

## Prediction of Polymer Densities

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### Synopsis

A method is proposed for predicting the density of a linear, amorphous polymer. The method is based on the additivity of group increments for the molar volume of a polymer unit. It is analogous to the published methods for predicting the molar volume of organic liquids. The method may be improved as additional experimental values on polymer densities become available.

### Introduction

Density may be regarded as one of the most important polymer properties. This is obvious in so far as polymer density in practical applications is concerned. But also from a theoretical point of view the density of a polymer is an important property. For the calculation of a number of other properties (e.g., thermodynamic quantities) knowledge of density is necessary. It is also used for the characterization of polymers. Within a given family of polymers, for instance, density is closely related to the degree of crystallinity. Moreover, polymer density can be easily determined experimentally.

In this connection the lack of data on polymer densities is surprising. There are only few literature surveys in this field.<sup>1,2</sup> Several articles list a number of properties for given groups of polymers, but only occasionally are densities mentioned.

Therefore a method for predicting polymer density as a function of polymer structure could be useful. As far as the authors are informed, no such method has yet been proposed. There are methods available, however, for the prediction of the densities of organic liquids. They calculate the molar volume by addition of increments for given structural units.

Application of these values to the densities of amorphous polymers does not lead to a close correspondence. Apparently, modified increment values must be chosen. The present article should be considered a first attempt at a derivation of such a method. As more experimental data become available, the method will have to be revised.

### Methods for Predicting the Molar Volume of Organic Liquids

All methods published calculate the molar volume of an organic liquid by the addition of increments, each of which corresponds with a given struc-

tural element. According to the nature of the structural elements three methods can be distinguished.

**Atomic Increments.** These were proposed many years ago by Traube<sup>3</sup> and by Le Bas.<sup>4</sup> Additional atomic increment values have been published by Davis<sup>5</sup> and by Harrison.<sup>6</sup>

**Group Increments.** Accurate comparison of molar volumes for related compounds, as made by Davis for instance, revealed that atomic increments should have different values, according to the nature of neighboring atoms. This has led to the introduction of group increments. A number of group increments have been calculated by Exner.<sup>7</sup> Recently, this method has been used by Rheineck and Lin.<sup>8</sup>

**Bond Increments.** This method has been applied by Tatevskii<sup>9</sup> to the molar volume (and to other properties) of hydrocarbons. For this class of compounds, only two atom combinations are possible, viz. C—C and C—H bonds. Different values for the bond increments are used, however, dependent on the other bonds of the carbon atoms involved.

For practical purposes, the method of group increments is to be preferred. The use of atomic increments proved to be too simplistic, unless different increments were used for the same atom in different groups. On the other hand, the use of bond increments leads to an unpractically large number of increments, because the number of combinations is some factorial function of the number of elements.

There is an interesting difference between the two oldest methods published, which is also of importance with regard to other methods. Traube added to the sum of the atomic increments for a given compound a constant value, which was called residual volume. As this was not done by Le Bas, his atomic increments were always larger than the corresponding values of Traube, as appears from Table I. Traube's values are in much better agreement with those obtained by later investigators. His method was used by van Krevelen<sup>10</sup> for the calculation of densities of coal constituents. The method of Le Bas is still used in some fields, e.g., for the prediction of

TABLE I  
Atomic Increments

	Atomic increment, cm <sup>3</sup> /g-atom	
	Traube <sup>3</sup>	Le Bas <sup>4</sup>
C	9.9	14.8
H	3.1	3.7
O (in C = O)	5.5	7.4
O (in ethers)	5.5	11.0
S	15.5	25.6
F	5.5	8.7
Cl	13.2	21.6
Br	13.2	27.0
I	13.2	37.0
Residual volume	26.0	—

diffusion coefficients.<sup>11</sup> Porter and Johnson<sup>12</sup> compared measured molar volumes for some polymers with values calculated according to Le Bas.

A confirmation of the additivity of molar volume increments can be obtained from the study of homologous series. This method has been applied to hydrocarbons by Kurtz,<sup>13</sup> van Nes and van Westen,<sup>14</sup> and Tatevskii.<sup>9</sup> A connection between the empirical relations derived and the cell theory of liquid structure has been laid down by Simha and Hadden.<sup>15</sup> Several series of compounds with increasing number of  $\text{CH}_2$  groups lead to rather accurate values for the increment of molar volume for this group. A number of values found by several investigators are mentioned in Table II. Except for the much too high value given by Le Bas, the data show a good correspondence.

TABLE II  
Molecular Volume Increments for the Methylene Group — $\text{CH}_2$ —

Reference	Molecular volume increment, $\text{cm}^3/\text{g-atom}$
Traube <sup>3</sup>	16.1
Le Bas <sup>4</sup>	22.2
Kurtz and Lipkin <sup>13</sup>	16.3
Simha and Hadden <sup>16</sup>	16.5
van Nes and van Westen <sup>14</sup>	16.5
Harrison <sup>6</sup>	16.4
Davis and Gottlieb <sup>5</sup>	16.6
Exner <sup>7</sup>	16.6
Tatevskii <sup>9</sup>	16.1
Rheineck and Lin <sup>8</sup>	16.5

The successful use of group increments for describing the molar volumes of homologous series suggests application of the same method to families of polymers.

#### Difficulties in Applying Increment Methods to Molar Volumes of Polymers

The increment methods mentioned above deal with the molar volume of organic compounds of low molecular weight at room temperature (about 25°C) in the liquid state. At this temperature, however, polymers are generally in the solid state. This is a reason why different increment values may apply to polymers.

At room temperature many polymers are in the glassy amorphous state, which shows a certain correspondence with the liquid state in that long-range order does not exist. A number of polymers show a specific structure, which is connected with a certain degree of crystallinity. In this case, the density is higher than for the amorphous polymer. The glassy state of solid polymers may therefore be considered to be the form which shows the greatest correspondence with the liquid state of organic com-

pounds. The correlations mentioned in this article will be confined to the densities of purely amorphous polymers at (about) 25°C.

Unfortunately, densities of purely amorphous polymers have been reported for a limited number of polymers only. Most data rely to samples of unknown degree of crystallinity. In this case it can merely be concluded that density of the amorphous state should be lower than or equal to the reported value. Densities of partly crystalline polymers may be up to 1.2 times the amorphous densities.

In the present study the polymer will be assumed to consist of an infinite number of equal units. Calculations will be based on molecular weight and molar volume of these units. The effect of the presence of endgroups, not included in the polymer unit, on the density may be expected to be less than 1% for normal values of the degree of polymerization.

TABLE III  
Group Increments for the Molecular Volume of Amorphous Polymers  
 $V_i$  (25°C) and Comparison with van der Waals Volume Increments  $V_w$

	$V_i$ , cm <sup>3</sup> /g-atom	$V_w$ , cm <sup>3</sup> /g-atom	$V_i/V_w$
<b>Tetravalent</b>			
	5.58	3.33	1.68
<b>Trivalent</b>			
	11.47	6.78	1.69
	21.40	13.48	1.59
<b>Bivalent</b>			
	16.13	10.23	1.58
	28.38	16.94	1.68
	69.27	43.32	1.60
	7.61	3.7	2.1
	9.88		2.7
	21.43	15.2	1.41
	23.37	—	—
<b>Monovalent</b>			
	22.10	13.67	1.62
	69.67	45.84	1.52
	17.53	11.62	1.51
	9.71	5.72	1.70

### Derivation of Group Increments for the Molar Volume of Amorphous Polymers

As was stated before, none of the published increment methods for the molar volume of organic compounds leads to accurate values if applied to polymers. Therefore new group increment values have been derived, starting from literature data for polymer densities.<sup>1,2,16-33</sup>

Only for a limited number of polymers, densities for the completely amorphous state have been published. For most of the other data the degree of crystallinity is unknown. These density values could be used, however, for the determination of lower limits for the molar volume increments. The study has been restricted to a limited number of structural groups, as mentioned in Table III.

For the derivation of group increments from the available data, by using the formula

$$d_{\text{am}} = M_u / \sum V_i$$

where  $d_{\text{am}}$  is the density of amorphous polymer,  $M_u$  is the molecular weight of a polymer unit, and  $V_i$  is the volume increment, a linear programming method has been derived. This program contained the desired group increments as adjustable parameters. The objective function aimed at minimum differences between calculated and experimental molar volumes for the completely amorphous polymers. The limiting values for the

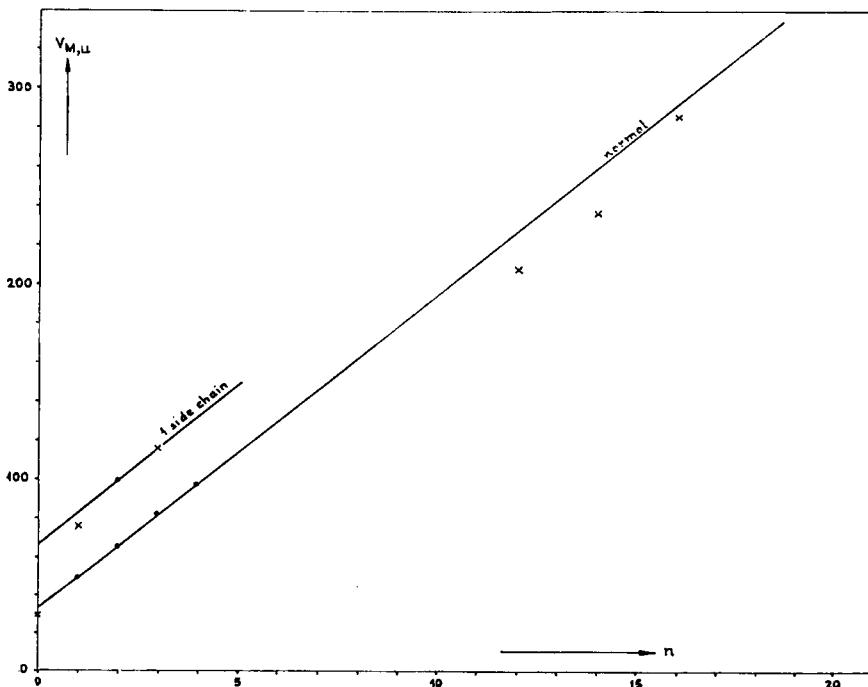


Fig. 1.  $V_{M,u}$  vs.  $n$  for polyolefins.

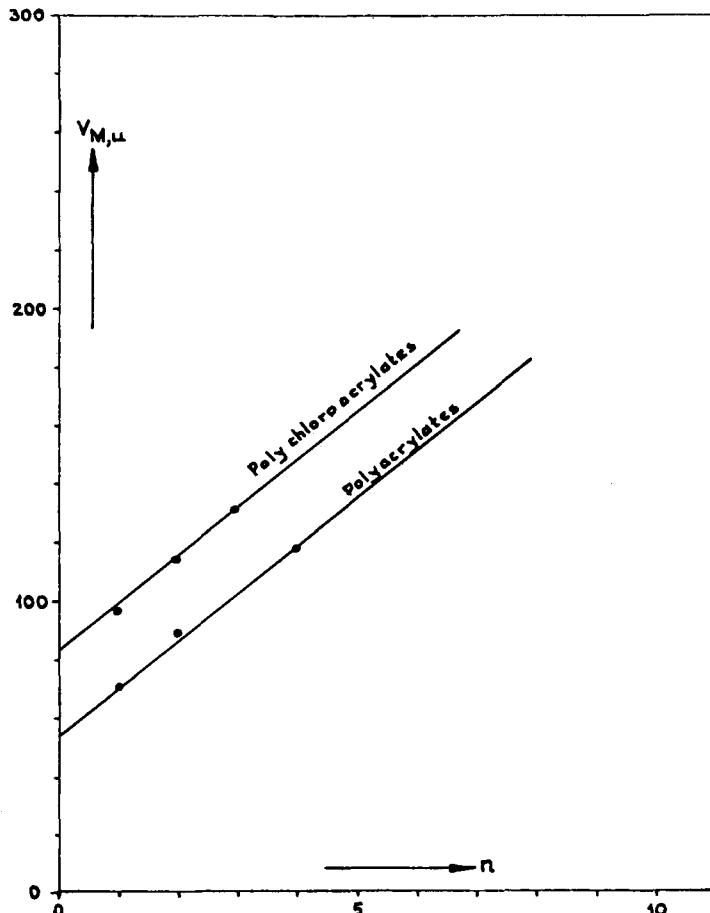
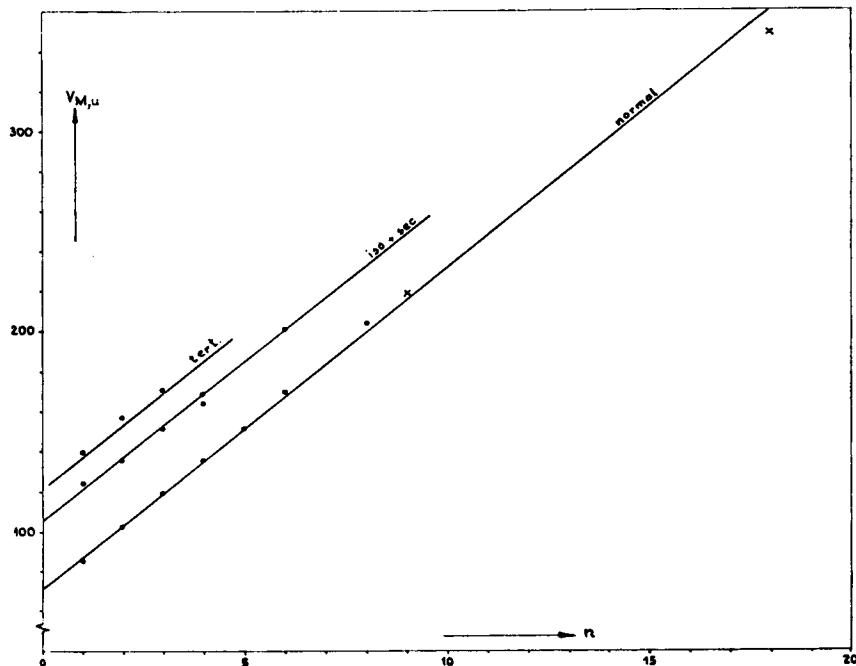
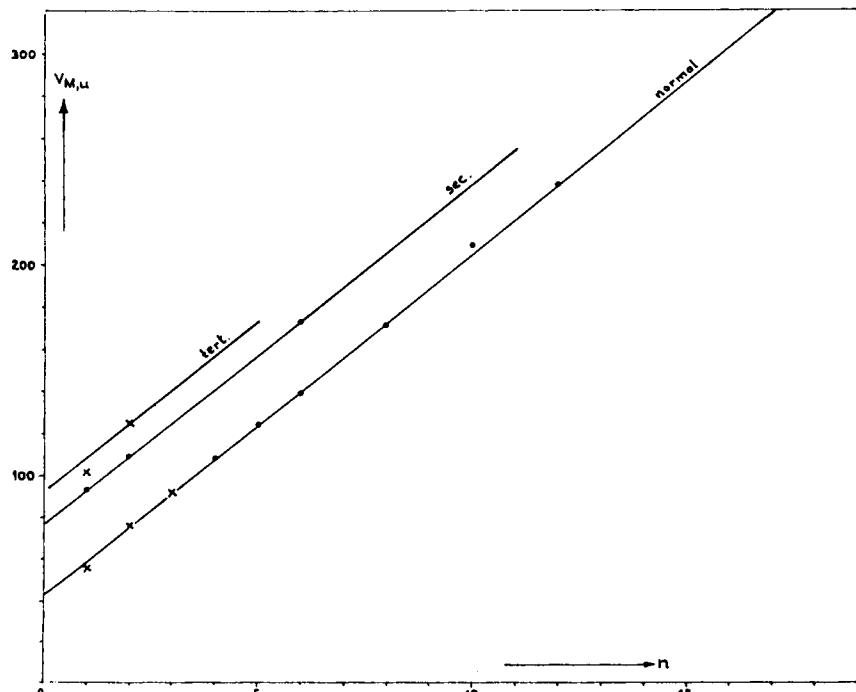


Fig. 2.  $V_{M,u}$  vs.  $n$  for polyacrylates.

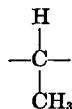
molar volumes of the other polymers, as mentioned above, entered into the program as constraints.

As a start, a complete distinction was made between groups occurring in the main chain and the same groups in side chains. For most groups nearly the same increment values were found, whether they occurred in the main chain or in a side chain. In these cases, only one increment value has finally been used. For ether groups, however, the correlation could be improved substantially if different increment values were used for the main and side chains.

It should be remarked that a number of group increment values are only found in fixed combinations. This is caused by our restriction to units of linear polymers, which as a whole are always bivalent groups. Therefore, only for bivalent groups can independent increment values be calculated. The mono-, tri- and tetravalent groups always occur in bivalent combina-

Fig. 3.  $V_{M,u}$  vs.  $n$  for polymethacrylates.Fig. 4.  $V_{M,u}$  vs.  $n$  for poly(vinyl ethers).

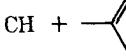
tions. For instance, one trivalent CH group and one monovalent CH<sub>3</sub> group form together the bivalent group,



As it is preferred to use separate values for the subgroups, the increment values had to be split up quite arbitrarily. A directive could be found in the increment values proposed by Bondi<sup>34</sup> for the van der Waals volume of structural groups.

The proposed values for the group increments can be found in Table III, where they are compared with increment values for the van der Waals volume. For most groups the ratio between the two increments is between 1.5 and 1.6. In Table IV, the proposed increment values for bivalent groups have been compared with values given by other authors.

TABLE IV  
Comparison of Group Increments for the Molar Volume  
as Proposed by Various Authors

	group increments for molar volume $V_{M,u}$ , cm <sup>3</sup> /mole				
	this paper <sup>a</sup>	Traube <sup>b</sup>	Exner <sup>b</sup>	Davis <sup>b</sup>	Rheineck and Lin <sup>b</sup>
—CH <sub>2</sub> —	16.1	16.1	16.6	16.6	16.4
—O— main chain	7.6				
—O— side chain	9.9	5.5	6.7	6.8	
—C—O—	21.4	20.9	19.5	15.5	
—C—N—	23.4	20.0	17.5		
—C—C— H    H	28.4	24.3		27.0	
— 	69.3	58.6		61.5	
CH + CH <sub>3</sub>	33.6	32.2		33.2	33.5
CH + — 	81.1	74.7		78.2	74.5
CH + Cl	29.0	26.2			23.5
CH + F	21.2	18.5			
C + 2CH <sub>3</sub>	49.8	48.3		49.8	

<sup>a</sup> For glassy polymers.

<sup>b</sup> For liquid organic chemicals.

### Discussion

For several families of polymers, calculated values for  $V_{M,u}$  the molar volume per structural polymer unit in the amorphous state, have been plotted in Figures 1 to 5 as a function of the number  $n$  of methylene groups

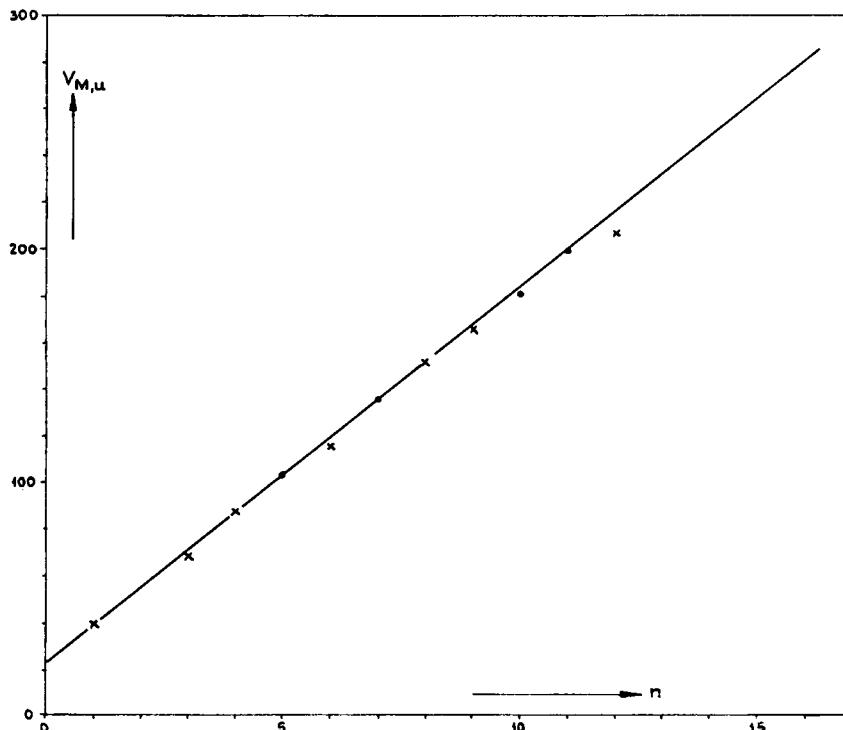


Fig. 5.  $V_{M,u}$  vs.  $n$  for polyamides with one amide group per unit.

per structural unit (solid lines). They can be compared with published values for amorphous polymers (dots) and for polymers with an unknown degree of crystallinity (crosses). In Figures 3 and 4, the terms normal, iso, sec and *tert* refer to the structure of the alcoholic group in the polymer unit. The data for amorphous polymers not covered by the figures have been reported in Table V.

The general agreement between experimental and calculated densities is satisfactory. For a total number of 85 amorphous polymers, the mean deviation is 1.3%. The greatest disagreement is found for polyisobutene, where the calculated density is 0.85, while an experimental value of 0.91 has been reported. Further, some polyesters with a large number of methylene groups per unit show calculated densities for the amorphous polymers higher than reported values for unknown degree of crystallization.

The method proposed in this paper may be used for a prediction of the density of an amorphous polymer, with an accuracy sufficient for many investigation purposes. Further improvement of the increment values may be obtained if more experimental data will be reported. If density values are needed with an accuracy of within 1%, however, experimental determination remains necessary.

TABLE V  
Calculated and Experimental Densities for Some Amorphous Polymers

Polymer	$d_{\text{am}}$ , g/cm <sup>3</sup>	
	Experimental	Calculated
Polyethylene	0.855–0.887	0.869
Polystyrene	1.047–1.057	1.070
Poly- <i>α</i> -methylstyrene	1.063–1.066	1.042
Poly- <i>p</i> -methylstyrene	1.04	0.994
Poly- <i>p</i> - <i>tert</i> -butylstyrene	0.95	0.950
Polyisobutene	0.913	0.851
Poly(vinyl chloride)	1.385	1.385
Poly(vinylidene chloride)	1.66	1.709
Polytetrafluoroethylene	2.00	2.000
Polychlorotrifluoroethylene	2.032–2.11	2.015
Polytrifluoropropene	1.580	1.542
Poly(2-chloro-sec-butyl acrylate)	1.24	1.228
Poly(2-chloroisopropyl acrylate)	1.27	1.278
Poly(2-chloromethyl acrylate)	1.45–1.49	1.458
Poly(1,3-dimethylbutyl methacrylate)	1.005	0.998
Poly(1,2,2-trimethylpropyl methacrylate)	0.991	0.998
Poly(phenyl methacrylate)	1.21	1.202
Poly(1-phenylethyl methacrylate)	1.129	1.129
Poly(benzyl methacrylate)	1.179	1.125
Poly(diphenylmethyl methacrylate)	1.168	1.168
Poly(1,2-diphenylethyl methacrylate)	1.147	1.147
Poly(2-chloroethyl methacrylate)	1.32	1.292
Poly(2,2,2-trifluoro-1-methylethyl methacrylate)	1.34	1.349
Poly(vinyl acetate)	1.191	1.210
Polybutadiene	0.892	0.892
Poly-2-methylbutadiene	0.904–0.910	0.899
Polypentadiene	0.89	0.899
Poly-2-chlorobutadiene	1.243	1.243
Nylon 66	1.069–1.09	1.088
Nylon 610	1.041	1.036
Poly(glycolic acid)	1.60	1.54
Poly(3-hydroxybutyric acid)	1.23	1.233
Poly(ethylene sebacate)	1.113	1.118
Poly(ethylene terephthalate)	1.33	1.331
Polyformaldehyde	1.25	1.263
Poly(ethylene oxide)	1.13	1.103
Poly(propylene oxide)	1.002	1.038
Polyacetaldehyde	1.071	1.071
Polyepichlorohydrin	1.37	1.343

The density of a polymer in the crystalline state  $d_{\text{cr}}$  can be estimated by approximation only, as

$$d_{\text{cr}} \approx (1 + 0.15\alpha)d_{\text{am}}$$

where  $\alpha$  is the degree of crystallinity.

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