A Novel Parameter of Polymer Structure

WILLIAM S. BAHARY, *TEXUS Research Center, Texas-U. S. Chemical Company, Parsippany, New Jersey*

Synopsis

A need exists for a simple and reliable heterogeneity index to determine the presence of high molecular weight components which may be branched in complex polymers and copolymers. On the basis of theoretical considerations, a proposal is made to employ the ratio of concentrated solution to intrinsic or Mooney viscosity as a heterogeneity index. The basis for the index is that the concentrated solution or melt viscosity is a function of a higher moment of the molecular weight distribution than either the intrinsic or Mooney viscosity. Experimental evidence in the form of light-scattering measurements and osmometry support the validity of the index when the range of intrinsic viscosities is narrow and other assumptions cited are justified. It is further shown that the heterogeneity index correlates well with the processibility of *cis*-polybutadiene.

Introduction

A need exists for a simple and reliable method to determine the breadth of the molecular weight distribution of complex polymers and copolymers such as polybutadiene and styrene–butadiene. Complicating factors in determining the heterogeneity of these types of elastomers are microgel and branching. For example, the presence of variable amounts of microgel confounds the results obtained for the weight-average molecular weight obtained by light scattering,[1-4] and the variable degree of branching which usually increases with molecular weight,[5] complicates fractionation.[6]

A simple heterogeneity index which is relatively insensitive to the presence of microgel is proposed in order to measure the comparative breadth of the distribution. The index is based on concentrated and dilute solution viscosities.

Theoretical Considerations

The concentrated solution viscosity (η_s) is related to the molecular weight of narrow linear fractions by the equations:[7]

$$\eta_s = K_1 M \qquad \text{For } M < M_b \qquad (1)$$

and

$$\eta_s = K_2 M^{3.5} \qquad \text{For } M > M_b \qquad (2)$$

where K_1 and K_2 are constants for a given temperature and solvent–polymer system, M is the molecular weight, and M_b is the critical molecular weight, which is about two times the entanglement molecular weight. For a polydisperse polymer, the concentrated solution viscosity will be equal to the sum of the contribution of the various molecular species and can be represented by eq. (3):

$$\eta_s = K_1 \sum_i W_i M_i + K_2 (\sum_j W_j M_j)^{3.5} \tag{3}$$

where W_i is the weight fraction of all fractions of molecular weight M_i below the critical molecular weight, and W_j the weight fraction of all fractions of molecular weight M_j, above the critical molecular weight.

A similar equation can be written for the intrinsic viscosity:[8]

$$[\eta] = K_3 M^\alpha$$

or

$$[\eta] = K_3 \sum_k W_k M_k^\alpha \tag{4}$$

where K_3 is a constant similar to K_1 and K_2; W_k is the weight fraction of fractions of all molecular species M_k below and above the critical molecular weight; and α is the fractional exponent in the Mark-Houwink equation. With styrene–butadiene copolymers, α is equal to 0.66 for hot[9] and 0.71 for cold types.[10] From the above equations, the concentrated solution viscosity is a function of a higher moment of the distribution than the intrinsic viscosity. Therefore a heterogeneity index based on concentrated solution and intrinsic viscosities should be possible.

Defining ROV as the ratio of the two viscosities, the following statement may be made:

ROV $\equiv \eta_s / [\eta]$ = a function of the relative breadth of the molecular

weight distribution for a given polymer   (5)

The conditions and assumptions involved in eq. (5) are as follows: (1) microstructure is constant; (2) composition is constant in the application of this relationship to copolymers; (3) the polymer contains some molecules having a molecular weight greater than the critical value; (4) the range of intrinsic viscosities to be compared is narrow; (5) variation in branching and/or effect of branching is small. The justifications for these assumptions are considered below.

Experimental Evidence

Experimental evidence in support of ROV as a heterogeneity index is provided in Table I. The three samples of styrene–butadiene copolymer employed and some of their molecular parameters have been previously reported.[2] Sample 110 is a cold type, 115 is a hot type, and 116 is a special blend; all three were completely soluble in good solvents. For the un-
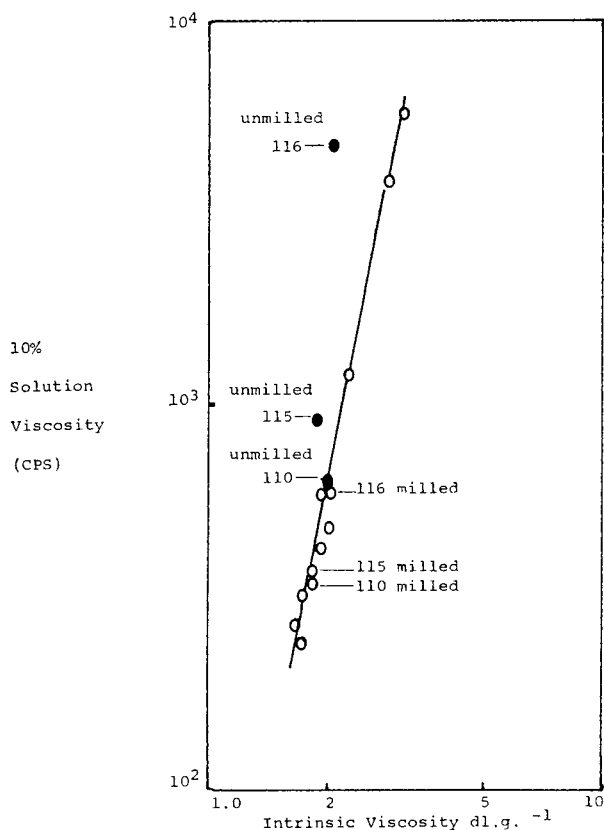
Fig. 1. Relationship between 10% solution viscosity and intrinsic viscosity: (O) styrene–butadiene copolymers of similar heterogeneities; (●) copolymers of similar intrinsic viscosities but different heterogeneities.

milled samples, the ROV increases in the order: sample 110 < 115 < 116, whereas $\bar{M}_w/\bar{M}_n$ is indeterminate for 115 and 116 due to the presence of microgel.[2] Upon cold milling of the samples in order to break down some of the microgel, the ROV follows the same order as $\bar{M}_w/\bar{M}_n$.

Three features of the results shown in Table I need to be mentioned. First, the samples chosen meet the first two conditions cited, since they have the same per cent cis, trans, vinyl in the butadiene portion and styrene in the copolymer; 15, 68, 17, and 23%, respectively. Secondly, the high weight-average molecular weights obtained justify assumption 3. Thirdly, it is important that the samples have the same intrinsic viscosities, within a few per cent, since the concentrated and intrinsic viscosities for linear fractions are related by eq. (6):[11]

$$\log \eta_s = K + (B/\alpha) \log [\eta] \qquad (6)$$

where K and B are constants for a given polymer–solvent system and temperature when the molecular weight is greater than the critical value.

TABLE I

Molecular Weight Parameters of Unmilled and Milled Styrene–Butadiene Copolymers

Sample	$[\eta]$, dl./g.	10% SV, cp.[a]	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	ROV	$\bar{M}_w/\bar{M}_n$	Mooney C viscosity	ROVM
Unmilled 110	2.00	629	0.9	8.22	3.1	9.1	50	13
Unmilled 115	1.89	915	0.6	∞	4.8	—	48	19
Unmilled 116	2.11	4844	0.5	∞	23.0	—	48	101
Milled 110[b]	1.85	348	0.9	3.4	1.9	4	40	9
Milled 115	1.86	367	0.6	9.5	2.0	16	29	13
Milled 116	2.04	617	0.5	34.5	3.0	69	31	20

[a] 10% solution viscosity in centipoise.
[b] 100 g. polymer, 10 passes, nip 0.01 in. at 20°C.
[c] ML-4 at 100°C., ASTM D 1646-63.

The relationship of eq. (6) for a series of unfractionated cold-polymerized styrene–butadiene copolymers of varying molecular weights and samples 110, 115, and 116 is shown in Figure 1.

It is interesting to note that the slope shown in Figure 1 is equal to 5.0. If the value of B for these commercial samples is taken at 3.5 as in the case of linear narrow fractions, then α is equal to 0.70. It is perhaps coincidental that this value of α agrees well with the value of 0.71 reported for cold-type styrene–butadiene.[10] Although both B and α may change with small variations in polydispersity and branching, it appears that their ratio remains constant for a series of polydisperse, moderately branched polymers. For very heterogeneous polymers containing high molecular ends which may be branched, the relationship between intrinsic and concentrated solution viscosities breaks down, as in the case of samples 115 and 116.

The justification for assumption 5 is not clear, since there is some ambiguity in the literature on the effect of branching on concentrated solution and melt viscosities. The data of Schaefgen and Flory[12] and Fox and Allen[13] support, and the results of Berry[14] contradict the contention of Bueche[15] that branching lowers the viscosity. Kraus and Gruver[16] show that at low molecular weights, the bulk viscosities of branched polybutadiene are lower, whereas at very high molecular weights the viscosities are higher than for the corresponding linear polymer.

It is difficult at present to assess the relative contributions of branching and molecular weight distribution to ROV. From data presented here, polydispersity increases ROV, but branching cannot be ruled out. Since both branching and broad molecular weight distributions increase the non-Newtonian behavior of polymers,[17] this does not hinder significantly the operational value of the ROV parameter. With many polymerization systems, the mechanism that produces long-chain branches also broadens the distribution,[18] so that the ROV is one way of determining the presence of these high molecular ends.

In place of ROV, a simpler and more useful parameter may be used with elastomers. Since the intrinsic viscosity and the Mooney viscosity[19] are linearly related,[20] the Mooney viscosity may be used in place of the former. The associated heterogeneity index is then called ROVM (ratio of solution viscosity to Mooney viscosity). The ROVM is less accurate although simpler to use than ROV, since a standard measurement on elastomers is the Mooney viscosity. The experimental evidence for using ROVM as a heterogeneity index is shown in Table I. The advantages of using ROV or ROVM as heterogeneity indices is their simplicity, reliability, and reproducibility.

Experimentally, 10% solution viscosities were run by using the Brookfield viscometer at room temperature. Corrections for temperature and ethanol–toluene extractables were made by empirically determined equations. The procedures for light scattering, osmometry, and intrinsic viscosity measurements have been described.[2]

TABLE II
Relation between ROV and ROVM Parameters for
cis-Polybutadiene and Ease of Carbon Black Incorporation

Sample	ML-4 at 100°C.	$[\eta]$, dl./g.	10% SV, cp.[a]	ROV	ROVM	Process-ibility rating[b]
A	43	2.43	1235	5.1	28	1
B	42	2.46	1657	6.7	38	2
C	43	2.44	2211	9.1	51	3

[a] 10% solution viscosity in centipoise.
[b] 1 denotes best processibility.

It has not been possible as yet to establish a unique relationship between ROV and $\bar{M}_w/\bar{M}_n$ for SBR polymers due to the presence of long "tail" ends which have a pronounced effect on $\bar{M}_w/\bar{M}_n$. Such a relationship is currently being studied with the simpler polybutadiene system. It is of interest that the ROVM values for *cis*-polybutadiene show a broad range, and preliminary experiments indicate that the ROVM correlates with ease of carbon black incorporation. Some data in support of the above are shown in Table II. Further elaboration plus the application of ROV and ROVM to structure and processibility will be published in forthcoming papers.

References

1. Cooper, W., D. E. Eaves, and G. Vaughan, *J. Polymer Sci.*, **59**, 241 (1962).
2. Bahary, W. S., and L. Bsharah, paper presented at the 146th ACS meeting, Philadelphia, Pennsylvania, April 1964, *ACS Polymer Preprints*, **5**, No. 1, 1 (1964).
3. Muus, L., and F. Billmeyer, *J. Am. Chem. Soc.*, **79**, 5079 (1957).
4. Pebbles, L., *J. Am. Chem. Soc.*, **80**, 5603 (1958).
5. Schneider, N. S., *J. Polymer Sci.*, **68**, 179 (1965).
6. Blachford, J., and R. F. Robertson, *J. Polymer Sci.*, **A3**, 1289 (1965).
7. Bueche, F., *Physical Properties of Polymers*, Interscience, New York, 1962, pp. 61–83.
8. Flory, P. F., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953, p. 312.
9. French, D. M., and R. H. Ewart, *Ind. Eng. Chem., Anal. Ed.*, **19**, 165 (1947).
10. Noirkov, A. S., M. B. Kharkina, T. V. Dorokhina, and M. J. Arkhangelskaya, *Colloid J. (USSR)*, **15**, 51 (1953); see also reference 6.
11. Busse, F., and R. Longworth, *J. Polymer Sci.*, **58**, 49 (1962).
12. Schaefgen, J., and P. J. Flory, *J. Am. Chem. Soc.*, **70**, 2709 (1948).
13. Fox, T. G, and V. Allen, paper presented at the 141st ACS meeting, Washington, D. C., March 1962, *ACS Polymer Preprints*, **3**, No. 1, 6 (1962).
14. Berry, G. C., *Rheol. Bull.*, **33**, No. 4, 11 (1964).
15. Bueche, F., *J. Chem. Phys.*, **40**, 484 (1964).
16. Kraus, G., and J. T. Gruver, *J. Polymer Sci.*, **A3**, 105 (1965).
17. Kraus, G., and J. T. Gruver, *J. Appl. Polymer Sci.*, **9**, 739 (1965).
18. Beasley, J. K., *J. Am. Chem. Soc.*, **75**, 6123 (1953).
19. Dinsmore, R. P., and R. D. Juve, *Synthetic Rubber*, G. S. Whitby, Ed., Wiley, New York, 1954, p. 376.
20. Pike, M., and W. F. Watson, *J. Polymer Sci.*, **9**, 229 (1962).

Résumé

Il existe un besoin de disposer d'un indice d'hétérogénéité simple et reproductible afin de déterminer la présence de composés de poids moléculaire élevé qui peuvent être ramifiés en polymères complexes et copolymères. Sur la base de considérations théoriques, une proposition est faite afin d'employer le rapport de la viscosité en solution concentration à la viscosité intrinsèque ou viscosité Mooney comme indice d'hétérogénéité. La base de cet indice réside en ce que la viscosité en solution concentrée ou à l'état fondu dépend plus fortement du moment de la distribution des poids moléculaires que la viscosité intrinsèque ou la viscosité Mooney. Des mesures de diffusion lumineuse et de pression osmotique confirment la validité de cet indice lorsque le domaine de viscosité intrinsèque est étroit et que les autres hypothèses énoncées sont justifiées. On montre en outre que l'indice d'hétérogénéité établit une bonne corrélation avec la processabilité du polybutadiène-*cis*.

Zusammenfassung

Es besteht ein Bedarf für einen einfachen und verlässlichen Heterogenitätsindex, um die Anwesenheit hochmolekularer, eventuell verzweigter Komponenten in komplexen Polymeren und Kopolymeren zu bestimmen. Auf der Grundlage theoretischer Betrachtungen wird die Verwendung des Verhältnisses der Viskosität einer konzentrierten Lösung zur Intrinsic- oder Mooney-Viskosität als Heterogenitätsindex vorgeschlagen. Der Index beruht darauf, dass die Viskosität einer konzentrierten Lösung oder Schmelze eine Funktion eines höheren Moments der Molekulargewichtsverteilung ist als die Intrinsic- oder Mooney-Viskosität. Versuchsergebnisse für Lichtstreuungs- und osmotische-Druck-Messungen bestätigten die Brauchbarkeit dieses Index, da der Bereich der Intrinsic-Viskosität eng ist und die anderen gemachten Annahmen gerechtfertigt sind. Weiters wird gezeigt, dass der Heterogenitätsindex in guter Korrelation zur Verarbeitbarkeit von *cis*-Polybutadien steht.