

## New Technique for Polymer Density Estimation

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### Synopsis

A general equation is derived for estimating polymer density for amorphous polymers. The method is based on the molecular weight and parachor of the polymer repeat unit to give the limiting density.

### INTRODUCTION

Polymer density, although one of the most basic measurements for obtaining polymer properties, is not always reported or used.<sup>1,2</sup> The importance of density is appreciated by studying the recent work of Holiday and Holmes-Walter.<sup>3</sup> Undoubtedly, further work will find additional applications of density to the elucidation of polymer properties.

The method of Van Krevelen and Hoftyzer<sup>4</sup> for predicting polymer densities based on polymer repeat unit structure has the serious limitation of requiring hard-to-obtain experimental data and of rigorously applying only to those polymers with previously investigated structural units. Since many new polymers are synthesized daily, this report presents a method for estimating polymer densities unfettered by the limitations of the structural unit molar volume technique. Combining this work with that of Holiday and Holmes-Walker will provide the researcher with a powerful predictive tool in selecting those polymer structures having desired properties in advance of synthesis.

### THEORY

Recently, the utility of refractive index measurements for polymer characterization was demonstrated.<sup>5,6</sup> Those investigations demonstrated that the ratio of parachor to molar volume for a homologous series approached a limiting value (Table I). The parachor expressed as a general power series in terms of molar volume,

$$P = a_0 + a_1V_m + a_2V_m^2 + \dots \quad (1)$$

TABLE I  
Parachor/Molar Volume Ratio for Selected Homologous Series

Compound	Density <sup>20</sup> <sub>4</sub>	Molecular weight	Molar volume $V_m$	Parachor $P$	$P/V_m$
$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	0.6262	72.151	115.220	231.9	2.012
$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	0.6603	86.178	130.513	272.2	2.088
$\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	0.7685	212.422	276.411	634.9	2.299
$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$	0.77331	226.449	292.831	675.2	2.304
$\text{CH}_3(\text{CH}_2)_{20}\text{CH}_3$	0.8124	450.883	555.001	1320.0	2.381
$\text{CH}_3(\text{CH}_2)_{21}\text{CH}_3$	0.8136	464.910	571.423	1360.3	2.381
$\text{CH}_3(\text{CH}_2)_{22}\text{CH}_3$	0.8148	478.937	587.797	1400.6	2.381
$\text{CH}_3(\text{CH}_2)_{23}\text{CH}_3$	0.8157	492.964	604.345	1440.9	2.387
$\text{CH}_3\text{OH}$	0.7914	32.042	40.488	85.3	2.105
$\text{CH}_3\text{CH}_2\text{OH}$	0.7893	46.069	58.367	125.3	2.146
$\text{CH}_3(\text{CH}_2)_2\text{OH}$	0.8035	60.096	74.793	165.3	2.212
$\text{CH}_3(\text{CH}_2)_3\text{OH}$	0.8098	74.123	91.532	205.3	2.242
$\text{CH}_3(\text{CH}_2)_4\text{OH}$	0.8273	144.258	174.372	405.3	2.326
$\text{CH}_3(\text{CH}_2)_5\text{OH}$	0.8297	158.285	190.774	445.3	2.336
$\text{CH}_2\text{CH}_2\text{CH}_2$	0.9757	196.295	201.184	486.6	2.421
$\begin{array}{c} \emptyset \\   \\ \text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2 \\   \quad   \\ \emptyset \quad \emptyset \end{array}$	1.0172	300.448	295.368	734.4	2.488
$\begin{array}{c} \emptyset \quad \emptyset \quad \emptyset \\   \quad   \quad   \\ \text{CH}_2(\text{CH}_2\text{CH})_2\text{CH}_2\text{CH}_2 \\   \quad   \quad   \\ \emptyset \quad \emptyset \quad \emptyset \end{array}$	1.0215	404.602	396.086	982.2	2.481

can be truncated to a linear relation,\*

$$P = a_0 + a_1 V_m \quad (2)$$

and was rearranged,

$$P/V_m = a_0/V_m + a_1 \quad (3)$$

so that a limit in a value of  $V_m$  was approached, a condition always fulfilled for high polymers:

$$\begin{aligned} \text{Lim} \left( \frac{P}{V_m} \right) &= a_1 \\ V_m &\rightarrow \infty. \end{aligned} \quad (4)$$

Parachor and molar volume were related to surface tension and density (Sugden's<sup>7</sup> relationship):

$$\gamma = \frac{P^4(D - d)^4}{M^4} \quad (5)$$

\* Note added in proof: A general power series was used to fit data; however, through examination of experimental data, a linear fit was found adequate to express  $P$  as a function of  $V_m$ , which is consistent with Sugden's relationship. A linear fit gave  $P = -4.482 + 2.460V_m$ , and a cubic fit gave  $P = -4.807 + 2.478V_m - 3.113 \times 10^{-5}V_m^2 + 1.267 \times 10^{-8}V_m^3$ . In every case the fraction of the variability in the data accounted for by the regression equation is essentially unity, with consequent negligible residual variability (the example used was linear alkanes as polyethylene models). Thus, a linear relation was evaluated at the Lim ( $P/V_m$ ) as  $V_m \rightarrow \infty$ .

where  $\gamma$  is the surface tension,  $D$  and  $d$  are densities of a liquid and its vapor, respectively,  $P$  is the parachor, and  $M$  is the molecular weight. Hence, neglecting  $d$ , eq. (5) reduced to

$$\gamma = P^4/V_m^4 \quad (6)$$

where  $V_m$  was the ratio  $M/D$ ; i.e.,  $\gamma^{1/4}$  equals  $a_1$  of eq. (4):

$$P/V_m = \gamma^{1/4} = a_1. \quad (7)$$

In Table II are found values of  $\gamma^{1/4}$  which are constant for a wide range of polymer types and structures.

TABLE II  
Values\* of  $\gamma^{1/4}$

Polymer	$\gamma$	$\gamma^{1/4}$
Poly(vinyl fluoride)	28	2.3003
Poly(tetrafluoroethylene)	30-35	2.3403-2.4323
Poly(1,1-dihydroperfluorooctyl methacrylate)	30	2.3403
Amylopectin	35	2.4323
Poly(chlorotrifluoroethylene)	31	2.3596
Polyethylene	31	2.3596
Poly(hexafluoropropylene)	31.5	2.3691
Poly(decamethylene sebacamide)	32	2.3784
Poly(methyl methacrylate)	33-34	2.3968-2.5755
Polystyrene	33-35	2.3968-2.4323
Poly(11-aminoundecanoic acid)	33	2.3968
Cellulose	44	2.5755
Poly(vinylidene chloride-co-acrylonitrile)		
80:20	38-44	2.4828-2.5755
91:9	38	2.4828
Poly(octamethylene suberamide)	34	2.4147
Poly(nonamethylene azelaamide)	36	2.4495
Poly(vinyl alcohol)	37	2.4663
Amylose	37	2.4663
Starch	39	2.4990
Poly(vinyl chloride)	39	2.4990
Polyacrylamide	35-40	2.4323-2.5149
Poly(vinylidene chloride)	40	2.5149
Poly(6-aminocaproic acid)	42	2.5457
Poly(ethylene terephthalate)	42.5-43	2.5533-2.5607
Casein	43	2.5607
Poly(heptamethylene pimalamide)	43	2.5607
Wool	45	2.5900
	average <sup>b</sup>	2.466 ± 0.031

\* Values from reference 1.

<sup>b</sup> 95% Confidence interval estimate.

A relationship was obtained for the limiting density  $\rho_{lim}$  for any high molecular weight polymer as a function of the molecular weight  $M_{ru}$  and a parachor  $P_{ru}$  of the repeating unit,

$$\rho_{lim} = a_1 \frac{M_{ru}}{P_{ru}} \quad (8)$$

The derivation of eq. (8) followed from the previously reported<sup>5</sup> dependency of refractive index upon density  $\rho$ , the specific refractivity per electron  $K_\alpha$ , molecular weight  $M$ , and the total number of electrons  $g$  in the chromophoric center:

$$\left( \frac{\eta - 1}{K_\alpha} \right) \frac{M}{g} = \rho \quad (9)$$

In a polymer,  $M$  and  $g$  were composite terms equal to the sum of endgroup (eg) and repeating unit (ru) contributions:

$$\left( \frac{\eta - 1}{K_\alpha} \right) \frac{2M_{eg} + XM_{ru}}{2g_{eg} + Xg_{ru}} = \rho \quad (10)$$

As  $X$ , the number of repeating units approached an infinitely large number  $\rho$  approached  $\rho_{lim}$ :

$$\rho_{lim} = \frac{\eta - 1}{K_\alpha} \left( \frac{M_{ru}}{g_{ru}} \right) \quad (11)$$

The equation was simplified to eq. (8) using a relation previously derived<sup>6</sup> between the refractive index  $\eta$ , the molar volume  $V_m$ , and the number of bonds per parachor at high molecular weight,  $\beta_{lim}$ :

$$\eta - 1 = \frac{K_\alpha \beta_{lim} P}{V_m} = a_1 K_\alpha \beta_{lim} \quad (12)$$

Table III illustrates the general utility of eq. (8) for polymers of widely varying structure.

TABLE III  
Comparison of Calculated and Experimental Densities for Some Amorphous Polymers

Polymer	$\rho$ , g/cm <sup>3</sup>	
	Calculated	Experimental
Polyethylene	0.86	0.855–0.887
Polystyrene	1.04	1.04–1.057
Poly(methylpentene-1)	0.86	0.83
Poly(tetrafluoroethylene)	2.02	2.00
Polyformaldehyde	1.24	1.25
Poly(dimethylsiloxane)	1.13	1.14
Poly(ethylene oxide)	1.09	1.13
Nylon 66	1.01	1.069–1.09
Poly(vinyl acetate)	1.16	1.191
Poly(vinyl fluoride)	1.25	1.385

## CONCLUSIONS

A simple but general equation based upon tabulated<sup>7</sup> parachor values has been derived for estimating polymer densities from only repeat unit structures. The advantage of this method over others was that no new experimental information was necessary to obtain a good approximation to polymer density.

Holiday and Holmes-Walker<sup>3</sup> used density to estimate such polymer properties as bulk modulus, Young's modulus, hardness, and coefficient of expansion. Future work will undoubtedly appear showing density to be applicable in calculating other polymer properties hopefully facilitated by the general method described above.

## References

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