

A Method of Calculating Densities of Polymers

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Synopsis

Molar volumes of substantially amorphous polymers may be calculated by using additive constants derived from constitutive atomic and structural parachor contributions. For 34 polymers, ranging in density from 0.83 to 2.03 g/cm³, the greatest error in the calculated molar volume compared with the measured value was 13.9%, while for 30 of the polymers the error was less than $\pm 7\%$, with a mean error of $\pm 3.9\%$.

INTRODUCTION

The development of new polymers having predetermined physical properties would be greatly facilitated if these properties could be predicted from a knowledge of chemical structure alone. Investigation of the relationship between polymer physical properties and structure, with particular reference to glass transition temperature (T_g), is of special interest since at the T_g many properties having technological importance show a marked change in magnitude or in temperature dependence. For instance, elastomers do not show elastomeric behavior below the T_g .

The relationships between T_g and several parameters, including cohesive energy (C.E.) and cohesive energy density (C.E.D.), have been studied.¹ These parameters can be calculated, using additive constants,² from a knowledge of the structural formula of a polymer if the density is known. Molar refractivity, refractive index, molar polarization, and the parachor are other examples of molar additive properties which are a function of density and one other parameter. The additivity of molar volume (molecular weight/density) has been examined³ and accurate density calculations can be made for many polymers for which additive group contributions are available. However, an insufficient number of reliable density measurements are available to enable a comprehensive list of all the molar volume contributions of groups found in polymers to be compiled. A means of estimating molar volume, or density, of polymers accurately with wide applicability would be of great value, especially for use in the prediction of important physical properties of hypothetical polymer structures which may contain unusual groups.

The use of the parachor for calculating molar volumes of substantially amorphous polymers to within a mean error of 4% of the observed values is described here.

APPLICATION OF THE PARACHOR TO POLYMERS

At temperatures considerably removed from the critical temperature, the following relationship⁴ was proposed for liquids:

$$P = \gamma^{1/4} \cdot V \quad (1)$$

where P = parachor, γ = surface tension of liquid (dynes/cm), and V = molar volume.

The parachor for any substance is a constant, relatively independent of temperature, which, for a liquid, Sugden⁴ showed is both an additive and a constitutive property. The contributions⁵ to the parachor of a compound made by various atoms, bonds, and structures are given in Table I. The concept of surface tension has been successfully applied to polymers for which critical surface tension values (defined as the lowest surface tension a liquid can have while still exhibiting a contact angle of greater than zero degrees on the polymer surface), have been published⁶ and to solid surfaces in general.⁷ It seems reasonable, therefore, to apply the parachor to polymers, especially when they are in their liquid states.

For a polymer, $V = M/d$, where M and d are the molecular weight and density of the repeating unit, respectively. From eq. (1), the value of the parachor calculated from the repeating unit of a polymer should be proportional to V or $1/d$ at a temperature where the surface tension is at a standard or reference value for all polymers. Although the surface tensions of polymers vary over a wide range at ambient temperatures, γ is to the power $1/4$, and so large variations in surface tension are accompanied by only small variations in molar volume or density. For instance, the critical surface tension of poly(ethylene terephthalate) has been quoted⁶ as 43 dynes/cm at room temperature. The density calculated from the value of the parachor (386.9) and the molecular weight of the repeating unit (192) is 1.271 g/cm³ at this temperature. However, if the temperature of the polymer is such that the surface tension is lowered to 37 dynes/cm, the calculated density is 1.224 g/cm³. Thus, a change of about 14% in surface tension is accompanied by a change of only 3.7% in density.

TABLE I
Atomic and Structural Parachor Contributions

Atom	Parachor contribution	Bond or structure	Parachor contribution
Carbon	4.8	double bond	23.2
Nitrogen	12.5	triple bond	46.6
Hydrogen	17.1	semipolar bond	-1.6
Oxygen	20.0	3-membered ring	16.7
Fluorine	25.7	4-membered ring	11.6
Phosphorus	37.7	5-membered ring	8.5
Sulfur	48.2	6-membered ring	6.1
Chlorine	54.3	naphthalene ring	12.2
Bromine	68.0	ester	-3.2
Iodine	91.0		

TABLE II
Parachors and Molar Volumes of Various Polymers

Polymer	Parachor	Molar volume, cm ³
Polyethylene	78.0	34.6
Polyisobutylene	156.0	61.4
Polypropylene	117.0	49.4
Polybutadiene (trans)	145.0	58.1
Polyisoprene (cis)	184.0	74.7
Polychloroprene (trans)	172.2	72.0
Polystyrene	250.9	100.0
Poly(4-methylstyrene)	289.9	125.2
Poly(1-butene)	156.0	64.4
Poly(1-pentene)	195.0	82.5
Poly(chlorotrifluoroethylene)	141.0	57.4
Poly(vinyl alcohol)	97.0	34.7
Poly(vinyl chloride)	115.2	44.3
Poly(vinylidene chloride)	152.4	58.4
Poly(butyl vinyl ether)	254.0	108.8
Poly(ethylene oxide)	98.0	38.9
Poly(methylene oxide)	59.0	24.0
Poly(propylene oxide)	137.0	58.1
Poly(methyl methacrylate)	224.0	84.1
Poly(N-isopropylacrylamide)	272.6	105.8
Poly(hexamethylene adipamide)	545.2	209.3
Poly(hexamethylene sebacamide)	701.2	271.3
Poly(6-aminocaproic acid)	272.6	102.9
Poly(ethylene terephthalate)	386.9	144.4
Poly(tetramethylene isophthalate)	418.5	173.7
Poly(5-methylresorcinol isophthalate)	517.6	198.5
Poly(5-methylresorcinol 5-methyl isophthalate)	556.6	233.2
Poly(5-butylresorcinol isophthalate)	634.6	237.8
Poly(5-hexylresorcinol isophthalate)	712.6	279.3
Poly(5-octylresorcinol isophthalate)	790.6	303.4
Poly(5-tridecylresorcinol isophthalate)	985.6	380.2
Polyester from 1,5-bis(3-carboxyphenyl)decafluoropentane and hexafluoropentanediol	929.4	375.2
Polyimide from 1,3-bis(3-aminophenyl)hexafluoropropane and 1,3-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride	1074.4	413.2
Poly[1,3-bis(3-hydroxyphenyl)hexafluoropropane carbonate]	602.4	224.9

Published values⁶ of critical surface tensions of 24 homopolymers range from ca. 10.6 to 46.0 dynes/cm, but 18 of the 24 homopolymers have values in a much narrower region, between 25 and 43 dynes/cm. Changes in surface tension within this range should therefore not affect molar volume values greatly; and if the parachors of polymers are plotted against their molar volumes, a linear plot with limited scatter of points should be obtained. Table II gives values of the parachors of the repeating units of a

variety of polymers, calculated from the data given in Table I, together with their molar volumes derived from density values. These values were either measured on quenched samples using the weighing bottle technique or were obtained from published data for polymers in the amorphous state.⁸

DETERMINATION OF POLYMER DENSITY FROM THE PARACHOR

The parachors of the 34 polymers listed in Table II are plotted against their molar volumes in Figure 1. Their densities range from 0.85 to 2.03 g/cm³ and their repeating unit molecular weights vary between 28 and 628. The straight line through the points was calculated from the data in Table II using a linear least-squares regression and gave a slope of 2.596 and an intercept on the ordinate at -7.7 .

From Figure 1, therefore,

$$P = 2.596V - 7.7$$

or

$$V = \frac{P + 7.7}{2.596} \quad (2)$$

Since $V = M/d$, M can be summed for the repeating unit and d obtained directly.

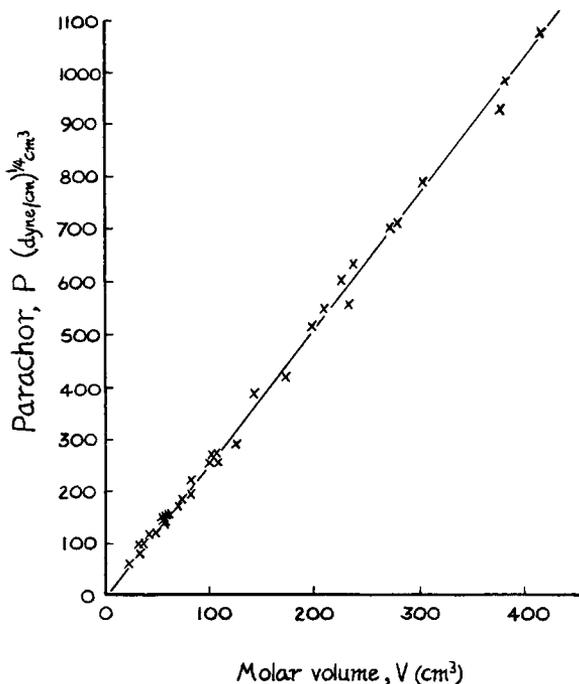


Fig. 1. Relationship between parachor and molar volume for various polymers.

DISCUSSION

The standard deviation of the differences between observed molar volumes and values calculated from eq. (2) is 6.0 for the 34 polymers given in Table II. The relationship between parachor and molar volume given in eq. (2) for polymers having a wide range of molecular weights and densities should therefore enable molar volumes of most other polymers to be calculated within $\pm 12 \text{ cm}^3$ of the observed values. It follows that percentage errors in calculating molar volume will be greater the lower the value of the parachor. The greatest error between predicted and measured molar volumes is, in fact, 13.9% for poly(vinyl alcohol), which has a parachor of only 97.0. Calculated molar volumes are within 7% of the measured values for 30 of the 34 polymers considered, and for 12 polymers the error is less than 2%. The mean of the percentage errors for the 34 polymers is 3.9%. This method of calculating molar volume is especially suitable for polymers containing structural groups for which no group contributions to the molar volume are available, e.g., the poly(resorcinol isophthalates) and the polyimide in Table II. Using available group contributions⁹, however, the mean error for molar volume estimation for the remaining polymers in Table II is about 3%.

Equation (2) may be expressed as

$$V = \frac{P}{2.596} + 2.966.$$

If the atomic and structural contributions in Table I are divided by 2.596, therefore, the molar volume of a polymer may be obtained directly by summing the new values of the contributions and adding 2.966. Table III gives the values of the parachor contributions in Table I divided by 2.596 for use in the above expression. Atomic contributions to molar volume have been published previously¹⁰; for the polymers in Table II, the mean

TABLE III
Atomic and Structural Molar Volume Contributions*

Atom	Contribution, cm ³	Bond or structure	Contribution, cm ³
Carbon	1.849	double bond	8.937
Nitrogen	4.815	triple bond	17.951
Hydrogen	6.587	semipolar bond	-0.616
Oxygen	7.704	3-membered ring	6.433
Fluorine	9.900	4-membered ring	4.468
Phosphorus	14.522	5-membered ring	3.274
Sulphur	18.567	6-membered ring	2.350
Chlorine	20.917	naphthalene ring	4.700
Bromine	26.194	ester	-1.233
Iodine	35.054		

* 2.966 cm³ must be added to the total contributions of atoms and structures to the polymer repeating unit when calculating molar volumes.

error in molar volume is $\pm 6\%$. This concept of the additivity of atomic contributions, derived from the parachor, to the molar volume is contrary to the opinion of Exner.¹¹

The presence of a small intercept, of the same magnitude as the standard deviation, in the statistical relationship in Figure 1 indicates that insufficient polymers have been included, or that the parachor contributions given in Table I are slightly incorrect when applied to polymers, or reflects small errors arising from the assumption of equal surface tensions of polymers. However, the statistical relationship is close to a line which could be drawn through the origin, so that the error between the two relationships would be small, especially in cases where the molar volume is large. It is surprising that the intercept is negative because many polymers contain ordered regions which make their observed densities higher than might be anticipated from the properties of liquids.

The estimated density of poly(tetrafluoroethylene) is 2.22 g/cm^3 in the amorphous state, for which measured values are unavailable. This compares well with the published⁸ crystalline density range of $2.35\text{--}2.40 \text{ g/cm}^3$.

CONCLUSIONS

Molar volumes and, therefore, densities of polymers may be calculated by using additive constants derived from the parachor contributions of the constitutive atoms and structures in the repeating units. Assuming that the 34 polymers are a representative sample, the standard deviation of the differences between observed and calculated molar volumes indicates that the great majority of predicted results should lie within $\pm 12 \text{ cm}^3$ of the observed values at ambient temperatures; nearly 90% of the calculated molar volumes lie within $\pm 7\%$ of the actual values at ambient temperatures. The greater the value of the molar volume or parachor, the less should be the percentage error.

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