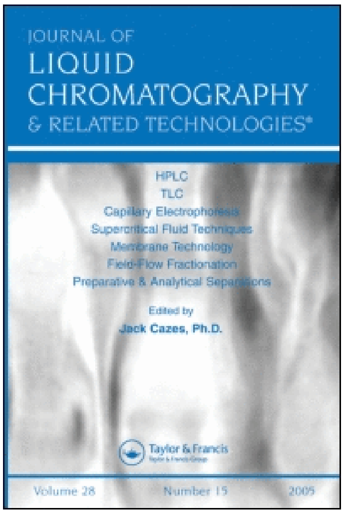

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

A Review of Polymer Shear Degradation in Size-Exclusion Chromatography

H. G. Barth[a]; F. J. Carlin Jr.[a]
[a] Hercules Incorporated, Research Center, Wilmington, Delaware

To cite this Article Barth, H. G. and Carlin Jr., F. J.(1984) 'A Review of Polymer Shear Degradation in Size-Exclusion Chromatography', Journal of Liquid Chromatography & Related Technologies, 7: 9, 1717 — 1738
To link to this Article: DOI: 10.1080/01483918408068832
URL: http://dx.doi.org/10.1080/01483918408068832

JOURNAL OF LIQUID CHROMATOGRAPHY, 7(9), 1717-1738 (1984)

A REVIEW OF POLYMER SHEAR DEGRADATION IN SIZE-EXCLUSION CHROMATOGRAPHY

H. G. Barth and F. J. Carlin, Jr.
Hercules Incorporated
Research Center
Wilmington, Delaware 19894

ABSTRACT

Although there have been only a few studies involving shear degradation of polymers in size-exclusion chromatographic (SEC) columns, it appears that the potential for degradation exists when analyzing high molecular weight polymers. Because of the complex hydrodynamics associated with SEC systems, it is very difficult to arrive at simple correlations between SEC operational parameters and the onset of shear degradation. Also, the dependency of shear degradation on polymer concentration, structure, and the nature of the mobile phase further complicates this issue. Nevertheless, guidelines involving operational parameters are presented based on published data and estimated shear rates produced in various parts of a SEC system.

INTRODUCTION

The introduction of high-performance packings in size exclusion chromatography (SEC) has brought about a significant decrease in analysis time and an increase in resolving power. Like other high-performance liquid chromatographic techniques, the current trend is to use smaller particle size packings to obtain maximum column efficiency. However, most analysts forget

0148-3919/84/0709-1717$3.50/0

that high molecular weight polymers, whether synthetic or naturally occurring, are fairly sensitive to shear forces which can lead to chain rupture. As compared with conventional SEC in which mobile phase flow velocities range from about 0.02 to 0.10 cm/sec, velocities used in HPSEC are typically 5 times greater. Also, because of the much smaller particle sizes used in SEC, the shear rates generated in these columns are significantly greater than obtained in conventional columns. As a result, shear degradation of polymers during elution through a column is possible.

Presented are a discussion on the theory of polymer shear degradation, estimates of shear rates which can occur in chromatographic columns, and a review of reports published in this area of study. Guidelines are also given for minimizing the occurrence of polymer shear degradation during SEC.

THEORY

The relationship between shear stress (applied force per unit area) and shear rate of a Newtonian liquid under laminar flow is given by:

$$\tau = \eta\dot{\gamma} \qquad (1)$$

where τ is shear stress (dynes/cm^2), η is viscosity of the solution (poise, g$\bullet$cm^{-1}$\bullet$sec^{-1}), and $\dot{\gamma}$ is shear rate (sec^{-1}) or the velocity gradient (dv/dy) formed perpendicular to the direction of flow.

In calculating the shear rate of a packed column, we assume that the column consists of a bundle of capillaries in which the capillary radius can be estimated from the bed hydraulic radius:

$$R_h = D_p \varepsilon/3(1-\varepsilon) \qquad (2)$$

where D_p is the diameter of the packing and ε is the porosity of a packed column ($\varepsilon = 0.36$) (1). Thus, the shear rate in a packed column, assuming Newtonian behavior, is readily calculated using:

$$\dot{\gamma} = 4\ \bar{v}/R_h = 4Q/\varepsilon A R_h \quad (3)$$

where $\bar{v}$ is the average linear velocity, Q is the flow rate, and A is the cross-sectional area of the column. For open tubes, ε is unity and the tube radius is equal to R_h.

DEGRADATION MECHANISMS

Because of velocity gradients generated during flow, a polymer becomes extended. Bonds near the middle of the chain become stretched and can rupture if shear rates are great enough. The end segments of a chain maintain their coiled shape; thus, the maximum strain is usually focused near the center of the polymer. To a first approximation, the strain generated in a polymer is proportional to the square of its length (2, 3). The weak points along a polymer chain are determined by its length and structure. According to Bird et al. (4), there is no reliable quantitative theory of mechanical stability of polymers, and the stability of each polymer must be determined experimentally under strictly defined conditions.

In addition to shear forces, extensional flow components may also play a significant role in polymer degradation. These flow components would cause more stress on the chain than that produced by a laminar flow. Extentional flow occurs at capillary entrances and exits and at convergent-divergent flow paths in packed beds (5-8). Recently, Giddings (25) had shown extentional flow in packed columns multiplies the shear effect by about 10^3 beyond that of tangential shear.

When shear is applied, the most probable sites of stress concentration on the polymer chain are (3):

1. Side chain linkages to main chain, i.e., branch points.
2. Crosslink points in networks.
3. Points of inclusion of heteroatoms and quaternary carbon atoms.
4. Dissymmetry between adjacent atoms which promotes rupture of the chain by stretching forces.

Chain entanglements are also quite sensitive to shear stress. Junction points of entangled chains concentrate energy due to stress and thus can break. The mechanism depends on the time scale of shear deformation, temperature, probability of entanglement, and slippage of junction points (9-11). Thus, polymer solutions which contain entangled chains are more shear sensitive than more dilute solutions in which entanglements have not occurred. The extent of chain entanglement also depends on the nature of the solvent (4). Recently, Yu et al. (12) have studied the concentration dependency of shear degradation and have postulated that both entanglements and inhibition of molecular extention by surrounding molecules in concentrated solutions are contributing factors. Therefore, although entanglements which occur at high polymer concentrations may favor shear degradation, molecular extensions are inhibited by surrounding molecules.

Polymers that are extended in solution, i.e. dissolved in good solvents, exhibit a higher sensitivity toward shear degradation than more randomly coiled polymers (13-15). For example, the rate of mechanical chain scission of dextran is approximately 100 times lower than for polyacrylamide (13).

With sufficiently high internal stresses, bonds rupture and produce radicals. In the presence of radical acceptors, e.g., oxygen, radicals that are formed are stabilized resulting in a decrease in molecular weight. However, in the absence of radical acceptors, branching and crosslinking are possible (3).

There are two popular theories regarding the mechanism of shear degradation with respect to molecular weight (3). One theory proposes that during degradation a limited molecular weight is approached (16). Once this limited or critical molecular weight (or more precisely chain length) is reached, no further chain scission can occur (17). This critical chain length is short enough that it can adjust to the applied stress by moving with respect to its sheath of solvent molecules rather than by rupturing primary bonds. The second theory, postulated by Rodriguez and Winding (18), states that there is no critical molecular weight which is resistant to degradation at a given shear rate. There is, however, a decreased probability that degradation will occur as the molecular weight decreases.

POSSIBLE SOURCES OF POLYMER SHEAR DEGRADATION IN SEC

In size-exclusion chromatography, the following are potential sources of polymer shear degradation:

Injection valve
Capillary tubing
Column frits
Packed column

It should be emphasized that shear degradation may also occur during sample preparation. In view of this, it is advisable to use low shear rate conditions such as tumbling and low speed stirring.

The following are estimated shear rates calculated from Equation 3. Because of the many factors which influence polymer degradation, these values are used to demonstrate the magnitude of shear rates which can be developed in various parts of the chromatographic systems.

Injection Valves

Typical sample loop sizes are shown in Table 1 with the corresponding shear rates produced assuming a 1 ml/min flow rate. Also included are shear rates developed in the smallest flow passages of the valve.

Capillary Tubing

Capillary tubes, which are used for column and detector connections as well as for sample loops in injection valves, usually range in ID from 0.01 to 0.04 inches. As shown in Table 2, the shear rates generated in these tubes can be quite high.

Frits

Commonly used stainless steel frits have an average channel radius of about 1 μm. Assuming a flow rate of 1 ml/min through a 6-mm diameter disc (ϵ ~0.3), the estimated shear rate generated is about 7.8×10^3 $\sec^{-1}$.

Shear Rate in Packed Columns

The shear rates generated in columns as a function of particle diameter are shown in Figure 1 for 0.5 and 1.0 ml/min flow rates. Results were calculated assuming a 4-mm ID column. As indicated, columns packed with >40 μm particles exhibit relatively low shear rates of less than 1000 $\sec^{-1}$. For high performance packings of 10 μm, the shear rate ranges from 4-8 $\times 10^3$ $\sec^{-1}$. Packings of 5 μm, which represent about the smallest D_p of commercial SEC packings, will generate shear rates between 0.8 to 1.6 $\times 10^4$ $\sec^{-1}$.

TABLE 1

Estimated Shear Rates Produced in Injection Valves*

Sample Loop Capacity (µl)	ID, inches	$\dot{\gamma}$, sec^{-1}
10	0.012	6×10^3
20 to 100	0.020	1.3×10^3
Passages in Rotor Seal	0.018	1.8×10^3

*Assume 1 ml/min flow rate. Dimensions are for a Rheodyne 70-10 sample injection valve. Calculated using Equation 3 and setting ε to unity.

TABLE 2
SHEAR RATE PRODUCED IN DIFFERENT DIAMETER CAPILLARY TUBING AT 1 ML/MIN

ID, inches	$\dot{\gamma}$, sec^{-1}
0.01	1.0×10^4
0.02	1.3×10^3
0.03	3.8×10^2
0.04	1.6×10^2

The effect of flow rate on shear rate for 4-mm diameter columns packed with 5, 10, and 20 µm particles is shown in Figure 2. For 10-µm packings, the shear rate can be kept below 1×10^4 sec^{-1} by employing flow rates less than 1 ml/min. For flow rates less than 0.1 ml/min, shear rates of $<1 \times 10^3$ sec^{-1} can be achieved for both 5 and 10-µm diameter packings.

As will be discussed, a shear rate below about 1×10^4 sec^{-1} is probably sufficiently low to avoid shear degradation of most polymers of $<1 \times 10^6$ molecular weight. Thus for

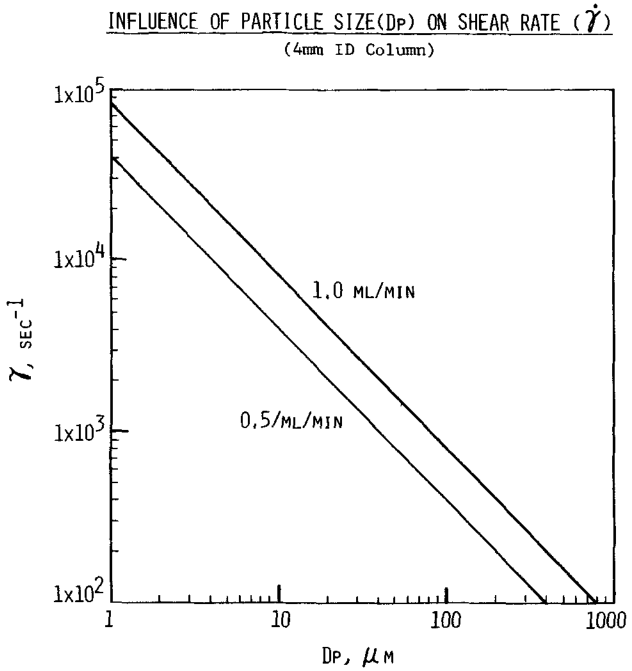

FIGURE 1. Shear rate generated in a 4-mm ID column versus particle diameter at 0.5 and 1.0 ml/min flow rates. Shear rates were calculated using Equation 3.

high performance packings of 10μm, flow rates of less than 1 ml/min are recommended for 4mm-ID columns. For ultrahigh molecular weight (>1 x 10^6) samples, flow rates <0.1 ml/min may be necessary. Because of the inverse logarithmic relationship between D_p and shear rate (Figure 1), the use of SEC packings much lower than 5μm is questionable. These high efficiency packings should be used only for lower molecular weight polymers to avoid shear degradation. Obviously, lower velocities can be easily obtained using wider diameter columns. For decreased analysis times, short columns at low flow rates

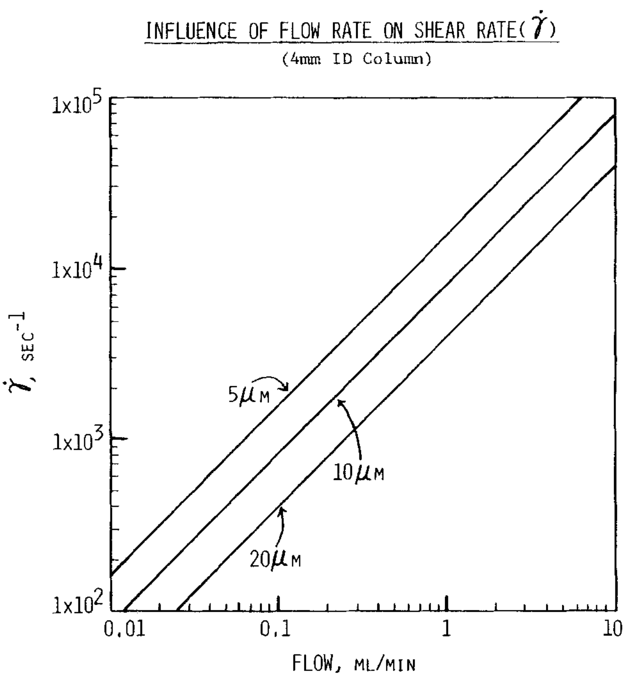

FIGURE 2. Shear rate versus flow rate produced in 4-mm ID columns packed with 5, 10, and 20μm diameter particles. Shear rates were calculated using Equation 3.

may be optimal. For an excellent discussion of the influence of particle size on both critical molecular weight and column efficiency see Giddings (25). Also, as reported by Giddings, elongational strain rates may have a more pronounced effect on polymer chain rupture than shear rate.

The calculated shear rates found in column frits are relatively high. Thus, low porosity frits should be avoided. If possible, 5μm or larger frits should be employed. Capillary tubing appears to be a major potential source of shear degradation. Since most high performance injectors, detectors, and column connections utilize 0.01 inch ID capillary tubes to reduce band broadening, fairly high shear rates can be produced in these systems. As shown in Table 2, capillary tubes of 0.02 inches ID or greater should be employed when analyzing high molecular weight samples. It should be emphasized that capillary tubing incorporated into detectors can also be a significant source of shear. For example, the Waters 401 refractometer utilizes 0.009 inch ID tubing for the detector inlet. This would generate 1.4×10^4 sec^{-1} at 1 ml/min flow.

A comparison of shear rates in a high performance versus a conventional SEC system is shown in Table 3. As indicated, shear rates generated in high performance systems are one to two orders of magnitude higher.

CRITICAL MOLECULAR WEIGHTS AND SHEAR RATES

It should be emphasized that the shear rates estimated for high performance SEC should serve only as a rough guide when relating these values to critical shear rates (or stress) and critical molecular weights established in other types of shear fields, e.g., capillary tubes, concentric cylinders, or high speed stirring. The hydrodynamics associated with an SEC system, from injector to detector, are highly complex and dependent on the geometry of flow channels, structure of the packed bed, production of local points of turbulence, and

Table 3

Comparison Of Shear Rates Generated In High Performance Versus Conventional SEC Systems

	$\dot{\gamma}$, sec^{-1}	
Source of Shear	High Performance(1)	Conventional(2)
Capillary Tubing	1×10^4	1.6×10^2
Frits	7.8×10^3	2.2×10^2
Column	8×10^3	3.6×10^2

(1) Flow: 1 ml/min; column: 4 mm ID; D_p: 10 µm; capillary: 0.01 inch ID; frit: 2µm; R_h: 1.86µm (velocity through column: 0.37 cm/sec).

(2) Flow: 1 ml/min; column: 7.9 mm ID; D_p: 56 µm; capillary: 0.04 inch ID; frit: 10µm; R_h: 10.4 µm (velocity through column: 0.095 cm/sec).

inhomogeneity of shear fields. For example, if turbulence were present, different segments of the chain may be caught in eddies moving in various directions thus producing additional strain on the polymer. Thus, the shearing conditions in SEC are very difficult to define.

There appears to be no adequate model to predict shear sensitivity of a given polymer (4). Critical molecular weights and shear rates must be determined experimentally (25). Even when these values are known, they are highly dependent on experimental conditions and the technique used to generate the shear rate or stress (2). Furthermore, it has been proposed that entangled chains rather than individual molecules are more shear sensitive because of the concentration of energy at junction points (9, 11, 19).

Frenkel (2), who did not take into account entanglements, estimated that the critical shear rate for a polymer of degree of polymerization of 10^3 is 10^5 sec^{-1}. From experimental work and thermodynamic considerations, Morris and Schnurmann (20) reported that shear rates of more than 1.6×10^6 sec^{-1} would be required for shear degradation of hydrocarbon polymers of molecular weights of 2.5×10^4 and less. At 10^5 sec^{-1} under laminar flow conditions, polymers of molecular weights $>10^5$ were degraded.

DEGRADATION OF POLYMERS DURING SEC

Surprisingly, there have been only a relatively small number of papers describing shear degradation of polymers in SEC (19, 21-26). Slagowski et al. (21) have demonstrated that both 4.37×10^7 and 2.73×10^7 molecular weight polystyrene degrades during SEC using a conventional system (Styragel) at flow rates as low as 0.25 ml/min ($\dot{\gamma} = 95$ sec^{-1}). A chromatographed sample of the 4.37×10^7 polystyrene run at 1 ml/min ($\dot{\gamma} = 380$ sec^{-1}) was collected and from viscosity measurements was found to have a reduced viscosity of 25.6 dl/g as compared to 64 dl/g for the initial sample. At 1 ml/min, a 9.6×10^6 molecular weight polystyrene showed no apparent degradation as determined from elution volume measurements.

Using high performance SEC, Kirkland (18) has shown that 7.1×10^6 polystyrene was shear degraded above 0.1 cm/sec ($\dot{\gamma} = 2.7 \times 10^3$ sec^{-1}) using 8μm-silica particles.

Rooney and VerStrate (19) employed an on-line, low-angle laser light-scattering detector (LALLS) to study polymer degradation in SEC columns (μBondagel and Shodex 800 series) and found that polystyrene and several polyolefins of molecular weight $\geq 6.7 \times 10^5$ degraded above 0.5 ml/min flow rate. These authors also undertook a brief study of the effect of polymer concentration on shear degradation. Although they claim to see a small concentration dependency, the scatter about the data points appeared to be too high to warrant any conclusions. Their results suggest that shear rates as low as $2.7\text{-}6.4 \times 10^3$ sec^{-1} (calculated from Equation 3) were sufficient to obtain noticeable shear degradation of polymers $\geq 6.7 \times 10^5$ molecular weight. It should be noted, however, that the $\bar{M}_w$ results obtained at flow rates of 1.0 ml/min and greater may be in error because of excess light scattering presumably caused by thermal and/or flow inhomogeneities in the detector cell. In addition, contributions from peak broadening generated within the column and between the LALLS and differential refractometer may have complicated the results (28).

Huber and Lederer (26) measured the $\bar{M}_w$ of 1×10^6 molecular weight poly(isobutylene) as a function of flow rate employing a LALLS detector and Styragel columns. Polymer degradation was first noticeable at flow rates greater than 10 ml/hr ($\dot{\gamma}$ = 77 sec^{-1}). At a flow rate of 2 ml/min (930 sec^{-1}), $\bar{M}_w$ decreased by almost a factor of two. It should be noted, as described above, that no band broadening corrections were employed; thus the $\bar{M}_w$ data obtained on-line may be in error.

Using both Shodex and silica high performance columns (8 mm ID), Ye and Shi (23) studied shear degradation effects of polystyrene calibrants of molecular weights of 2.7 x 10^6 to 7 x 10^6 using a flow rate of 2 ml/min. (Equivalent to 0.5 ml/min for a 4-mm ID column.) Measurements were made using an off-line LALLS photometer and intrinsic viscosity measurements of collected samples. No molecular weight decrease was observed for the Shodex column; whereas, for the silica column (particle size not given), some degradation was obvious. The authors claim that since the pressure across the silica column was greater than for the Shodex column, pressure was a contributing factor.

Rand and Mukherji (24) investigated polystyrene shear degradation using two high-performance silica columns, μBondagel (4mm ID) and Zorbax Bimodal columns (6.2 mm ID), and an on-line LALLS detector. Although there was scatter in the data, it appeared that shear degradation had occurred for 3 x 10^6 and 7 x 10^6 molecular weight polystyrene standards at flow rates as low as 0.5 ml/min. Little shear degradation of polystyrenes in the molecular weight range of 5×10^4 to 1.8×10^6 was evident at flow rates of 0.5-1.5 ml/min using either of the silica columns.

Giddings (25) developed a relationship between the critical molecular weight of a polymer and shear stress in packed beds and uniform channels. Polyacrylamide ($\bar{M}_w$ ~6.2×10^6) was used as the test polymer and shear degradation was determined by measuring the reduction of intrinsic viscosity of the polymer after it passed through a column packed with controlled-pore glass (70µm). The experiment consisted of pumping two column volumes of polymer solution (0.05 and 0.10 wt%) through the column. Substantial viscosity loss was apparent at velocities as low as 0.025 cm/sec. Polymer degradation using nonporous glass particles of the same size as the SEC packing was about 25% lower, suggesting that polymer chains are more prone to rupture as they diffuse into and out of pores. Giddings also presented several useful equations that can be used to establish guidelines for avoiding polymer shear degradation and, at the same time, maximizing column efficiency.

In our laboratory, we have observed shear degradation of polystyrene calibrants using Zorbax PSM silica packings. Figure 3 is a polystyrene calibration curve obtained on a set of Du Pont Zorbax Bimodal columns using THF as the mobile phase. The backward curve of the high-molecular-weight end of the

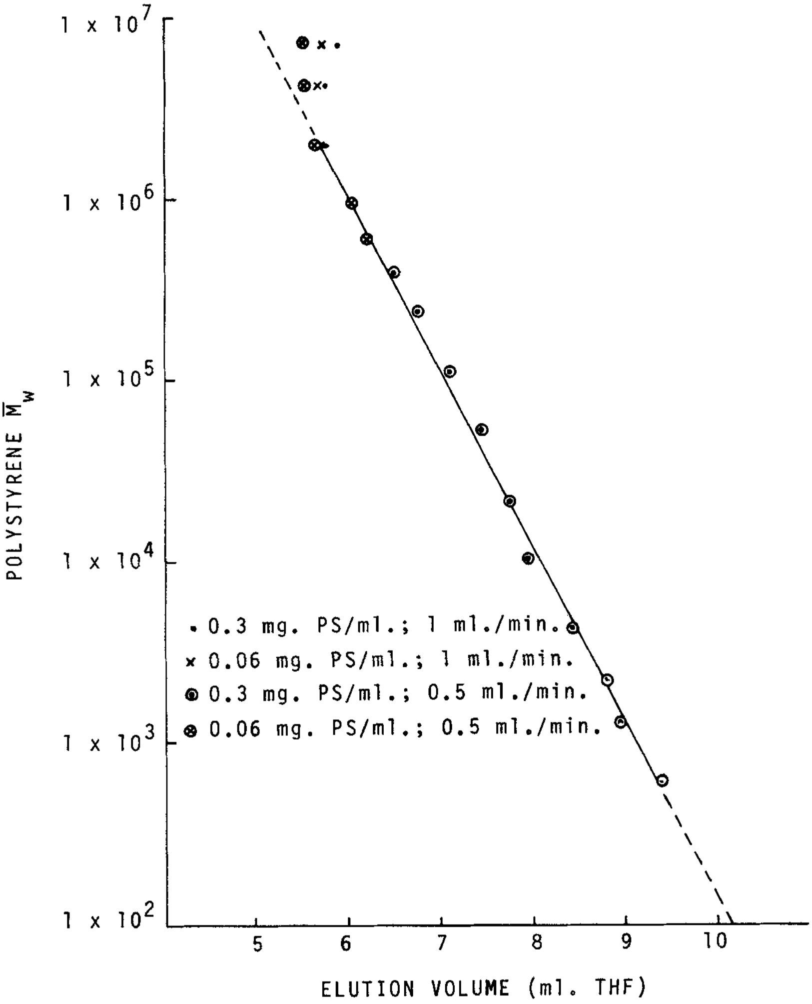

FIGURE 3. **Polystyrene calibration curve showing the effect of sample concentration and flow rate on elution volume. A Zorbax PSM 60-S and PSM 1000-S column-set (6.2mm diameter) was used with tetrahydrofuran as the mobile phase and 100-μl injection volumes.**

polystyrene calibration curve could be indicative of shear degradation. The 7×10^6 molecular weight polystyrene peak elutes near the 9.5×10^5 peak, and the 4.1×10^6 polystyrene elutes between 1×10^6 and 2×10^6 molecular weight polystyrene standards. The amount of shear degradation increased with mobile phase flow rate and with polymer concentration. It should be recognized, however, that other flow rate and concentration dependent effects could contribute to these observations.

CONCLUSIONS

Because of the complex hydrodynamics involved in SEC systems, it is very difficult to arrive at a simple correlation between operational parameters, such as flow rate and particle size, and onset of shear degradation. Also, the dependency of shear degradation on polymer concentration, chemical structure, and solvent further complicates this issue. Nevertheless, guidelines can be established, based on published data and estimated shear rates produced in various parts of an SEC system.

Because of the appearance of degradation with conventional columns in which very low $\dot{\gamma}$ are produced within the column, it is obvious that degradation may be occurring in capillary tubing associated with the system. As suggested by Giddings (25), elongational forces within the packed bed may have a more pronounced effect on polymer degradation than do tangential shear forces. Because of the high shear rates that can be generated in high-performance columns, it is advisable to measure elution profiles of samples as a function of flow rates. If an on-line light scattering photometer is available, the occurrence of degradation can be more readily determined. However, one should be aware of elution volume-flow rate dependence (27) and additional band broadening that can occur between concentration and LALLS detectors used in series (28).

Capillary tubing of large ID should also be employed providing that column efficiency is not sacrificed. Since HPLC detectors contain small (<0.010 inch) ID tubing, alternative detection systems may be required. Because of the inverse relationship between shear rate and particle radius, it is doubtful that small diameter SEC packings (<10μm) would prove useful for the analysis of high molecular weight polymers unless short, wide columns are used to obtain sufficiently low flow rates at acceptable analysis times.

Finally, since shear degradation of polymers may occur more readily with increased polymer concentration, fairly dilute polymer solutions may be required. The use of dilute solutions is also needed to avoid chromatographic effects such as macromolecular crowding and viscous fingering.

As can be seen, a significant amount of work is needed before we can fully understand and predict the extent of polymer degradation in chromatographic systems.

REFERENCES

1. McHugh, A. J., Liquid Chromatography of Polymer Latexes, in Advances In Emulsion Polymerization And Latex Technology, 9th Annual Short Course, Lehigh Univ., G. Poehlein, Editor, Vol. 1, 1978.

2. Frenkel, Y. I., Orientation and Rupture of Linear Macromolecules in Dilute Solution under the Influence of Viscous Flow, Acta Physiochim. USSR, 19, 51 (1944).

3. Casale, A., Porter, R. S. and Johnson J. F., The Mechanochemistry of High Polymers, Rubber Chem. and Technol., 44, 534 (1971).

4. Bird, R. B., Armstrong, R. C. and Hassager, O., Dynamics of Polymeric Liquids, Vol. 1, John Wiley & Sons, N.Y., 1977, p. 61.

5. Payatakes, A. C. and Neira, M. A., Model of the Constricted Unit Cell Type for Isotropic Granular Porous Media, A.I.Ch.E.J., 23, 922 (1977).

6. Neira, M. A. and Payatakes, A. C., Collocation Solution of Creeping Newtonian Flow Through Periodically Constricted Tubes, A.I.Ch.E.J., 24, 43 (1978).

7. Durst, F. and Haas, R., Elongated Flows with Dilute Polymer Solutions: A Theoretical Model and its Experimental Verification, Rheol. Acta, 20, 179 (1981).

8. Durst, F., Haas, R. and Kaczmar, B. U., Flows of Dilute Hydrolyzed Polyacrylamide Solutions in Porous Media under Various Solvent Conditions, J. Appl. Polym. Sci., 26, 3125 (1981).

9. Arisawa, K. and Porter, R. S., The Degradation of Polystyrene During Extrusion, J. Appl. Polym. Sci., 14, 879 (1970).

10. Porter, R. S. and Johnson, J. F., The Entanglement Concept in Polymer Systems, Chem. Rev., 66, 1 (1966).

11. MacArthur, A. and McIntyre, D., A Model of Chain Degradation in Very Dilute Solutions of High Molecular Weight Linear Polymers, ACS Polym. Prepr., 24 (2), 102 (1983).

12. Yu, J. F. S., Zakin, J. L. and Patterson, G. K.,

Mechanical Degradation of High Molecular Weight Polymers in Dilute Solution, J. Appl. Polym. Sci, 23, 2493 (1979).

13. Basedow, A. M., Ebert, K. H. and Hunger, H., Effects of Mechanical Stress on the Reactivity of Polymers: Shear Degradation of Polyacrylamide and Dextran, Makromol. Chem., 180, 411 (1979).

14. Nakaro, A. and Minovra, Y., Relationship between Hydrodynamic Volume and the Scission of Polymer Chains by High-Speed Stirring in Several Solvents, Macromolecules 8, 677 (1975).

15. Nakaro, A. and Minovra, Y., Degradation of Aqueous Poly(Acrylic Acid) and its Sodium Salt Solutions by High-Speed Stirring, J. Appl. Polym. Sci., 22, 2207 (1978).

16. Johnson, W. R. and Price, C. C., Shear Degradation of Vinyl Polymers in Dilute Solution by High-Speed Stirring, J. Polym. Sci., 45, 217 (1960).

17. Abdel-Alim, A. H. and Hamielec, A. E., Shear Degradation of Water-Soluble Polymers: Degradation of Polyacrylamide in a High-Shear Covette Viscometer, J. Appl. Polym. Sci., 17, 3769 (1973).

18. Rodriguez, F. and Winding, C. C., Mechanical Degradation of Polyisobutylene Solutions, Ind. Eng. Chem., 51, 1281 (1959).

19. Rooney, J. G., and VerStrate, G., On-line Determination by Light Scattering of Mechanical Degradation in GPC, in Liquid Chromatography Of Polymers And Related Materials, J. Cazes, Ed., Vol. 3, M. Dekker, N.Y., 1981, p. 207.

20. Morris, W. J. and Schnurmann, R., Mechanical Degradation of Large Molecules, Nature, 160, 674 (1947).

21. Slagowski, E. L., Felters, L. J. and McIntyre, D., Upper Molecular Weight Limit for the Characterization Of Polystyrene by GPC, Macromolecules, 7, 394 (1974).

22. Kirkland, J. J., Porous Silica Microspheres for High-Performance Size Exclusion Chromatography, J. Chromatogr. 125, 231 (1976).

23. Ye, M.-L. and Shi, L.-H., A Study of Mechanical Degradation of Polymers in High Performance GPC, J. Liq. Chromatogr, 5, 1259 (1982).

24. Rand, W. G. and Mukherji, A. K., Molecular Weight Determination of Polystyrene using SEC Interfaced with a Low-Angle Laser Light Scattering Photometer: The Influence of Flow Rate, J. Polym. Sci.: Polym. Letter Ed., 20, 501 (1982).

25. Giddings, J. C., Analysis of Fundamental Obstacles to SEC of Polymers of Ultrahigh Molecular Weight, Adv. Chromatogr., 20, 217 (1982).

26. Huber, C. and Lederer, K. H., Flow-Rate Dependent Degradation of High Molecular Weight Polyisobutylene in GPC, J. Polym. Sci., Poly. Letter Ed., 18, 535 (1980).

27. Aubert, J. H. and Tirrell, M., Flow Rate Dependence of Elution Volumes in SEC: A Review, J. Liq. Chromatogr., 6 (S-2), 219 (1983).

28. Bressau, R., Problems in Multiple Detection of GPC Eluents, in Liquid Chromatography Of Polymers and Related Materials, J. Cazes, Ed., Vol. 2, M. Dekker, N.Y., 1980, p. 73.