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Physicochemical Characterization of Poly(vinyl chloride). II. Molecular Weight Distributions

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SUMMARY

Molecular weight distributions in poly(vinyl chloride) resins have been determined from simple viscosity measurements. Ratio of 11% solution viscosity to intrinsic viscosity yielded a figure which has been correlated with molecular weight distributions obtained (1) from the ratio of weight-average to number-average molecular weights and (2) from gel permeation chromatography. Ratio of viscosities is thus a useful short-cut technique for obtaining approximate molecular weight distributions in poly(vinyl chloride) resins which have $0.77 < [\eta] < 1.15$ and $1.6 < \overline{\text{ROM}} < 2.8$.

INTRODUCTION

The effect of molecular weight distribution (molecular heterogeneity or polydispersity) on the physical properties of polymers has been well documented [1-4]. It is therefore important that this parameter be well characterized.

There are several methods available by which one can determine polydispersity in polymers. For complete molecular weight distributions one must fractionate the polymer and construct integral and differential molecular weight distribution curves. This method has two disadvantages: (1) it is too time-consuming, and (2) no analytical method of general application is yet available for obtaining narrow fractions.

To obtain approximate value of the parameter one can make use of the several short-cut techniques available for this purpose. One such technique frequently employed calls for the ratio of weight-average to number-average molecular weights (ROM̄), ($\bar{M}_w/\bar{M}_\eta$) [5, 6] or ($\bar{M}_w/\bar{M}_\eta$) − 1 [7]. This method renders itself unsuitable for those polymers which have structural complications like microgel [8-11] and branching [12, 13]. Other measurements which can relate to approximate molecular weight distributions are the ratio of intrinsic viscosity in thermodynamically good and poor solvents [14], shear dependence of viscosity [15, 16], frequency dependence of a real part of complex viscosity [17], stress relaxation [18], and relaxation-time distribution [19]. However, some of these methods are tedious and other unreliable and so rarely used.

There is yet another short-cut technique [20] available for polydispersity characterization. It is of rather recent origin, but it holds promise. Very briefly the method relates approximate molecular weight distributions to the ratio of solution (or melt) viscosity to intrinsic (or Mooney) viscosity (ROV or ROVM) [21, 22]. Such is possible because solution (or melt) viscosity is related to a higher moment of molecular weight spread than intrinsic (or Mooney) viscosity. The method in question is still in the development stage, and as yet has been applied to two different systems. In the study of styrene butadiene rubber (SBR) complicated with microgel it has been partially successful [20], while in polypropylene glycol (PPG) and polyethyleneglycol (PEG) [23] it has been successfully tested.

To explore the usefulness of this technique in the measurement of molecular weight distributions in industrially important thermoplastics (which have both microgel and branching in their structure), poly(vinyl chloride) was selected and the results obtained are described and discussed in the following sections.

EXPERIMENTAL

The materials used for this study were industrially important products of commercial grade and were obtained from sources described below:

> Escambia PVC 4185 (Escambia Chemical Company); Diamond PVC 40, PVC 7-44, PVC 450 and PVC 500 (Diamond Alkali Company); Geon 103EP (B. F. Goodrich Chemical Company); Trulon 510 (Thompson Chemical Company); and Marvinol VR-53 (Uniroyal, Inc.). Viscosities were measured at room temperature in the THF solutions using Brookfield and Cannon-Fenscke viscometers.

Molecular parameters were obtained from the Mark-Houwink equation ($[\eta] = 1.50 \times 10^{-4} (M_w)^{0.77}$) [24], membrane osmometry, and gel permeation chromatography (ROĀ).

RESULTS AND DISCUSSIONS

Concentration dependence of viscosity was studied for all the resins described earlier and the results obtained are shown in Fig. 1. For the concentration region covered, these plots follow an exponential behavior which can be represented by

$$\eta = K^{S \cdot C} \qquad (1)$$

where η, K, S, and C represent solution viscosity, constant, slope, and concentration, respectively. The high rise in viscosity at rising polymer content is indicative of intermolecular interactions [25-29].

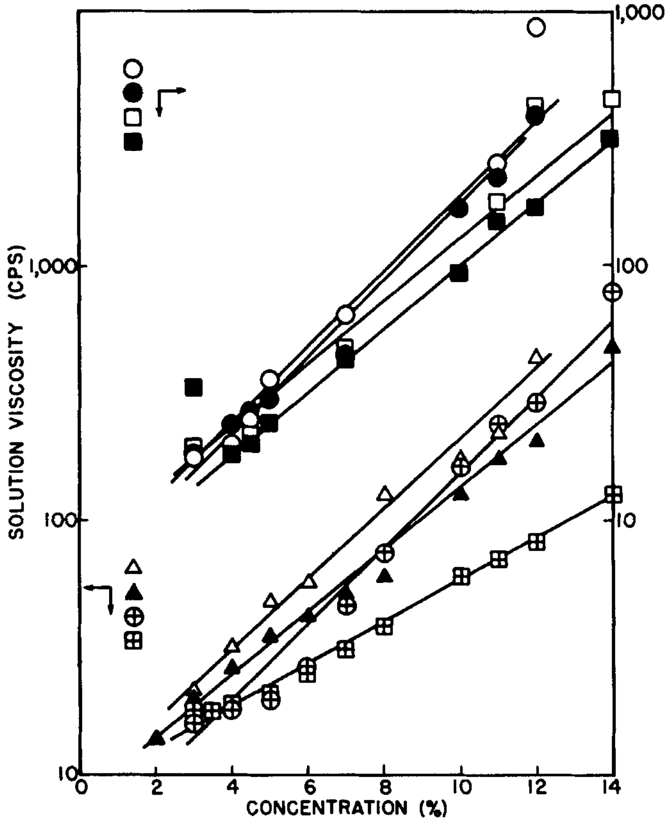

Fig. 1. Plots showing concentration dependence of viscosity. ○, PVC 500; ●, Marvinol VR-53; □, Trulon 510; ■, Geon 103EP; △, PVC 450; ▲, PVC 7-44; ⊕, PVC 40; ⊞, Escambia PVC 4185.

The relationship between solution and intrinsic viscosities is known to be linear and can be represented [30]

$$\eta = K'[\eta]^{B/a} \tag{2}$$

This was reconfirmed when a plot of 11% solution vs. intrinsic viscosity was found to be linear. This is shown in Fig. 2. The slope, B/a, was found to be 3.3 as compared to 5.0 in SBR [20] and 1.0 and 0.8 in PPG and PEG [23], respectively. The value of B determined was 3.0 and it was obtained from the plot shown in Fig. 3, which follows [30]

$$\eta = K'' (\overline{M}_w)^B \tag{3}$$

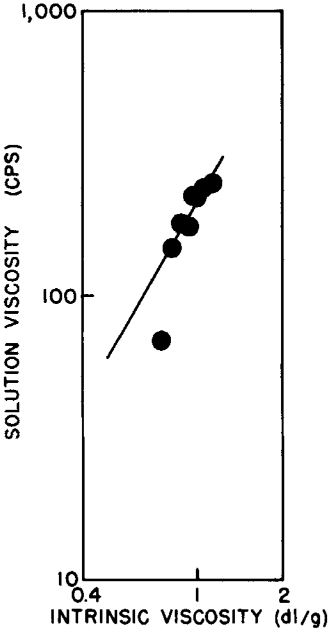

Fig. 2. Plot of 11% solution viscosity vs. intrinsic viscosity for PVC resins used.

For PPG, PEG, SBR, and PE values of B reported vary from 0.6 to 7.0 [23, 20, 30]. B/a and B values are structure-sensitive, as one would expect normally to be the case. The exponent, a, was calculated from the ratio of two slopes (Figs. 2 and 3) and was found to be 0.9, which is in fair agreement with published data [24]. Both the value of exponent a [31] and the sharp rise in viscosity at high poly-

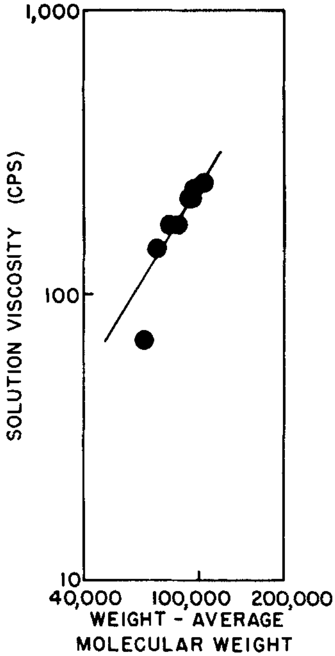

Fig. 3. Plot of 11% solution viscosity as a function of weight-average molecular weights for PVC resins used.

mer content [32, 33] reflect on the thermodynamic suitability of THF as a solvent for viscosity measurements on PVC. THF has also been reported by others [34-36] to be a suitable solvent for PVC.

In Table 1 molecular parameters for PVC resins studied are reported. Let us now focus our attention on ROV, RO$\bar{M}$, and RO$\bar{A}$ values. There is a fairly good agreement between these values for PVC (40, 7-44, 450, and 500), Geon 103EP, Trulon 510, and Marvinol VR-53. Escambia 4185 has ROV < RO$\bar{M}$ or RO$\bar{A}$. The different behavior of Escambia may also be noted in Figs. 2 and 3, where it falls off the linear plots. This is probably due to the low $[\eta]$ of this product as compared to others used. It is worthy of comment here that in order for RO$\bar{V}$ to be operative as a molecular heterogeneity index, the samples studied should not vary too much in their $[\eta]$ [20].

The results presented here then support the general conclusion that it is possible to obtain approximate molecular weight distributions from ROV ($\eta(11\%)/[\eta]$) for commercial PVC which may be characterized by $0.77 < [\eta] < 1.15$ and $1.6 <$ RO$\bar{M}$ < 2.8.

Table 1. Molecular Parameters for PVC Resins

Number of sample	Sample	$\eta(11\%)$, cps	$[\eta]$, dl/g	ROV	$\overline{M}_w \times 10^{-3}$	$\overline{M}_\eta \times 10^{-3}$	RO$\overline{M}$	$\overline{A}_w \times 10^{-3}$	$\overline{A}_\eta \times 10^{-3}$	RO$\overline{A}$
1	Escambia PVC 4185	70.0	0.77	0.9	65.3	34.0	1.9	1.9	0.9	2.1
2	PVC 40	148.0	0.83	1.8	72.1	42.7	1.7	2.4	1.1	2.2
3	PVC 7-44	177.0	0.89	2.0	79.7	42.9	1.9	2.4	1.0	2.4
4	PVC 450	175.0	0.94	1.9	85.4	50.7	1.7	3.0	1.3	2.3
5	Geon 103EP	220.0	0.99	2.2	91.7	49.5	1.9	3.0	1.3	2.3
6	Trulon 510	220.0	1.01	2.2	93.1	45.2	2.1	3.0	1.3	2.3
7	Marvinol VR-53	235.0	1.06	2.2	99.8	37.2	2.7	2.8	1.2	2.3
8	PVC 500	250.0	1.14	2.2	109.0	62.4	1.7	3.4	1.5	2.3

One might now argue against this general conclusion by saying that relative contributions of structural complications such as thermolabile associates, microgel, tacticity, and branching of the materials used have not been taken into account in obtaining the parameters reported. This argument is not a very strong one because of the following considerations:

1. The degree of aggregation of PVC in THF is very small at room temperature and it varies from 0 to 0.01% [37]. The polymer solutions used for this investigation were heated prior to any measurements to break down any temperature-sensitive aggregates that may have existed [38, 39].
2. As far as microgel is concerned, the $\overline{M}_w$ reported include their effect [24]. Drawing attention to Table 1 again, it can be observed that ROM have the effect of microgel incorporated in them while ROV and ROA do not take into account this structural complication, and yet there is a fair agreement between these parameters. This is indirect evidence of the effect of microgel on viscosity and gel permeation.
3. The tacticity of these materials is likely to have very little effect, if any, on these parameters. The reason for this is that the content of syndiotactic diads in these samples is about 0.55 [40-43], and they may be treated as nearly atactic structures for the purpose of this investigation.
4. The effect of branching is a priori unknown and cannot be discussed at this stage. The samples used may be characterized by (approximately) 1 branch per 100 monomer units [44].
5. ROV only affords an approximate molecular weight distribution.

From the above discussion one can now infer that ROV is a valid molecular heterogeneity index for screening PVC samples for molecular weight distributions. To make this technique a reliable quality control tool for industrial laboratories, one must extend this work to include the study of linear and variable branched PVC and also copolymers of VC with other monomers.

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