Solvent "Goodness" in Polymer Separation by Flow

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LETTER TO THE EDITOR

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It has been recently shown [1] that flow of a polymer solution through a tube should lead to a continuous separation of the polymer molecules according to size. The reason is that the average polymer velocity is greater than that of the fluid. The difference between both velocities is proportional to the effective radius of the polymer molecule. Consequently, larger molecules flow faster than smaller ones and a continuous separation occurs. Separation of polymer molecules according to size is important because polymer dimensions are proportional to some power of the molecular weight M, and separation of molecular weights is, thus, simultaneous with it.

The purpose of this letter is to point out that this separation of molecular weights by flow should become more effective with good solvents. The reason is, simply, that polymer dimensions are more strongly dependent on M when good thermodynamic conditions are present. For the mean square radius of gyration $\langle S^2 \rangle$, the well-known relationship $\langle S^2 \rangle \sim M^{1+\alpha}$ $(\alpha \geqslant 0)$ shows that the range of variation of $\langle S^2 \rangle$ with M, for a given polymer, is extended by solvent "goodness" $(\alpha > 0)$.

In the case of separation by flow, the relevant molecular dimension is the effective radius a, which is also a measure of the hydrodynamic volume ν [1]. For a random coil, $a \sim \langle S^2 \rangle^{1/2}$. Hydrodynamic dimensions are not strictly proportional to $\langle S^2 \rangle^{1/2}$, however, when excluded volume is present [2]. But in all instances, ν is related to M by the same functional form as $\langle S^2 \rangle^{3/2}$ is, namely: $\nu \sim M^{3/2+\epsilon}$ $(\epsilon \geqslant 0)$. The value of ϵ for a given polymer-solvent system may differ from $3/2\alpha$ if excluded volume affects the hydrodynamic and equilibrium molecular volumes differently, but in all cases ϵ increases as thermodynamic conditions are improved. In this way, the range of molecular radii on which the difference between polymer and fluid average velocities depend is expanded by use of a good solvent $(\epsilon > 0)$.

To get an idea of the magnitude of the influence of solvent "goodness" on separation of molecular weights by flow, we shall compare the values of

the elution volumes for different M's in two extreme cases: a θ-solvent ($\epsilon = 0$) and a very good solvent ($\epsilon = 0.3$) [3]. The relation between elution volume V_e and molecular size, given by DiMarzio and Guttman [1], is

$$V_e = \pi l r_0^2 \left[2 - (1 - R)^2 - 2\gamma R^2 \right]^{-1} \tag{1}$$

where r_0 and l are the tube radius and length, respectively, $R = a/r_0$, and γ is a parameter that measures the local retardation effect suffered by the polymer during flow [1]. Suppose that a certain polymer sample consists of different molecular weights between a minimum value M_1 and a maximum value M_2. The effectiveness of their separation depends on the range of elution volumes covered by the sample, i.e., on the difference $\Delta V_e = V_e(M_1) - V_e(M_2)$ between the slowest and fastest flowing molecules. The molecular weight ratio M_2/M_1 and the value of ϵ determine the ratio between the effective radius of the largest and smallest molecule as [4]

$$\frac{R(M_2,\epsilon)}{R(M_1,\epsilon)} = \left[\frac{M_2}{M_1} \right]^{1/2 + \epsilon/3} \tag{2}$$

In order to calculate ΔV_e from Eqs. (1) and (2), it is necessary to specify, in addition to M_2/M_1 and ϵ, the value of the relative radius R for one of the two molecular weights (M_1 or M_2).

The results obtained for the normalized elution volume difference $\Delta V = \Delta V_e/\pi l r_0^2$ (with ΔV_e computed using Eq. (1) in the simple case of no retardation, $\gamma = 0$) are shown in Table 1 for three different molecular weight ratios ($M_2/M_1 = 2, 5, 10$) and three different choices of relative radius [$R(M_1,\epsilon = 0) = 0.1, 0.05, 0.01$] covering a wide range of ΔV (the possible values of ΔV are in the range 0-0.5)[1]. For each $R(M_1,\epsilon = 0)$ the corresponding value of $R(M_1,\epsilon = 0.3)$ has been taken as $R(M_1,0.3) = 1.5R(M_1,0)$; i.e., the expansion factor for $R(M_1)$ in a good solvent has been set constant and equal to 1.5 [5].

Table 1 shows that the influence of solvent "goodness" on elution volumes can become large. In fact, the difference between ΔV for a good solvent and a θ-solvent (last column) is of an order of magnitude similar to ΔV itself. However, these numbers are for an extreme situation in which a very poor solvent ($\epsilon = 0$) is compared with a very good one ($\epsilon = 0.3$). Comparison between different solvent conditions for most practical cases should correspond to situations in between those tabulated.

Use of a good solvent should also decrease the spreading caused by

Table 1. Difference in Elution Volumes between the Highest and Lowest
Molecular Weights of a Polymer Sample

R $(M_1, \epsilon = 0)$	M_2/M_1	ΔV		$\Delta V (\epsilon = 0.3)$
		$\epsilon = 0$	$\epsilon = 0.3$	$- \Delta V (\epsilon = 0)$
0.10	2	0.048	0.070	0.022
	10	0.187	0.239	0.052
	50	0.318	–	–
0.05	2	0.031	0.051	0.020
	10	0.136	0.211	0.075
	50	0.279	0.362	0.083
0.01	2	0.007	0.014	0.007
	10	0.039	0.075	0.036
	50	0.100	0.195	0.095

Brownian diffusion on the elution volume peak of a given M. This is be-
cause spreading grows approximately as the inverse of the molecular
diffusion coefficient [1], and the influence of excluded volume on a given
polymer chain is to decrease its mobility [6].

ACKNOWLEDGMENT

REFERENCES

[1] E. A. DiMarzio and C. M. Guttman, *Macromolecules,* 3, 131 (1970),
and references therein to previous papers.

[2] As expressed by the fact that $[\eta] M/\langle S^2 \rangle^{3/2}$, where $[\eta]$ is intrinsic
viscosity, depends on excluded volume, [P. J. Flory, *Statistical
Mechanics of Chain Molecules,* Wiley (Interscience), New York, 1969,
footnote on p. 37].

[3] A typical value of the Mark-Houwink-Sakurada exponent for a
flexible polymer in very good solvent conditions is 0.3.

[4] In Eq. (2) it is assumed that the relationship $\nu \sim M^{3/2+\epsilon}$ has the same proportionality constant for M_1 and M_2.

[5] An example of this value is provided by PMMA ($M = 3.3 \times 10^5$) in chloroform at $20°C$, for which the expansion factor of $\langle S^2 \rangle^{1/2}$ is 1.50 (I. A. Katime and A. Roig, unpublished results from this laboratory).

[6] A. Horta and M. Fixman, *J. Amer. Chem. Soc.*, **90**, 3048 (1968).

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