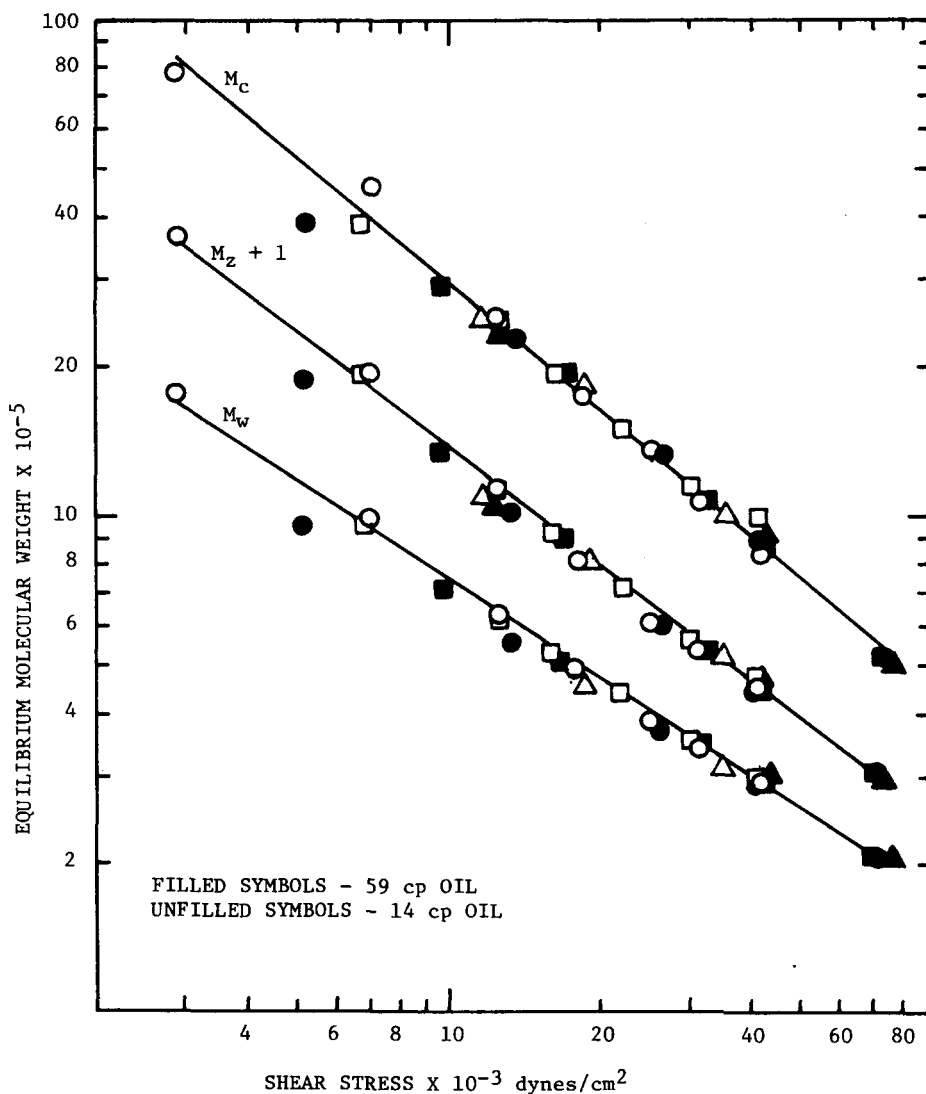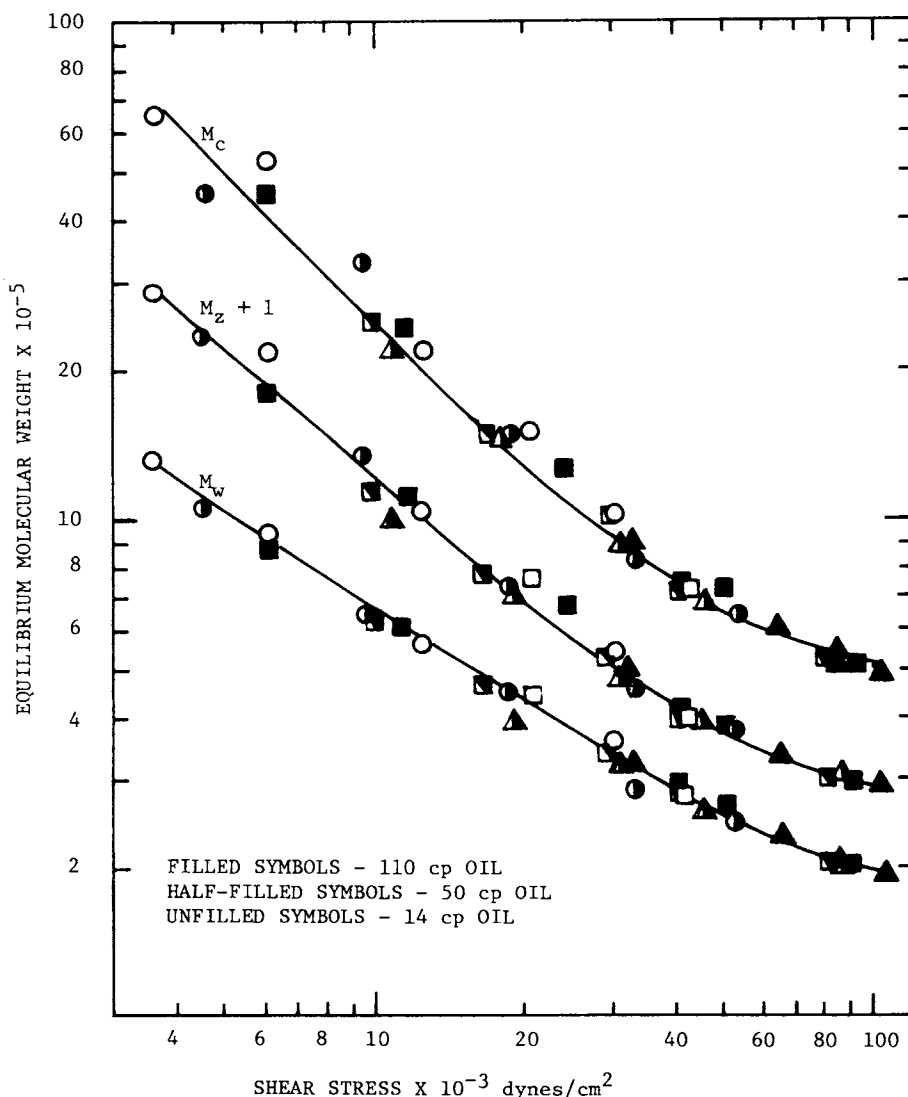

Fig. 3. Dependence of equilibrium MW on shear stress with different initial MWs and in various viscosities of solvents for 1% by weight of polyisobutene: (O) L-200; (□) L-140; (△) L-80.

three polyisobutene samples with different initial molecular weights in various viscosities of solvents.

An important finding is that all data points for different initial molecular weights and various viscosities of the solvents fall upon a straight line (Figs. 3 to 6). Therefore, shear degradation is independent of initial molecular weight and the viscosity of the solvent. However, whether the degradation is independent of other parameters of the solvent besides viscosity is not known because of the lack of variation in the other properties of solvent in the experiments. Table II shows that there was little difference in the aromaticity of the oils in which polyisobutene experiments were run.

At the same shear stress, the shear rate for the solution with a higher viscosity

Fig. 4. Dependence of equilibrium MW on shear stress with differential initial MWs and various viscosities of solvents for $\frac{1}{2}\%$ by weight of polyisobutene: (O) L-200; (□) L-140; (△) L-80.
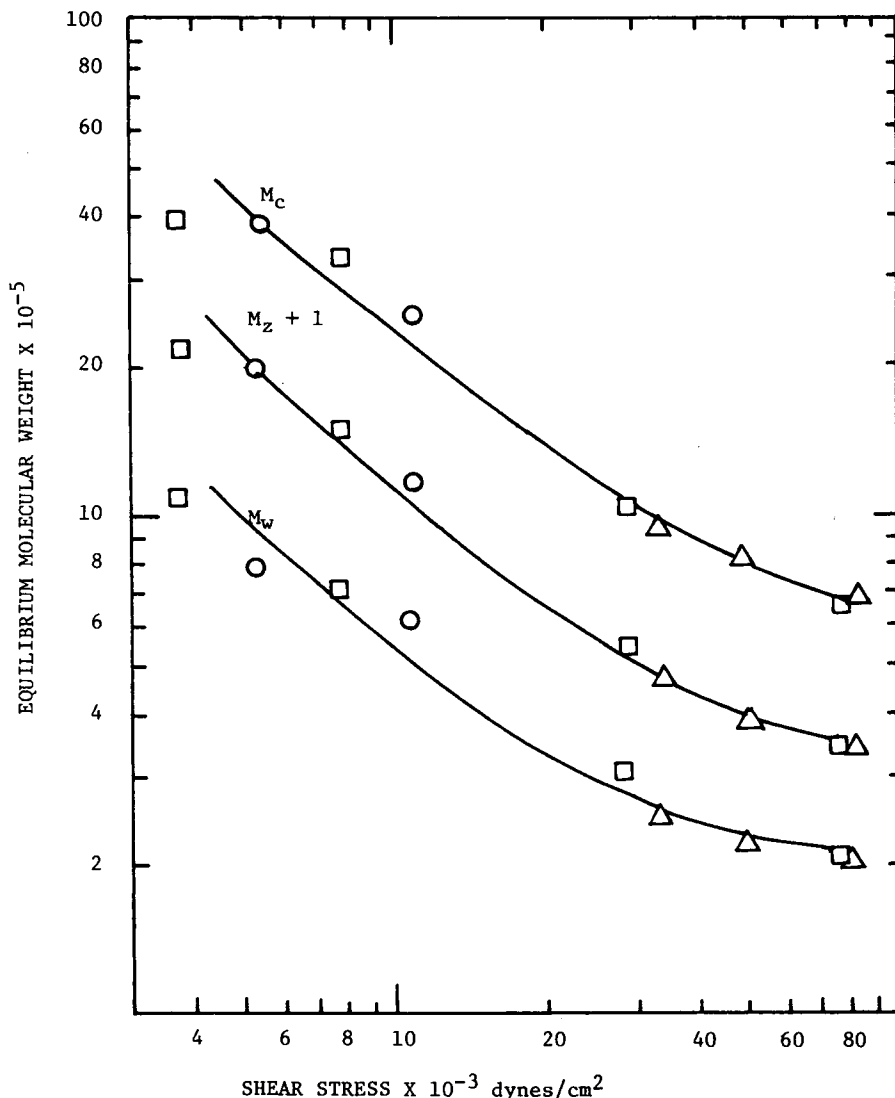
Fig. 5. Dependence of equilibrium MW on shear stress with different initial MWs for $\frac{1}{4}$% by weight of polyisobutene in 50 cp oil: (O) L-200; (□) L-140; (△) L-80.

is lower than that for the solution with a lower viscosity of solvent. However, both of them have an identical equilibrium molecular weight. This clearly shows that shear stress is the controlling parameter for shear degradation, not shear rate or the rate of energy input, which is shear stress multiplied by shear rate.

The dependence of equilibrium molecular weight on shear stress with different initial molecular weight for 1% by weight of polystyrene in 13 cp oil at 25°C is shown in Figure 7, for $\frac{1}{4}$% in Figure 8, and for $\frac{1}{10}$% in Figure 9. These figures indicate that the extent of degradation is independent of initial molecular weight for polystyrene also.
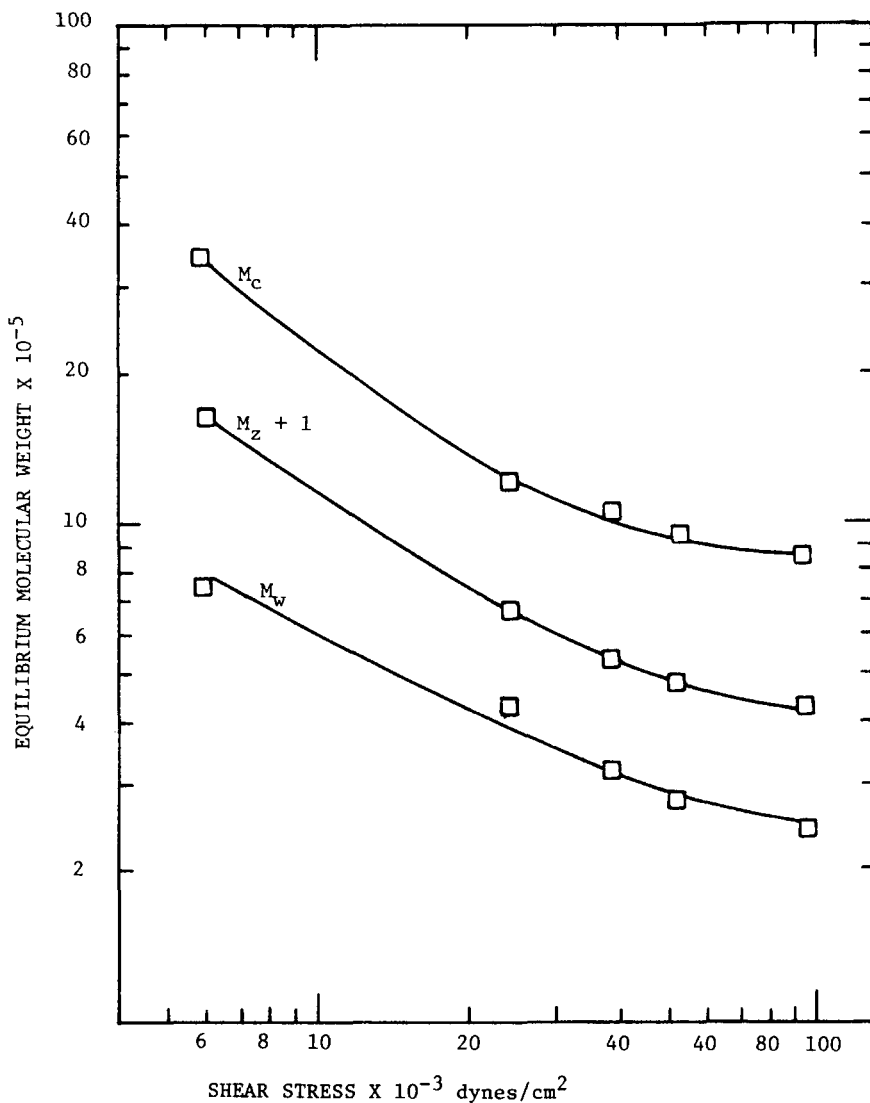
Fig. 6. Dependence of equilibrium MW on shear stress for ⅛% by weight of polyisobutene L-140 in 110 cp oil.

Undegradable Molecular Weight

For 0.5% by weight of polyisobutene, a logarithmic plot of equilibrium molecular weight versus shear stress is shown in Figure 4. The results are similar to those for 1% as shown in Figure 3, except that they deviate from a straight line at higher shear stresses (low molecular weight). This deviation may be explained by the effects of entanglements. There are fewer entanglements at a lower concentration than at a higher concentration. As the molecules degrade to a small size where they can adjust themselves and flow more freely in the shear field, degradation will be determined by the number of entanglements. Therefore, in the relatively low molecular weight region, the 1% polymer solution may degrade further with increasing shear stress while the 0.5% solution may
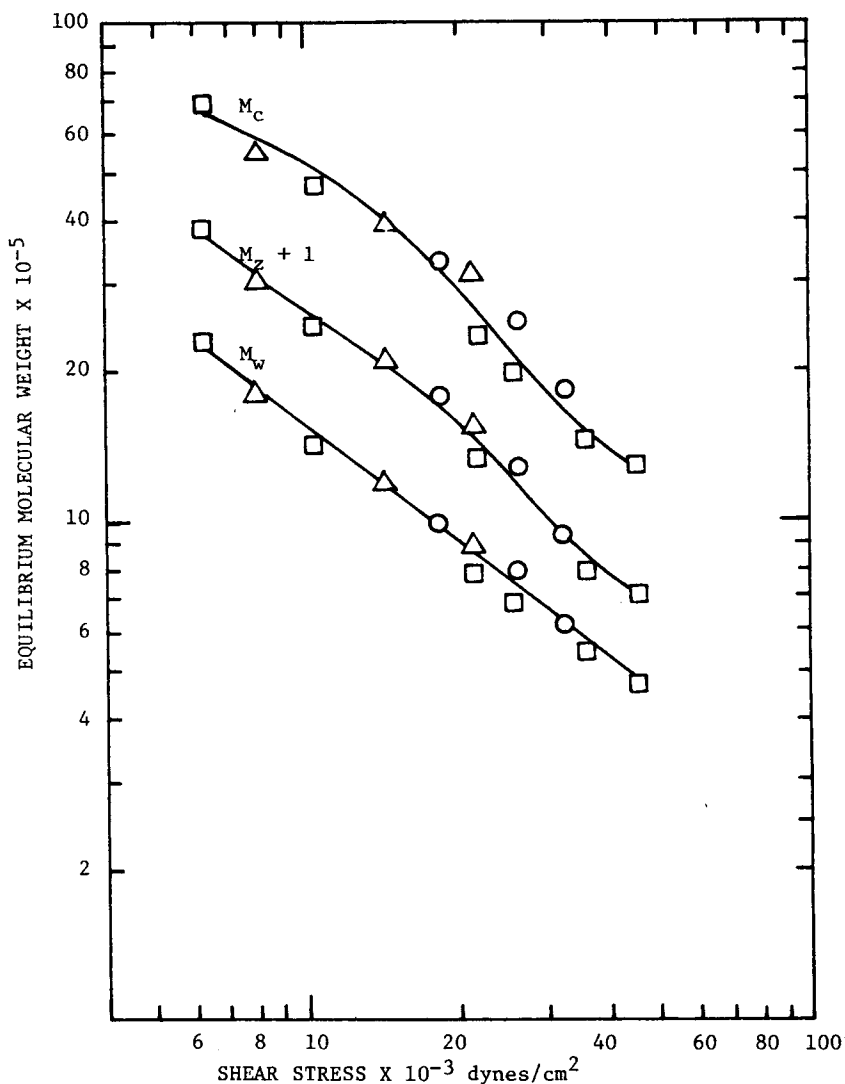
Fig. 7. Dependence of equilibrium MW on shear stress with different initial MWs for 1% by weight of polystyrene in 13 cp oil: (O) 7M; (□) 4M; (△) 2M.

not degrade as effectively since fewer entanglements are present. The effect of concentration on degradation in the region of relatively higher molecular weight will be discussed later.

Figure 4 shows a tendency to approach an undegradable molecular weight below which no further degradation is observed as shear stress increases. This tendency is more pronounced at lower concentrations (Figs. 5 and 6). For the 0.25% solutions, as shown in Figure 5, the results are similar to those for the 0.5% solution except that they start to level off at higher molecular weights. Figure 6 is for 1/8% solution, and the curves start to level off at even higher molecular weights. A logarithmic plot of undegradable molecular weight versus concentration is shown in Figure 10. A linear correlation may be seen. Hence, since
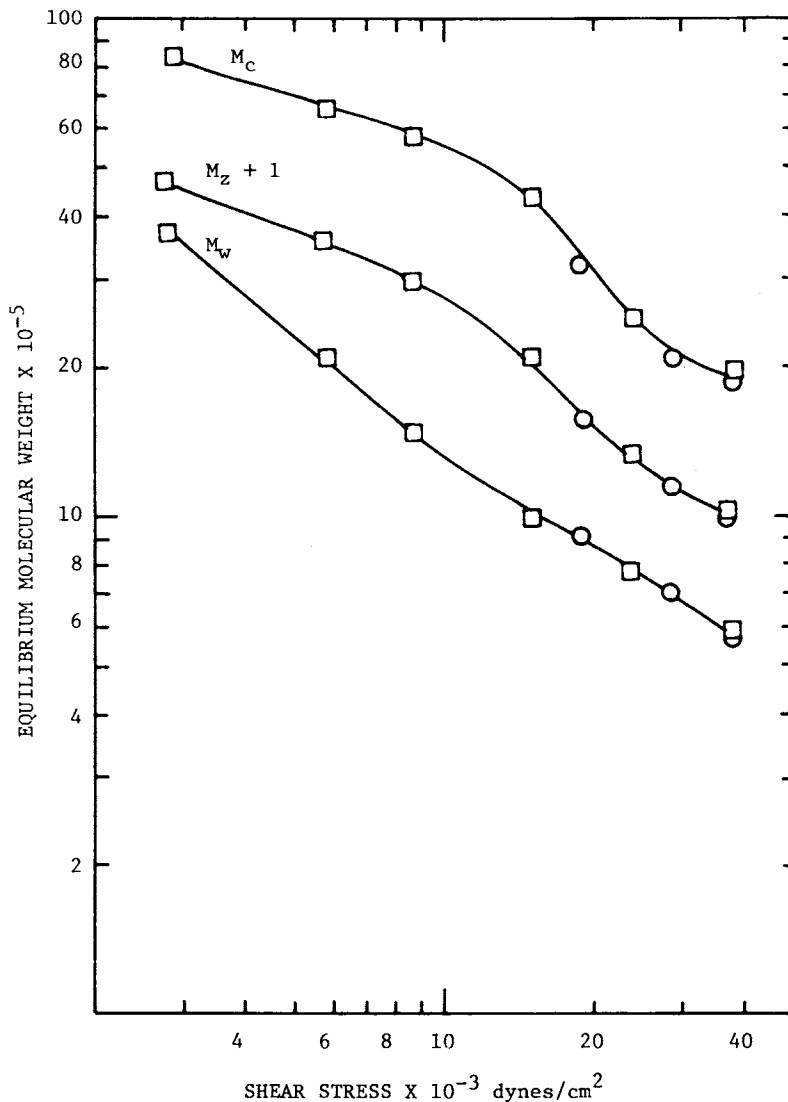
Fig. 8. Dependence of equilibrium MW on shear stress with different initial MWs for $\frac{1}{4}$% by weight of polystyrene in 13 cp oil: (O) 7M; (□) 4M.

undegradable molecular weight is lower at a higher concentration, it apparently depends on the number of entanglements present, increasing with decreasing number of entanglements, and vice versa.

No undegradable molecular weight can be seen in the data for polystyrene although the curves are flattening at low molecular weight. However, the maximum shear stress attainable in the lower viscosity oil (Figs. 7, 8, and 9) is less than half that attained with the polyisobutene solutions (Figs. 3–6), and an undegradable molecular weight for polystyrene might be observed at higher shear stresses.
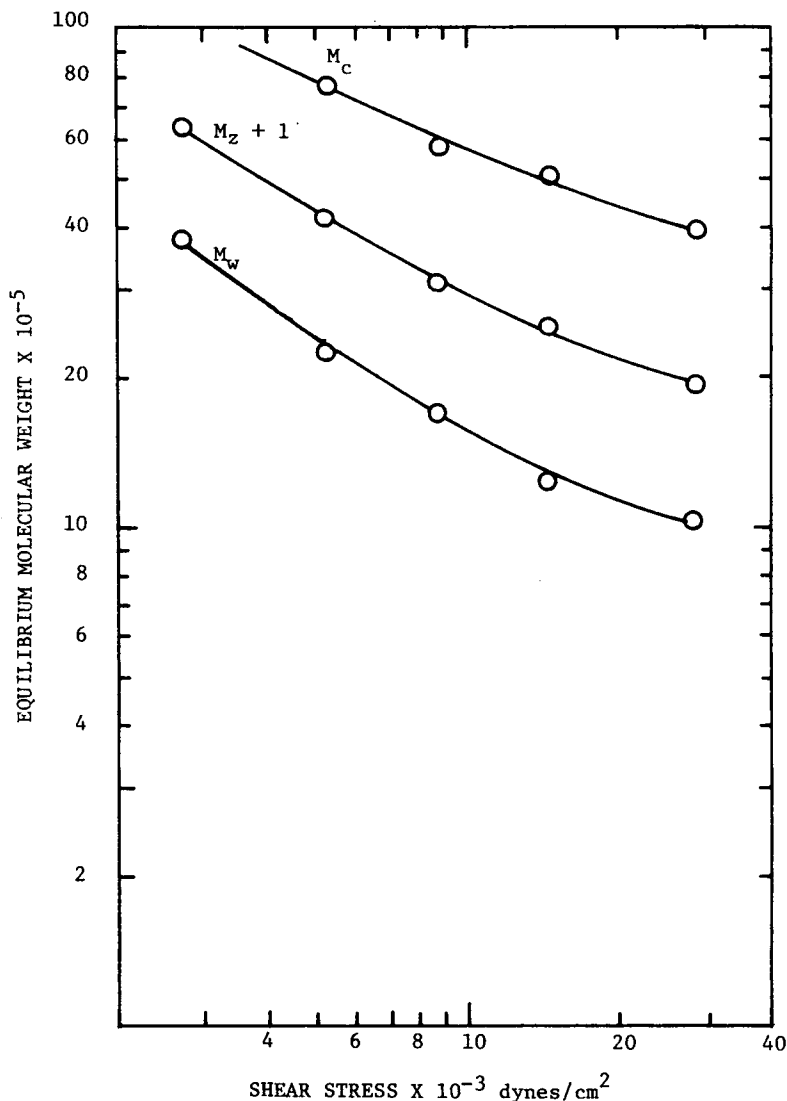
Fig. 9. Dependence of equilibrium MW on shear stress for 0.1% by weight of polystyrene 7M in 13 cp oil.

It should be noted that the undegradable molecular weight is not the same as the limiting molecular weight used by many other investigators. Many workers studied shear degradation with high-speed stirring or in capillary tubes. These methods cannot give a uniform shear field. Therefore, it takes a very long period of time to allow each molecule to experience the maximum shear stress and reach equilibrium molecular weight. They called this equilibrium molecular weight the limiting molecular weight at a given shearing condition. The undegradable molecular weight, however, means that the molecules will not degrade any further at any shear stress.
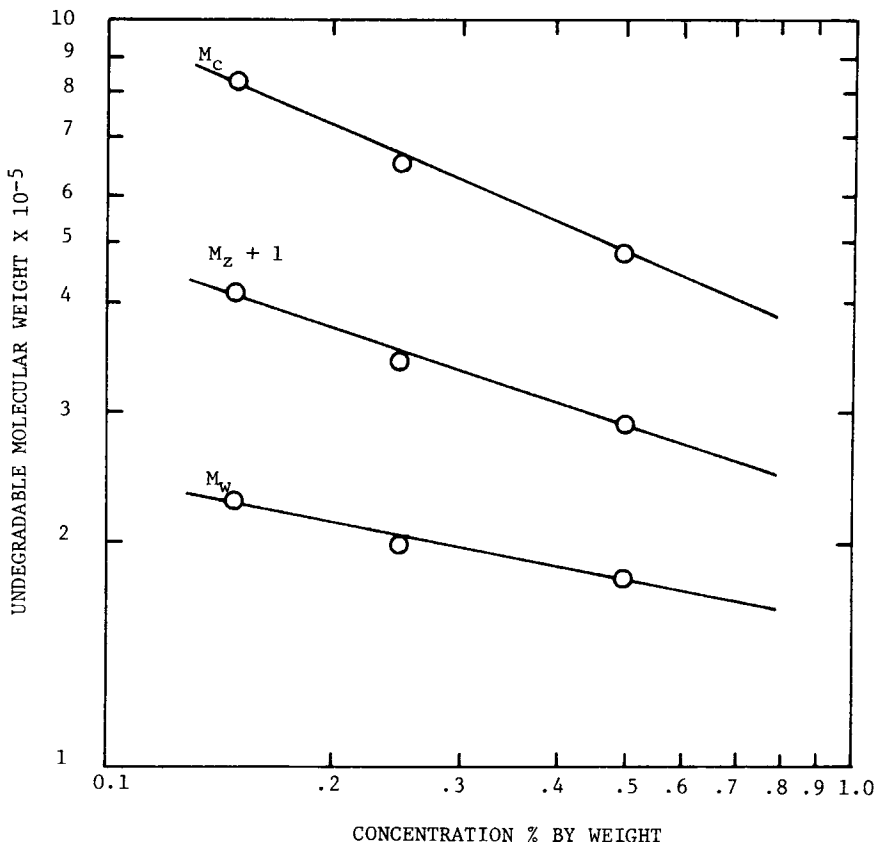
Fig. 10. Effect of concentration on undegradable MW for polyisobutene.

Effect of Concentration

For the sake of easily recognizing the effects of concentration on degradation, all the results at different concentrations of polyisobutene (Figs. 3–6) are plotted on the same graph (Fig. 11). In the region of low shear stress (relatively high molecular weight), it shows that degradation is more effective at lower concentration. This is a negative coefficient of the concentration dependence of the degradation effectiveness which contrasts with the positive concentration dependence found in the region of undegradable molecular weight (high-shear stress). If the entanglements are the only factor involved for shear degradation, the degradation effectiveness should always show a positive concentration dependence. However, these polyisobutene results show that this is not the case. Therefore, there must be some other factor besides entanglements involved in shear degradation. "Stretching" of the individual molecules could be another factor involved since "stretching" has a negative concentration dependence. At higher concentrations, molecular extensions are inhibited by the surrounding molecules. Therefore, degradation is limited at higher concentrations.

At high shear stresses, polystyrene also showed a positive concentration dependence (Figs. 7–9). At low shear stresses, however, the polystyrene results appear to have a zero concentration dependence, suggesting that neither of the effects is dominant in this region.
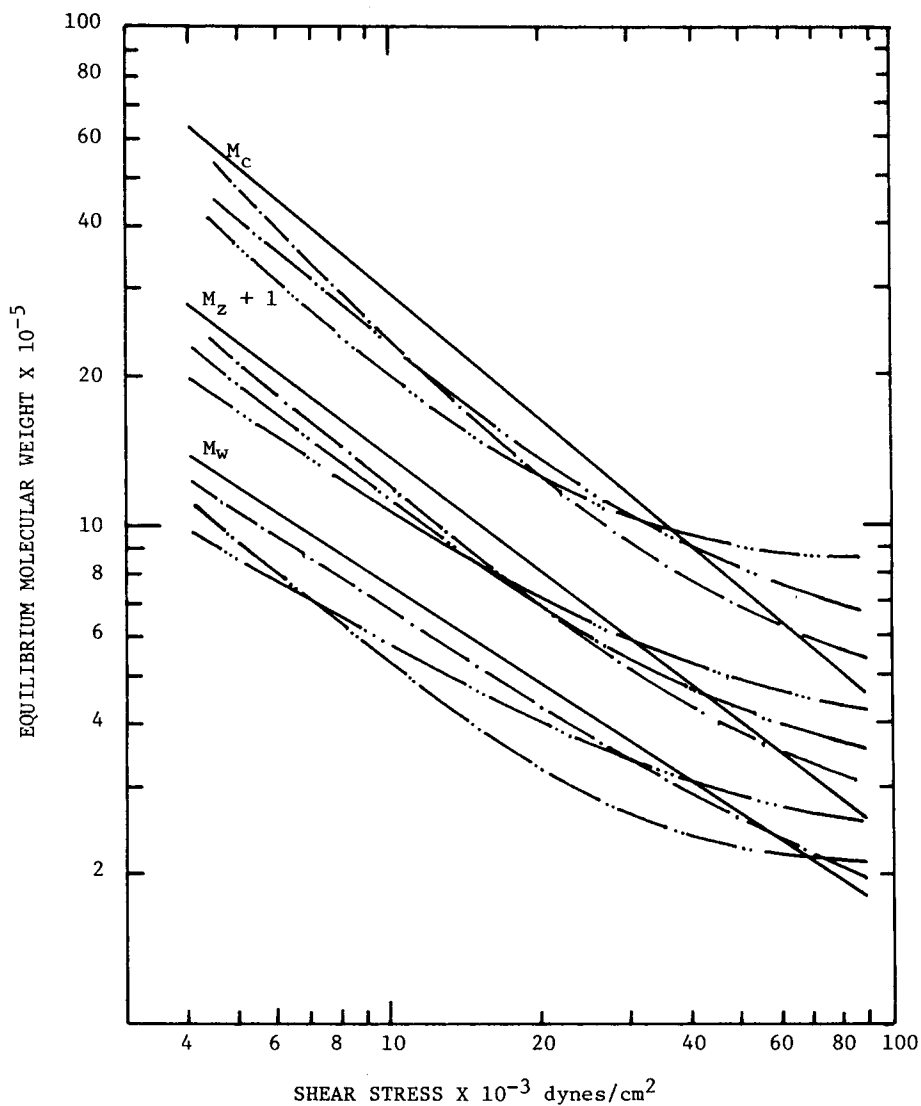
Fig. 11. Dependence of equilibrium MW on shear stress at various concentrations for polyisobutene: (—) 1%; (– · – ·) ½%; (– · · –) ¼%; (– · · · · –) ⅛%.

Literature reports show positive, negative, and zero concentration coefficients (Table V) for shear degradation.   Porter and Johnson,[25] Nakano and Minoura,[4] Ram and Kadim,[18] Goodman,[11] Yew and Davidson,[20] and other investigators reported negative concentration dependences.   This has been explained as the result of inhibition of molecular extension by surrounding molecules.

However, Rodriguez and Winding[43] were able to extrapolate to zero degradation at infinite dilution (positive concentration dependence).   They concluded that entanglements were the only factor for shear degradation at lower concentrations.   But recently, Zakin and Hunston[44] studied degradation at concentrations as low as 150 ppm and observed degradation with a negative concentration dependence in a thermodynamically "good" solvent and no concentration

TABLE V
Reports on Dependence of Mechanical Degradation on Concentration

Authors	Degradation methods	Polymers	Initial molecular weight	Solvents	Concentration range	Concentration dependence
Porter and Johnson[25]	concentric cylinder viscometer	polyisobutene	$M_v = 8.4 \times 10^5$ to 2.24×10^6	cetane (n-hexadecane) and 1,2,4-trichlorobenzene	4.2% and 9.6%	negative
Nakano and Minoura[4]	high-speed stirrer	poly(methyl methacrylate) polystyrene	$M_v = 6.2 \times 10^5$ $M = 2 \times 10^6$ nominal	chloroform, benzene, ethyl acetate methyl ethyl ketone, toluene, dioxane	0.04%-2%	negative
Ram and Kadim[18]	capillary tube	polyisobutene	$M_v = 6.4 \times 10^6$	decalin	0.26%-1.05%	negative
Goodman[11]	capillary tube	polyisobutene	$M_v = 1.74 \times 10^6$	cetane (n-hexadecane)	3%-5% 5%-20%	zero negative
Yew and Davidson[20]	capillary tube	DNA	not specified	water	0.5 ppm 5 ppm	negative zero
Zakin and Hunston[44]	high-speed stirrer	polystyrene	$M_w = 7.1 \times 10^6$ 4.1×10^6 2.4×10^6	toluene mixed solvent (poor solvent)	150-1000 ppm 150-1500 ppm	negative zero
Rodriguez and Winding[43]	high-speed stirrer	polyisobutene	$M_v = 2.0 \times 10^6$	solvent used in this concentration range not specified	0.05%-0.6%	positive
Johnson and Price[1]	high-speed stirrer	polyisobutene	$M_v = 1.2 \times 10^6$	cyclohexane	1% and 4.2%	zero
Minoura et al.[8]	high-speed stirrer	poly(ethylene oxide)	$M_v \sim 10^6$	benzene	2%-5%	zero
Nakano and Minoura[7]	high-speed stirrer	poly(ethylene oxide) poly(methyl methacrylate)	$M_v = 640,000$ $M_v = 770,000$	benzene benzene	1%-4% 1%-4%	zero zero
Abdel-Alim and Hamielec[27]	concentric cylinder viscometer	polyacrylamide	$M = 5.83 \times 10^6$	water	0.2% and 0.7%	zero
Kaverina[29]	concentric cylinder viscometer	polyisobutene	$M_v = 30,000$	mineral oil	5% and 20%	zero
Cavalieri and Rosenberg[45]	atomizer	DNA	$M_w = 3.5 \times 10^6$	water	0.03%-0.8%	zero

effect in a "poor" solvent.[‡] Therefore, it is not certain that entanglements are the predominant mechanism in dilute solutions. Other investigators such as Johnson and Price,[1] Minoura et al.,[8] Nakano and Minoura,[7] Abdel-Alim and Hamielec,[27] Kaverina,[29] and Cavalieri and Rosenberg[45] observed no concentration dependence. No obvious trend of the effect of concentration on the concentration dependence is apparent in these reports.

The conflicting results may be explained by the concept that two factors, entanglements and inhibition of molecular extension by surrounding molecules, are at work. Either may be dominant at a given set of conditions. Polymer concentration, polymer nature and molecular weight, solvent nature, and nature and intensity of the shear field are all factors which influence which mechanism is dominant.

CONCLUSIONS

As a result of this study the following conclusions can be made:

1. Mechanical shear degradation appears to be a nonrandom process.

2. Degrading a broad molecular weight distribution polymer such as polyisobutene narrows the distribution principally through the breaking down of the larger molecules.

3. Degrading a monodisperse polystyrene results in broadening of the distribution initially and then narrowing the distribution at higher shear stresses. At higher shear stresses, the distribution is not as broad as the low shear stress product but is still broader than that of the original polymer.

4. Breakage does not necessarily occur at the midpoint of the polymer chain. But the midpoint has the highest probability of being a breaking site.

5. There are two important factors for mechanical shear degradation: one is "entanglements," another is "stretching." At relatively low molecular weight (high shear stresses), "entanglements" are the dominant factor for degradation, i.e., positive concentration dependence; at relatively high molecular weight (low shear stresses), "stretching" is the dominant factor, i.e., negative concentration dependence.

6. An undegradable molecular weight, at which molecules will not degrade any further at any shear stress was observed for polyisobutene. This undegradable molecular weight decreases with increasing concentration.

7. Shear stress is the controlling parameter for mechanical shear degradation, not shear rate or the rate of energy input.

8. The shear degradation is independent of initial molecular weight and the viscosity of the solvent at a given shear stress.

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[‡] Solvent goodness was not a variable in the present investigation as the three oils used with polyisobutene were similar in their solvent nature (Table II). Variations in aniline point are due to differences in viscosity of the solvents.

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