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Calculation of Number-Average and Weight-Average Molecular Weight of Poly(vinyl Chloride) Polymers from Intrinsic Viscosity Measurements

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Synopsis

Consistent data are available from several authors to provide equations for the calculation of number-average and weight-average molecular weights of commercial poly(vinyl chloride) polymers from determinations of intrinsic viscosity in cyclohexanone solution at 30°C. Reasonable approximations of the molecular weights can be calculated quickly by use of the following simple equations: $\bar{M}_n = {}^1/_2[\eta] \times 10^5$; $\bar{M}_w = 0.9[\eta] \times 10^5$.

Many determinations have been made of the molecular weight of poly(vinyl chloride) based on osmometric, light-scattering, and viscosity measurements. Because no two authors have used the same polymers and their equations have differed in form, the variations have been more apparent than the extent of agreement. Since solution viscosities are readily measured it would be useful to have an accepted method for conversion of these measurements to molecular weights for commercial poly(vinyl chloride) polymers and copolymers. Five authors[1–5] have measured both solution viscosity and molecular weight by one of the absolute methods and have calculated the relationship between viscosity and molecular weight. Their equations are listed in Table I.

These equations have been recalculated to the units in current use in the United States, namely grams per 100 ml., and grouped as to method of determination of molecular weight (Table II). In all cases in Table II intrinsic viscosity is in units of deciliters per gram.

The form of Ciampa's equation for the data from osmometric measurements used here is that given by Kurata and Stockmayer,[6] who have also converted most of these equations to current units.

The determinations by osmometric measurements[2–4] are in good agreement. These authors have used unfractionated polymers prepared in the laboratory by a variety of methods and in the same solvent, cyclohexanone, for both viscosity and molecular weight measurements. By this procedure a number-average molecular weight is obtained. Danusso included two commercial polymers in addition to his laboratory prepared polymers.

TABLE I

Authors	Equation	Solution: Solvent, temperature	Solution: Concentration units
Mead and Fuoss[1]	$\lambda_0 = 7 \times 10^{-5} M$	Cyclohexanone, 25°C.	Monomeric units/l.
Breitenbach et al.[2]	$[\eta] = 1.16 \times 10^{-5} \bar{M}^{0.85}$	Cyclohexanone, 20°C.	g./l.
Danusso et al.[3]	$[\eta] = 2.4 \times 10^{-5} \bar{M}^{0.77}$	Cyclohexanone, 25–33°C.	g./l.
Ciampa and Schwindt[4]	$[\eta] = 1.1 \times 10^{-6} \bar{M}_w$	Cyclohexanone, 25°C.	g./l.
Batzer and Nisch[5]	$Z_{\eta_i} = 1.63 \times 10^{-4} \bar{P}^{0.92}$	Tetrahydrofuran, 20°C.	Monomeric units/l.

TABLE II

Author	Equation
$\bar{M}_n$, Standardized by Osmometry (Cyclohexanone)	
Breitenbach	$[\eta] = 1.16 \times 10^{-4} \bar{M}_n^{0.85}$
Danusso	$[\eta] = 2.4 \times 10^{-4} \bar{M}_n^{0.77}$
Ciampa	$[\eta] = 1.23 \times 10^{-4} \bar{M}_n^{0.83}$
$\bar{M}_w$, Standardized by Sedimentation or Light Scattering (Cyclohexanone)	
Mead and Fuoss	$[\eta] = 1.12 \times 10^{-5} \bar{M}_w$
Ciampa	$[\eta] = 1.10 \times 10^{-5} \bar{M}_w$
Standardized by Osmometry (Tetrahydrofuran)	
Batzer	$[\eta] = 3.63 \times 10^{-5} \bar{M}^{0.92}$

Ciampa also determined the molecular weight of the same polymers by light scattering, obtaining the weight-average molecular weight. He reports the same relation between intrinsic viscosity and molecular weight as previously reported by Mead and Fuoss. The molecular weight measurements by Mead and Fuoss were determined chiefly by osmometry. However, they measured closely fractionated polymers in which case, as discussed by Billmeyer,[7] number-average and weight-average molecular weights are expected to be identical. These data appear to support that generalization. The weight-average molecular weights obtained by Ciampa are almost twice as great as the number-average molecular weights and uniformly so for a variety of laboratory prepared polymers. This is considered to be evidence for a wide distribution in polymer size in PVC polymers by the usual procedures of preparation.

Finally Batzer made both viscosity and osmometric measurements in tetrahydrofuran as solvent and worked with fractionated commercial polymers. As would be expected, his values are closer to the weight-average molecular weights obtained with cyclohexanone as the solvent than they are to the number-average values.

TABLE III
Molecular Weight of PVC Polymers Calculated From Intrinsic Viscosity in Cyclohexanone, 30°C.
$[\eta] = K'\bar{M}^a$

Polymer	Intrinsic viscosity $[\eta]$, dl./g.	Number-average molecular weight: Breitenbach ($K' = 1.16 \times 10^{-4}$, $a = 0.85$)	Number-average molecular weight: Danusso ($K' = 2.4 \times 10^{-4}$, $a = 0.77$)	Number-average molecular weight: Ciampa ($K' = 1.23 \times 10^{-4}$, $a = 0.83$)	Number-average molecular weight: Rapid estimate ($K' = 2.0 \times 10^{-5}$, $a = 1.0$)	Weight-average molecular weight: Mead ($K' = 1.12 \times 10^{-5}$, $a = 1.0$)
PVC						
Escambia 2250	1.055	45,400	53,900	54,800	52,750	94,200
Escambia 2200	0.866	36,000	41,700	43,200	43,300	77,300
Opalon 630	0.840	34,750	40,300	41,700	42,000	75,000
Opalon 610	0.653	25,800	28,900	30,800	32,600	58,300
Geon 101 EP	1.128	49,100	58,700	59,400	56,400	100,100
Exon 965	0.488	18,300	19,800	21,700	24,400	43,600
Exon 924	0.840	34,750	40,300	41,700	42,000	75,000
Diamond PVC-40	0.893	37,300	43,400	44,900	44,700	79,700
Borden VC-32C	0.908	38,100	44,300	45,800	45,400	81,100
Acetate copolymers						
VYNW(3% acetate)	1.10	47,700	56,800	57,700	55,000	98,200
VYNS(10% acetate)	0.735	29,700	33,700	35,500	36,750	65,600
VYHH(13% acetate)	0.527	20,100	21,900	23,800	26,350	47,100
VYFS(13% acetate)	0.548	21,000	23,000	24,900	27,400	49,000
Exon 487(13% acetate)	0.495	18,600	20,200	22,000	24,750	44,200

Experimental

The intrinsic viscosity of fourteen commercial poly(vinyl chloride) polymers and copolymers have been calculated from dilute solution viscosity measurements in cyclohexanone at 30°C. The data are shown in Table III. In each case the number-average molecular weight has been calculated by each equation. It is obvious that the equations of Danusso and Ciampa are equivalent, and that of Breitenbach results in molecular weights of the same order of magnitude but somewhat smaller. Some, but not all, of this difference is due to the fact that his equation is based on measurements made at 20°C. The weight-average molecular weights of these commercial polymers have been calculated by the equation of Mead and are also shown in Table III.

Discussion

When the original data of these authors are plotted in the log–log form there is considerable scatter of the points about the straight line representing each equation. For this reason and from the nature of the intrinsic viscosity unit, one is inclined to question whether there is any significance to the numerical value of the constant (a) in the equation relating intrinsic viscosity and molecular weight, particularly in the case of polydisperse polymers such as commercial production poly(vinyl chloride). It is possible to approximate the same data with a very simple equation for the rapid estimation of molecular weight from measurements of intrinsic viscosities of polymers in cyclohexanone at 30°C. Number-average molecular weight is calculated by the equation

$$\bar{M}_n = {}^1/_2[\eta] \times 10^5$$

The values for these fourteen commercial polymers are shown in Table III in the column headed "Rapid estimate." Weight-average molecular weight is calculated by the equation of Mead in the form

$$\bar{M}_w = 0.9[\eta] \times 10^5$$

In the application of these equations relating viscosity and molecular weight to commercial polymers, the reasonable assumption has been made that the molecular size distribution of commercial polymers is similar to the size distribution obtained in laboratory preparations.

References

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Résumé

Suivant plusieurs auteurs, d'importantes données peuvent être obtenues à partir de certaines équations pour calculer le poids moléculaire moyen en nombre et en poids du chlorure de polyvinyle commercial. Ces équations sont obtenues par détermination de la viscosité intrinsèque dane une solution de cyclohexane à 30°C. Des approximations raisonnables des poids moléculaires peuvent être calculées rapidement par l'emploi des simples équations suivantes: $\bar{M}_n = {}^1/_2[\eta] \times 10^5$; $\bar{M}_w = 0.9[\eta] \times 10^5$.

Zusammenfassung

Es sind genügend konsistente Daten von verschiedenen Autoren vorhanden, um Gleichungen zur Berechnung des Zahlen- und des Gewichtsmittels des Molekulargewichts von handelsüblichen Vinylchloridpolymeren aus Bestimmungen der Viskositätszahl in Zyklohexanonlösung bei 30°C aufzustellen. Eine ausreichende Näherung für das Molekulargewicht kann aus den folgenden einfachen Gleichungen schnell berechnet werden: $\bar{M}_n = {}^1/_2[\eta] \times 10^5$; $\bar{M}_w = 0.9[\eta] \times 10^5$.

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