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THE RELATIONSHIPS BETWEEN POLYMERS AND GLASS TRANSITION TEMPERATURES

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PROJECT 7342, TASK 734203

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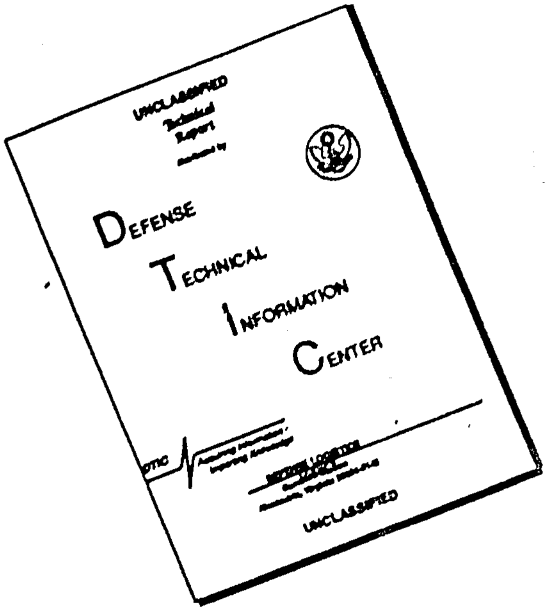

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FOREWORD

This report was prepared by the Central Research Division of American Cyanamid Company under USAF Contract No. AF 33(657)-11224. The contract was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena", Task No. 734203, "Fundamental Principles Determining the Behavior of Macromolecules". It was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, with Dr. Ivan J. Goldfarb as project engineer.

This report covers work conducted from June 1963 to May 1964.

The assistance of Dr. Maurice King in the mathematical analysis is gratefully acknowledged.

ABSTRACT

The parameter T_0 in the empirical equation

$$\log \eta/d = \log A_\eta + B_\eta/(T-T_0)$$

is being investigated as an indicator of glass formation in simple liquids for which viscosity η and density d have been published at various temperatures T. The parameter B_η was found to equal T_0 + 350° for polystyrene fractions, but this relation does not hold for the n-alkane series. Some correlations have also been discovered between the above constants and those in the Antoine equation for vapor pressure of the same liquid.

It was found that the Gibbs-DiMarzio theory correctly predicts the values of T_0 of the n-alkanes with a stiffness energy of 490 cal./mole. The predicted T_0 for polyethylene is 129°K, which corresponds to a well-known transition. A detailed study of steric factors in polymers is expected to lead to methods of predicting the stiffness energy and hence T_0.

A free volume theory has been developed which accounts satisfactorily for the change in viscosity with external pressure, and which separates the phenomenological effects of temperature and pressure from the structural and molecular factors involved in flow behavior. The adjustable constants have not yet been correlated with chemical structure, however.

This technical documentary report has been reviewed and is approved.

William E. Gibbs

WILLIAM E. GIBBS
Chief, Polymer Branch
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SYMBOLS

η	viscosity
d	density
A_η	pre-exponential constant in equation (1)
B_η	energy constant in equation (1)
$T_o(\eta)$	lower temperature limit for liquid state from equation (1)
V	molar volume
h	Planck's constant
N	Avogadro's number
ΔF^*	activation free energy in Eyring equation
R	gas constant
E	energy of vaporization
I	structural constant in Souders' relation
M	molecular weight
p	vapor pressure
A_p	pre-exponential constant in equation (4)
B_p	energy constant in equation (4)
$T_o(p)$	lower temperature limit for liquid state from equation (4)
x	number of chain atoms in polymer
$\overline{\Delta S}$	entropy of disorder per chain atom
Z	coordination number
Z'	valence of chain atom
v	free volume fraction
g	$\exp(-\epsilon/RT)$
ϵ	energy difference between rotational isomers

v_s	occupied volume
v_f	free volume
b	constant in equation (9)
K	constant (0.2058) in equation (9)
L	internal pressure factor in equation (9)

1. Introduction

Molecular theories of the liquid state are at present incapable of quantitatively predicting the effects of structure of the molecules on the formation of glasses, and reliance must be placed on empirical relations. The glass temperature has been defined(1) as that temperature at which the relaxation time becomes long compared with the duration of the experiment. Kauzmann(1) also pointed out that there is a close similarity between the relaxation processes which give rise to the change in liquid structure with temperature or pressure, and the molecular processes in viscous flow. It was therefore of interest to find that the best empirical equation for the effect of temperature on viscosity contains a parameter with the phenomenological characteristics of a glass transition. The equation is

$$\log \eta = \log A_\eta + B_\eta/(T-T_0), \qquad (1)$$

apparently first proposed independently by Fulcher(2), and Tammann and Hesse(3), although it is often referred to as the Vogel equation. The parameter T_0 has the physical significance of a lower limit to the liquid state. Miller(4) has pointed out that the WLF(5) equation, which is widely used to represent the effect of temperature on viscoelastic behavior of polymers, is equivalent to equation (1). Hence T_0 can be calculated from the reported WLF constants for polymers. Values have also been reported for a large number of low molecular weight liquids(3,6,7,8).

In spite of this large number of determinations of T_0, no correlation with molecular structure has yet been discovered. Part of the problem lies in the fact that the three parameters in equation (1) are highly correlated, which complicates the problem of calculating the best values from the experimental data. Some of the reported T_0 values may be unreliable, due to the use of measurements made over a small temperature range far above T_0, and improper weighting of the data. Ideally, the correlation with structure should be derived theoretically, and the adjustable parameters determined by direct comparison with experimental data.

Eyring et al.(9) arrived at the following expression for the viscosity of liquids, using the theory of absolute reaction rates:

$$\ln(V\eta) = \ln(hN) + \Delta F^{*}/RT \qquad (2)$$

where V = molar volume, N = Avogadro's number, h = Planck's constant and ΔF^{*} is the activation free energy. It was also proposed that

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$\Delta F^{*} = E/2.45$, where E is the energy of vaporization. Equation (2) is not a good representation of the effect of temperature on viscosity, since it fails to predict the rapid increase in viscosity as the glass temperature is approached. Furthermore, some trial calculations of the ratio $E/\Delta F^{*}$ indicated that this is highly variable. Nevertheless, the theory justifies the comparison of viscosity behavior with vaporization data, and such correlations will be discussed below.

Another correlation which has enjoyed some success is the Souders'(10) relation:

$$\log(\log \eta) = Id/M - 2.9 \qquad (3)$$

where I is a viscosity-constitutional constant, calculated from structural values which Souders has tabulated. This equation was tested against Doolittle's(11) data for tridecane and heptadecane, and the API(12) data for pentane. The plots were indeed linear, except at high densities, but did not show a common intercept at $d = 0$. Souders also claimed the same slope for all linear alkanes, but this was not confirmed either. The equation is not very useful as it stands, but it indicates one approach to a method of correlation with structure.

Equation (1) is of the same form as the Antoine equation for vapor pressure:

$$\log p = \log A_p - B_p/(T - T_o). \qquad (4)$$

Comparison of the constants in equations (1) and (4) for the liquids for which both have been reported revealed that T_o is roughly the same for both vapor pressure and viscosity, but B_p is several times larger than B_η. This is reasonable, since more energy is required to remove a molecule from a liquid than to simply move it to a new location within the volume of liquid. It would be enlightening to have a comparison of these parameters for a homologous series, to see if they follow the same trends with structure. Furthermore, since the energy of vaporization E can be calculated from B_p and $T_o(p)$ (assuming ideal vapor behavior and neglecting the liquid volume relative to the vapor), correlations of E with structure(13) could be translated into correlations for viscosity parameters.

Preliminary work with reported viscosity data indicated that kinematic viscosities obey equation (1) to even better precision than absolute viscosities. Statistical tests are required for confirmation of this observation.

2. Effect of Temperature on Viscosity

a. n-Paraffins

The effect of molecular structure on physical properties can be established by searching for a function which accurately represents the data for a homologous series of materials. For example, Small(13) found the parameter $(EV)^{1/2}$ to be linear in number of carbon atoms for several homologous series of liquids. The coefficient equals the group constant for a $-CH_2-$ group, and the intercept is that for the functional or end group. Since the parameters in equation (1) had not been reported for any homologous series, it was decided to determine them for the n-paraffin series, for which extensive data are available(11,12).

The Mathematical Analysis Group was requested to calculate the best values of log A_η, T_0 and B_η for each compound for which data was available. At the same time, the use of kinematic instead of absolute viscosity in equation (1) was investigated. The relation between the Antoine constants and those in equation (1) was also examined.

Table 1 gives the values of the parameters for both absolute and kinematic viscosity derived from the data of reference 12 by the use of a non-linear least squares method, programmed on the Datatron computer. Unfortunately, these data had been pre-smoothed according to some unknown scheme, and therefore no statistical tests can be made of the precision of the estimates. The residual mean square is substantially lower for kinematic viscosities of all the compounds except butane. As will be evident later, the data for butane are out of line in other respects as well.

Table 2 gives values of log A_η, B_η and T_0 for both kinematic and absolute viscosities, calculated from Doolittle's(11) data. 95% Confidence limits for the parameters are also included. Again the kinematic viscosity is represented more closely by equation (1).

For a comparison of Antoine constants with those in equation (1), vapor pressure data reported by Willingham, et al.(14) were treated by the same non-linear least squares method. The results are shown in Table 3 along with the T_0 values derived from the kinematic viscosities of reference 12. The 95% confidence intervals for the estimates of the parameters of the Antoine equation given in Table 3 are notably small since they do not include things such as an operator-to-operator or laboratory-to-laboratory component of error. Hence, estimates of these constants from other equally precise sets of data might very well seem not to be in agreement because of these other variance components. The comparison of $T_0(p)$ with $T_0(\eta)$ suffers accordingly, and it would be necessary to obtain very precise viscosity data in order to decide whether the two values are actually identical.

Table 1

ESTIMATES OF PARAMETERS IN EQUATION (1) FOR THE FIRST 20 n-PARAFFIN HYDROCARBONS BASED ON PRE-SMOOTHED DATA[*]

Number of Carbon Atoms in Compound	**Absolute Viscosity (η)**[**]				**Kinematic Viscosity (η/d)**[**]			
	log A_η	**B_η**	T_o	**Residual Mean Square x 10^5**	**log A_η**	**B_η**	T_o	**Residual Mean Square x 10^5**
1	-1.533	45.31	37.0	0.1226	-1.019	30.90	44.9	0.004221
2	-1.545	136.6	8.8	2.945	-1.076	90.70	25.8	1.951
3	-1.409	157.0	21.3	8.607	-1.065	128.2	28.4	2.374
4	-2.023	458.8	-68.7	0.07367	-1.374	261.8	-12.9	0.1225
5	-1.434	204.5	40.0	3.747	-1.073	154.7	54.5	1.161
6	-1.537	263.4	36.3	2.189	-1.130	187.8	58.9	0.6441
7	-1.520	273.8	51.6	3.845	-1.132	202.6	71.3	1.196
8	-1.634	345.4	41.2	1.632	-1.196	242.7	69.6	0.5356
9	-1.609	346.8	56.2	3.239	-1.191	252.1	81.2	0.9733
10	-1.698	412.6	46.2	2.567	-1.235	286.6	79.4	0.7570
11	-1.698	427.9	52.6	3.325	-1.236	300.1	85.4	0.9801
12	-1.749	477.3	46.2	3.263	-1.256	325.5	84.9	0.9803
13	-1.763	501.0	47.7	4.492	-1.259	339.9	88.1	1.333
14	-1.800	542.3	42.9	4.833	-1.271	360.1	88.2	1.420
15	-1.797	556.2	45.8	5.329	-1.265	369.3	91.8	1.493
16	-1.818	588.8	41.9	4.911	-1.270	385.7	91.7	1.424
17	-1.794	585.3	49.1	6.098	-1.254	387.9	96.9	1.747
18	-1.818	619.4	43.9	6.168	-1.258	402.8	96.4	2.019
19	-1.796	616.8	49.8	8.424	-1.238	402.2	101.6	2.629
20	-1.798	631.4	50.3	7.918	-1.237	411.4	103.1	2.355

[*] Data from reference 12.

[**] Viscosities are measured in centipoises (η) and centistokes (η/d); Temperature is in °K.

Table 2

ESTIMATES OF PARAMETERS IN EQUATION (1) WITH 95% CONFIDENCE LIMITS BASED ON RAW DATA ON (SELECTED) HYDROCARBONS[*]

Number of Carbon Atoms in Compound	Absolute Viscosity (η)[**]			Kinematic Viscosity (η/d)[**]		
	$\log A_\eta$	B_η	T_o	$\log A_\eta$	B_η	T_o
7	-1.794 ± 0.430	422.6 ± 273.8	-5.5 ± 101.7	-1.212 ± 0.153	238.3 ± 78.5	54.3 ± 41.5
8	-1.721 ± 0.362	397.4 ± 210.8	21.0 ± 76.0	-1.223 ± 0.143	256.7 ± 70.9	62.9 ± 33.5
9	-1.769 ± 0.195	441.8 ± 120.8	21.6 ± 41.2	-1.244 ± 0.076	280.7 ± 39.8	67.5 ± 17.8
11	-1.720 ± 0.107	440.6 ± 63.4	48.5 ± 20.5	-1.225 ± 0.043	295.1 + 22.2	87.3 ± 9.1
13	-1.735 ± 0.173	488.5 ± 110.0	49.9 ± 34.7	-1.242 ± 0.071	332.1 ± 39.2	90.4 ± 15.6
17	-1.952 ± 0.140	710.2 ± 115.2	12.3 ± 32.4	-1.318 ± 0.053	431.4 ± 36.0	80.0 ± 13.6
28	-1.801 ± 0.238	771.4 ± 203.5	31.4 ± 55.1	-1.249 ± 0.098	524.8 ± 72.5	86.1 ± 24.8
36	-1.605 ± 0.204	708.2 ± 160.2	64.3 ± 43.3	-1.121 ± 0.088	514.6 ± 61.5	105.9 ± 20.2
64	-1.230 ± 0.163	659.9 ± 113.4	107.1 ± 29.0	-0.829 ± 0.075	522.9 ± 48.0	133.7 ± 14.1

[*] Data from Reference 11.

[**] Viscosities are measured in centipoises (η) and centistokes (η/d); Temperature is in °K.

Table 3

ESTIMATES OF ANTOINE EQUATION CONSTANTS* FOR SELECTED n-PARAFFIN HYDROCARBONS WITH 95% CONFIDENCE INTERVALS

Number of Carbon Atoms in Compound	$\log A_p$	B_p	$T_o(p)$	$T_o(\eta)$
5	6.8474 ± 0.0004	-1062.4 ± 0.1	41.41 ± 0.03	54.5
6	6.8902 ± 0.0004	-1178.3 ± 0.2	48.02 ± 0.02	58.9
7	6.9052 ± 0.0008	-1269.7 ± 0.4	56.08 ± 0.05	71.3
8	6.9252 ± 0.0018	-1355.8 ± 1.0	63.60 ± 0.11	69.6
9	6.9522 ± 0.0005	-1439.8 ± 0.3	70.32 ± 0.04	81.2
10	6.9652 ± 0.0080	-1509.0 ± 5.3	77.82 ± 0.57	79.4
12	6.9782 ± 0.0094	-1624.4 ± 6.7	93.01 ± 0.72	84.9

*Data from Reference 14.
Vapor pressures are in mm.Hg.and temperatures in °K.

It was expected from the Eyring hole theory(9) that the parameters B_p and B_η would be closely related, since they are related to the activation energies for vaporization and flow, respectively. Figure 1 shows the correlation plot for B_η (kinematic viscosity) from Table 1 vs. B_p listed in Table 20k for reference 12.

The trend in T_0 with increasing number of C atoms shown in Tables 1 and 2 is somewhat irregular, making it difficult to extrapolate to the limiting value. Since this is the quantity we are primarily interested in correlating with structure, an effort was made to locate viscosity data on higher polymers. Tung(15) reported zero shear melt viscosities as a function of temperature for branched and unbranched polyethylene fractions, which should be suitable for calculation of T_0. However, the points were too scattered for a reliable estimate.

Aggarwal, et al.(16) reported viscosities at different temperatures for low density polyethylene fractions, and these were fitted to equation (1). Two of the sets of data were too scattered to be useful, and T_0 for the other three ranged from < 0 to > 220°K.

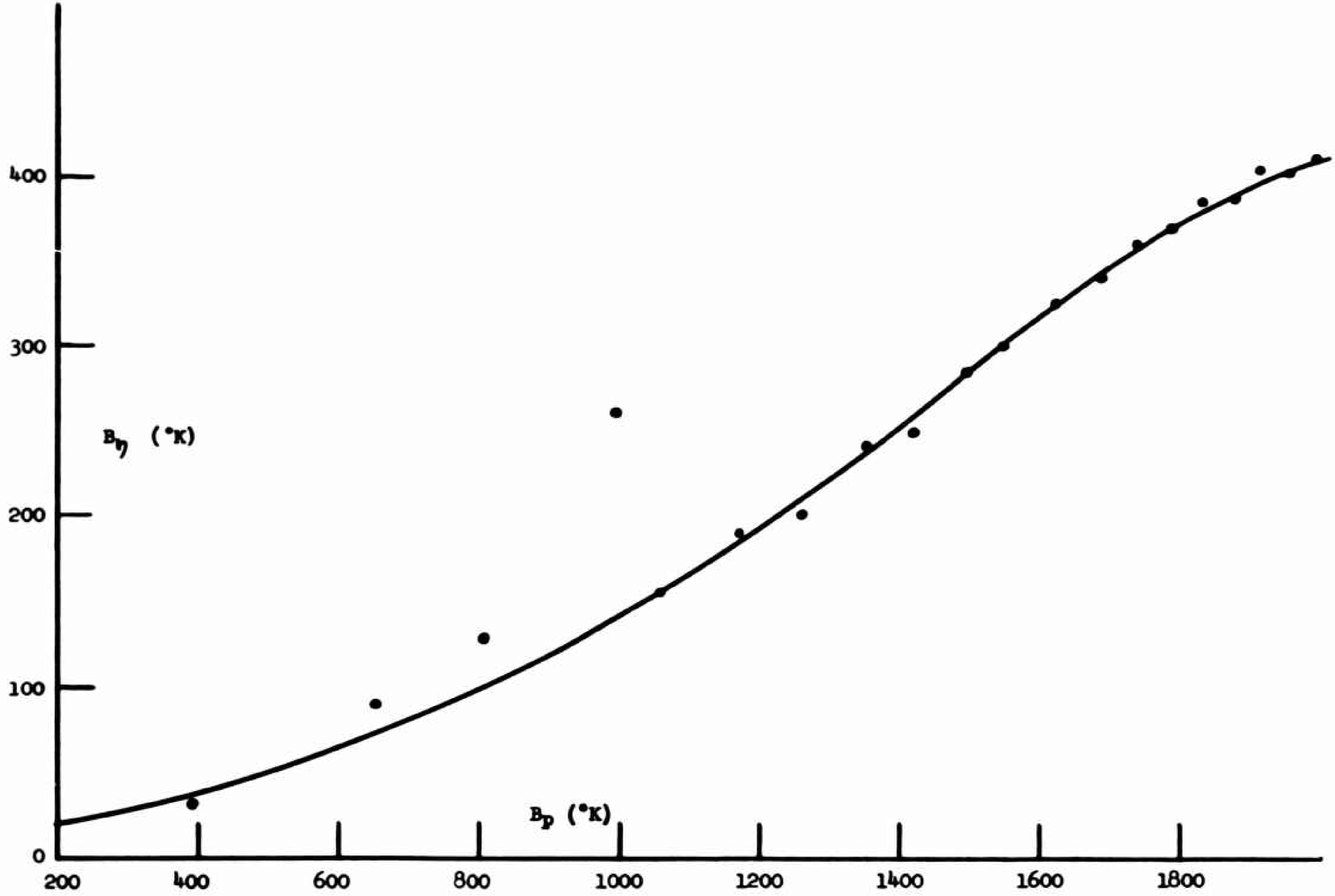
Marker, et al.(17) gave melt viscosities for a whole polymer of low density polyethylene with $\bar{M}_n = 33{,}330$. The data fit equation (1) with $T_0 = 33$°K and $B_\eta = 2{,}642$°K. These values do not seem to fit in with the results for the n-paraffin series. It was concluded that the available viscosity data on polyethylene are not sufficiently accurate for our purposes, possibly due to shear degradation or oxidative degradation.

While this work was in progress, the paper by Karapet'yants and Yan(18) appeared, giving the constants in equation (1) for 35 hydrocarbons. However, these workers found it necessary to use a separate set of constants for the upper (> 0.85 cp) and lower (< 0.85) ranges of values, making a total of six adjustable parameters for each liquid. Furthermore, many of their T_0 values are negative, in contrast to those in Tables 1 and 2, all of which (except for butane) are positive. Other workers(6,8) have also reported negative values of T_0. This seems to result from the use of viscosity data at temperatures far above T_0, and possibly from improper weighting of data.

b. Polystyrene

The viscosity data of Fox and Flory(19) on polystyrene fractions can be used to calculate log A_η, B_η and T_0 as a function of degree of polymerization, $\bar{P}$. The data had already been fitted to an equation of the same form as (1) by Williams(20), and as Miller(4)

Figure 1. B_η From Smoothed Kinematic Viscosities vs. B_p From Ref. 12.


400
300
200
100
0
B_η (°K)
B_p (°K)
200
400
600
800
1000
1200
1400
1600
1800

has pointed out, the constants in equation (1) can be obtained by a simple transformation. The resulting values of B_η and T_o are shown plotted against $\bar{P}$ in Figure 2. Both B_η and T_o approach limiting values above $\bar{P} = 200$, and drop off rapidly below that. The strong correlation between these constants is evident from Figure 2. There is an almost constant difference of 350° between B_η and T_o.

3. Correlations with Structure

A simple correlation between energy of vaporization E and chemical structure was proposed by Small(13), based on the observation that the function $(EV)^{1/2}$ is linear in number of repeating units in a homologous series. Small published a table of group values from which E can be calculated for any liquid, provided the molar volume V is known. This relation was checked against the selected values of E and V for the n-alkanes published by API Project 44(12), and was indeed found to be obeyed remarkably well, although the slope and intercept were slightly different from the values recommended by Small. Several drawbacks to this scheme should be pointed out, however. First is the requirement of having a measured value for the density of the liquid. Secondly, the correlation is known to be valid only at 25°C. and has not been tested at other temperatures. Third, the most serious objection is that the molar volume is a strong function of x, the number of carbon atoms, so that errors in prediction of E tend to be observed on a plot of $(EV)^{1/2}$ vs. x.

By analogy, it was thought that $(B_pV)^{1/2}$ should be linear in x, but this is not the case. It has been found, however, that

$$(B_pV)^{0.77} = 1{,}609\,x + 155 \qquad (5)$$

represents the n-alkane data very well.

Another function was found which gives the effect of structure (in the n-alkane series) on the Antoine constants with good precision, and does not require knowledge of the density:

$$(T_o/B_p)^{2.3} = 1.12 \cdot 10^{-4}x \qquad (6)$$

This result illustrates the fact that the parameters in equation (4) are highly correlated, and hence it should be possible to develop a relation with only one or two adjustable parameters.

The published data on n-alkanes have been submitted to the Mathematical Analysis Group in order to ascertain the best values of the constants in equations (5) and (6) and their confidence intervals.

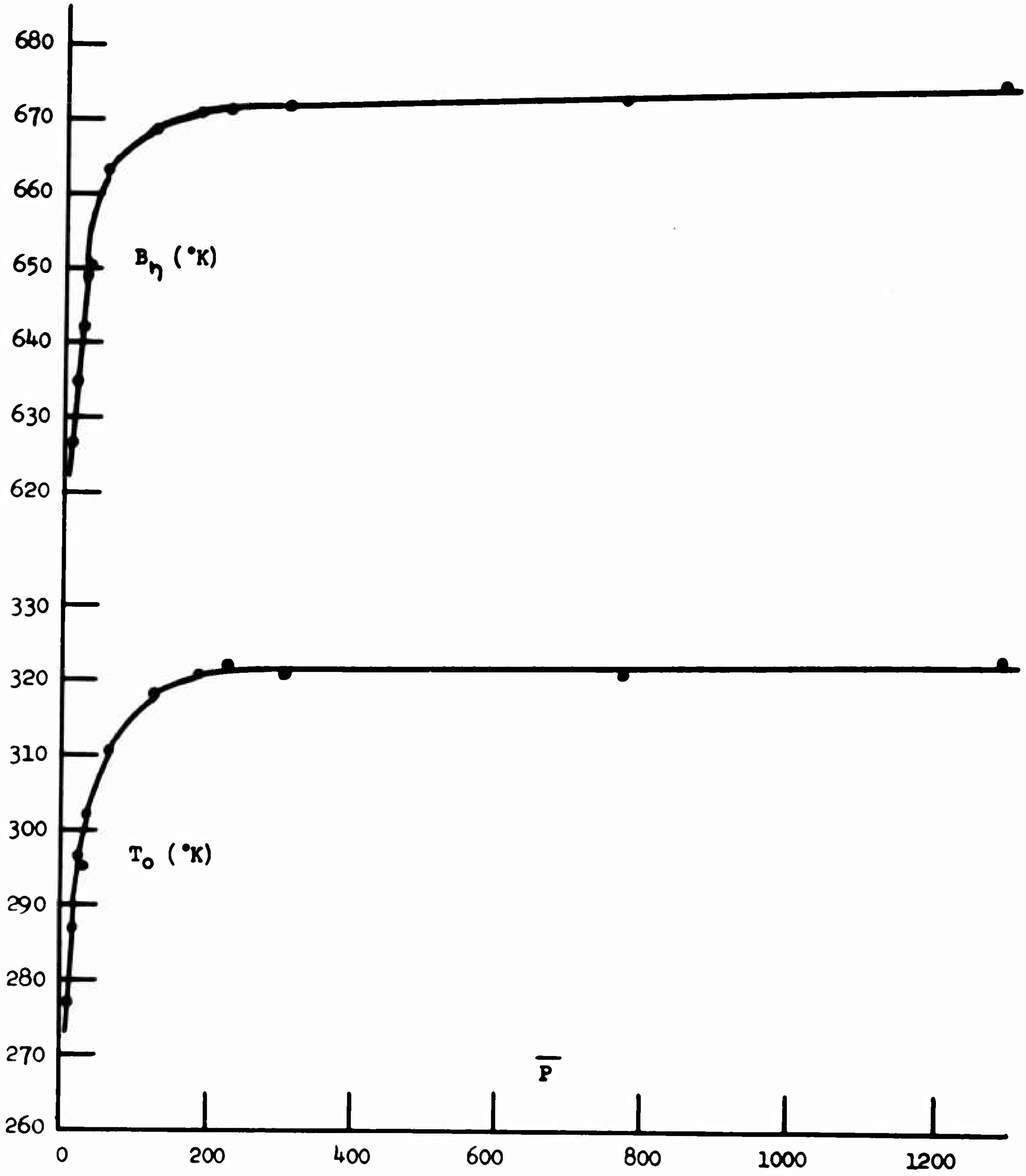


Figure 2. Constants in Equation (1) for Polystyrene.

The purpose of this line of approach is to find a means of relating intermolecular forces to structure, and use this in the prediction of glass temperatures. The product B_pV, for example, is roughly proportional to "a" in the van der Waals equation and hence can be used as a measure of cohesive energy. It would be highly desirable, however, to liberate this scheme from the requirement that the molar volume be known. Future work will be directed toward the estimation of B_p for other classes of compounds, and its relation to structural features rather than the molar volume.

The two correlations with structure discussed above [equations (5) and (6)] relate to the vapor pressure. Efforts to extend these to the viscosity parameters in equation (1) have not led to any useful result. However, a rough correlation has been found between $T_0(\eta)$ and B_p. The ratio $B_p/T_0(\eta)$ equals approximately 19 for straight-chain aliphatic liquids above butane, but varies over a wide range for other types of compounds, as shown in Table 4.

Table 4

CORRELATION OF B_p WITH $T_0(\eta)$

Liquid	$B_p/T_0(\eta)$	Liquid	$B_p/T_0(\eta)$
Methane	8.68	Ethylene bromide	18.99
Ethane	25.44	Acetic acid	20.24
Propane	28.63	Butyric acid	20.46
Butane	-73.33	Carbon Tetrachloride	17.02
Pentane	19.53	Cyclohexane	24.46
Hexane	19.89	Benzene	15.89
Heptane	17.79	Toluene	107.52
Octane	19.47	Chlorobenzene	44.86
Nonane	17.60	Nitrobenzene	21.58
Decane	18.91	Aniline	9.58
Undecane	18.41	Phenol	9.63
Dodecane	19.15	1,6-Dimethylnaphthalene	14.05
Tridecane	19.17		
Tetradecane	19.72		
Pentadecane	19.50		
Hexadecane	19.97		
Heptadecane	19.41		
Octadecane	19.92		
Nonadecane	19.31		
Eicosane	19.34		

The values in Table 4 were calculated from the data given by the American Petroleum Institute(12) for B_p of the n-alkanes, the $T_o(\eta)$ values (kinematic viscosity) for these liquids listed in Table 1, the values of B_p given by Dreisbach(21) for the liquids in column two, and the $T_o(\eta)$ values for these reported by Hoffmann and Rother(6). These are practically all the liquids for which both B_p and $T_o(\eta)$ have been reported. Further investigation along this line will require evaluation of raw data on viscosities or vapor pressures.

This correlation is potentially valuable, since it relates $T_o(\eta)$ to a parameter (B_p) which can in turn be correlated with structure through equation (5).

The empirical correlations discussed above are probably not sufficiently reliable for extrapolation to infinite molecular weight. Free volume theories are also of little use for this purpose, but the statistical mechanical theory of the glass transition proposed by Gibbs and DiMarzio(22) is on sufficiently firm grounds so that some degree of confidence can be placed in its predictions. The equations given in reference (22) yield the following expression for the entropy of disorder per atom, $\overline{\Delta S}$, when a chain of x atoms of valence Z' is placed on a lattice of coordination number Z:

$$\frac{\overline{\Delta S}}{R} = \frac{Z-2}{2}\cdot\frac{\ln v}{1-v} + \frac{1}{2}\left(Z-2+\frac{Zv}{1-v}\right)\ln\left[\frac{(Z-2)x+2}{Zxv}\cdot(1-v)+2\right]$$
$$+\frac{1}{x}\ln\frac{[(Z-2)x+2](Z-1)}{2} + \frac{x-3}{x}\left\{\ln[1+(Z'-2)g]+\frac{(Z'-2)g}{1+(Z'-2)g}\cdot\frac{\epsilon}{RT}\right\} \qquad (7)$$

where v is the fractional free volume, $g = \exp(-\epsilon/RT)$ and ϵ is the energy difference between rotational isomers. The point at which $\overline{\Delta S}$ decreases to zero is assumed here to equal $T_o(\eta)$. Application of this theory to glass temperatures of polymers yields reasonable values of ϵ, although there are no independently measured values for comparison. In order to evaluate the theory more critically, the values of $T_o(\eta)$ given in Table 1 for the n-alkanes were compared with the predictions of equation (7). For these liquids, ϵ is known from spectroscopic measurements(3) to be about 500 cal./mole.

Equation (7) has a number of interesting properties which are not immediately obvious. When $Z = Z' = 4$ and $x = 5$ or less, $\overline{\Delta S}$ is greater than zero for all positive values of ϵ/T. Nevertheless, reasonable values of ϵ/T_o are found for x = 6 or greater. Positive values of T_o cannot be obtained for pentane (x = 5) even if the free volume is decreased to zero. As a matter of fact, adjustment of v does little to improve the fit to the data above $x = 5$, and it seems expedient to eliminate this parameter from the theory.

It was noted that for long chains, increasing Z decreases the entropy. Unfortunately, for $x = 5$ the trend is reversed, as shown in Table 5, where the terms in equation (7) involving Z are evaluated for $v = o$. Coordination numbers less than 4 are physically unreasonable, so the best choice seems to be 4, which is the number used by Gibbs and DiMarzio.

Table 5

EFFECT OF COORDINATION NUMBER ON CONFIGURATIONAL ENTROPY

Z	x	$\frac{Z-2}{2} \ln \frac{(Z-2)\,x + 2}{Z\,x}$	$x^{-1} \ln [(Z-2)\,x + 2]\,(Z-1)/2$	$\overline{\Delta S}/R$
4	5	-0.511	0.578	0.067
4	∞	-0.693	0	-0.693
6	5	-0.620	0.801	0.181
6	∞	-0.81[illegible]	0	-0.811
8	5	[illegible]69	0.944	0.275
8	∞	[illegible].864	0	-0.864

One obvious defect in the Gibbs-DiMarzio theory is the failure to take into account the fact that rotations about successive bonds are interdependent, as discussed in the preceding monthly letter. The mathematical technique for handling this problem was developed by Lifson(24), and applied to the calculation of random coil dimensions by Nagai and Ishikawa(25) and Hoeve(26), and to the entropy of melting by Starkweather and Boyd(27). The decrease in entropy due to this effect is at a maximum for $\epsilon/T = 0$, and becomes negligible for $\epsilon/T \cong 5$(25,27). The formula given by Taylor(28) for the fraction of "forbidden" configurations yields 0.05 R for the decrease in entropy per atom in pentane, and even this maximum value is too small to resolve the difficulty with the calculation of T_o. For the infinite polymer $\epsilon/T_o \cong 3.9$ (for $v = o$ and $Z = Z' = 4$) and this increases as x decreases, so it appears that modification of the Gibbs-DiMarzio theory to include the pentane effect is hardly worthwhile.

Starkweather and Boyd(27) point out that lattice treatments are overly restrictive and underestimate the entropy of liquids. They propose addition of a contribution due to "long range disorder" on the order of 0.5 R. However, this would lead to negative values of T_o for all the n-alkanes below eicosane.

For the reasons given above, free volume and long range disorder were omitted, and Z was set equal to $Z' = 4$, to arrive at the final expression to be used for comparison with experiment:

$$0 = \ln\frac{x+1}{2x} + \frac{1}{x}\ln 3(x+1) + \frac{x-3}{x}\left[\ln(1+2q) + \frac{2q}{1+2q}\cdot\frac{\epsilon}{RT_0}\right] \qquad (8)$$

The energy difference between rotational isomers is generally lower in the liquid state than in the gas, hence the liquid state value should be used in equation (8). Data of this type are not plentiful, so the most practical way to estimate ϵ for polymers is by application of equation (8) to experimental measurements of T_0.

The Mathematical Analysis Group estimated the best values of ϵ in equation (8) for the set of $T_0(\eta)$ values listed in Table 1 (smoothed data) and 2 (raw data) for kinematic viscosities of the n-alkanes. These and the corresponding T_0 calculated for the infinite polymer are shown in Table 6. It was pointed out above that positive values of ϵ/T_0 are not obtained for x = 5 or less, so these data were omitted from the analysis. Furthermore, most of the error in estimation was contributed by hexane, x = 6, so a value is also shown with hexane omitted.

Table 6

ROTATIONAL ENERGY FOR n-ALKANES

	ϵ (cal./mole)	$T_0(\infty)$(°K)
Smoothed data	493.4	129.5
Smoothed data minus hexane	490.8	128.8
Raw data	467.4	122.6

The calculated energy differences are in excellent agreement with the spectroscopically measured values(23) of 450 for pentane, and 470 and 520 for two rotational isomers of hexane. Butane, for some reason, has a higher energy difference, 760 cal./mole, than the higher alkanes.

The limiting values of T_0 for $x = \infty$ all fall within a small range, and this seems to correspond to the well-known transition at about 120°K(29) in polyethylene.

In view of the success of the Gibbs-DiMarzio theory in predicting the magnitude of T_0, it becomes of pressing importance to find a correlation of ϵ with the structure of the repeating unit. The difficulty of this problem is illustrated by the situation in the methacrylate series, where the T_g of poly(methyl methacrylate), the parent member, varies over a range of at least 80° depending on stereoregularity. Simple additive schemes are basically incapable of accounting for such effects, and detailed examination of the molecular structure will be required.

With the above considerations in mind, an attempt was made to devise a scheme for representing diagrammatically the spatial requirements of polymeric chains, in hopes of demonstrating the steric effects which influence the behavior of polymers in bulk. In view of the variations in bond lengths and angles in different structures, and the large number of conformations available to each monomer unit, it is necessary to use some simplifying assumptions to make the problem tractable. Furthermore, this type of analysis is to be applied to polymers which have not yet been synthesized, so that knowledge of the crystal structure cannot be used as a basis.

The most satisfactory procedure found so far is as follows: the atoms are located on a tetrahedral lattice, shown in projection, with the relative levels of adjacent atoms depicted by means of the "flying wedge" symbol. Bonds between superimposed atoms therefore appear as in a Newman projection. Superimposed atoms are shown by circles of different sizes, small circles lying above the larger ones. Figure 3 illustrates the use of these diagrams in evaluating steric effects in the n-alkanes. Structures I-IV represent pentane, and V and VI are sections of a longer chain of methylene units.

The use of a tetrahedral lattice limits the conformation of each bond to the three isomers: trans, gauche (left) or gauche (right), labeled T, G and G′. Two types of steric interaction can be discerned. Hydrogen atoms may occupy adjacent lattice sites (structures II and III), which places them within their van der Waals radius of interaction, or may occupy the same site (structure IV), presumably a "forbidden" configuration. These atoms are 1,6 to each other in the first case and 1,7 in the second, arranged in the form of a cyclohexane ring, which can appear either flat or on edge. Interactions with more distant atoms can probably be neglected.

As Figure 3 shows, the all trans configuration is the most stable, while the sequence G G′ is forbidden. Since forbidden configurations occur first in pentane, Taylor(28) named it the "pentane effect".

Figure 3. Projections of Molecules on Diamond Lattice

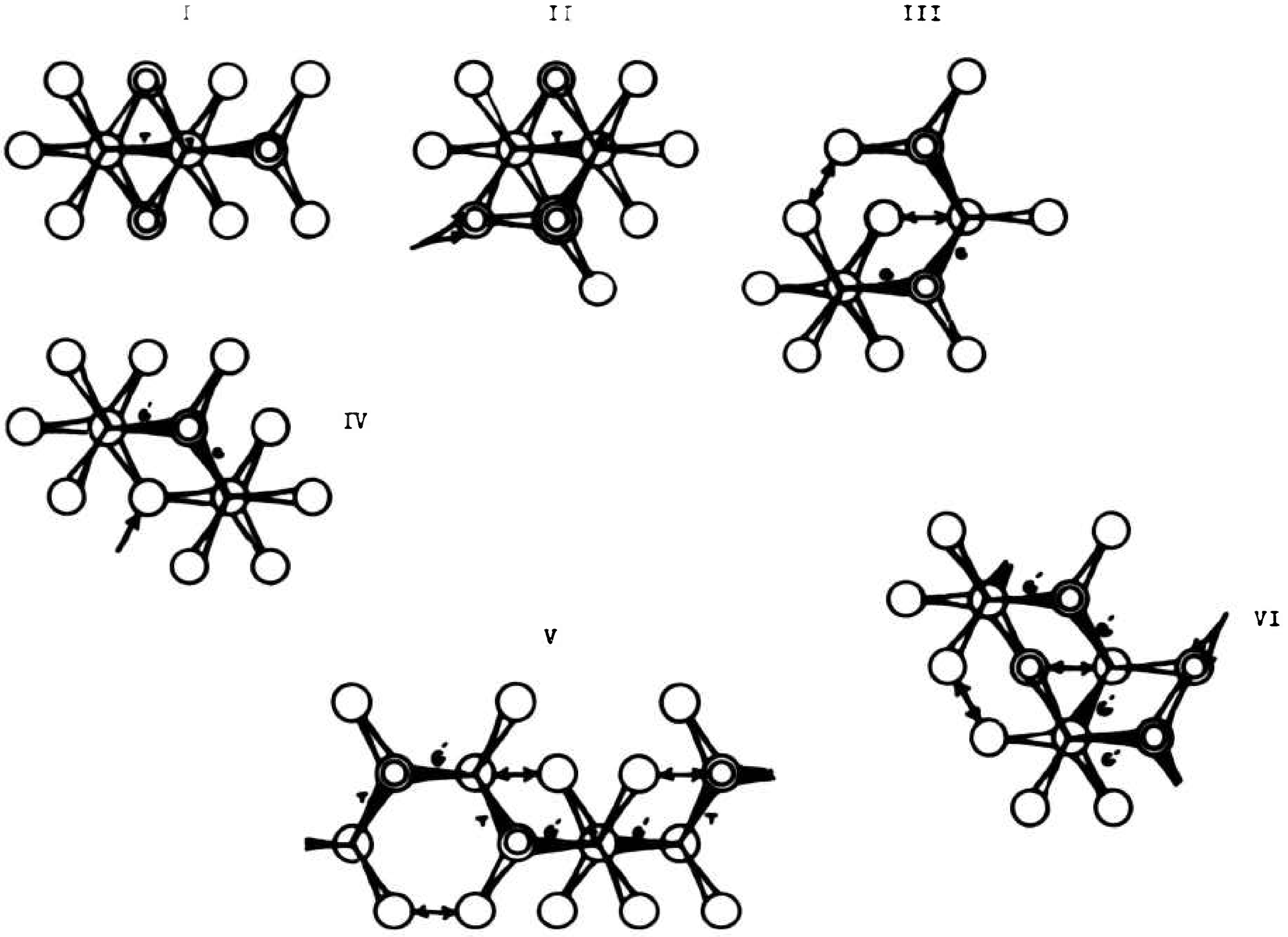


Figure 3. Projections of Molecules on Diamond Lattice

Substituents on the backbone can lead to double occupation of lattice sites in the all trans configuration, so that helical configurations tend to be favored. Two helical chains are depicted in Figure 3 to illustrate the manner in which they appear on this type of diagram. Structure V has six atoms per turn, and structure VI has four. When the backbone carries substituents it is not always possible to find a configuration free of the pentane effect. The important factor in chain stiffness is presumably the occurrence of one configuration which is strongly preferred over all others, although it may contain some double occupancies.

It will be necessary to examine a number of selected polymers for which ϵ has been determined by use of the Gibbs-DiMarzio theory, to see if interactions are evident on the diagrammatic projections which can account for the variations in stiffness energy. If this approach is successful, each type of interaction could be assigned an energy, depending on the nature of the atoms involved, and a small number of such values would suffice for the prediction of T_0 for a large number of different polymers.

4. Effect of Pressure on Viscosity

Although a number of studies have been made of the effect of pressure on viscosities of liquids, as yet no relation has been found which satisfactorily represents the isotherms observed. It would be highly desirable to be able to separate the phenomenological effects of both temperature and pressure from the structural and molecular factors involved in the viscoelastic behavior of polymers. This in fact is an essential first step in the correlation of structure with properties. An approach to the solution of this problem is described below.

The Doolittle(11) equation can be written

$$\ln \eta = \ln A_\eta + b v_s / v_f \qquad (9)$$

where ${}^{v_f}/v_s$ is the relative free volume, and b is a constant independent of temperature. Comparison with equation (1) shows that $\frac{v_f}{v_s}$ must be linear in T, when equation (1) is obeyed. Correspondingly, the influence of pressure can be explained in terms of a reduction in free volume as the pressure is raised. If it is assumed that the "occupied" volume, v_s, is independent of pressure, then a suitable equation of state will predict the effect of pressure on free volume and hence viscosity. Using the Tait equation and converting equation (9) to common logarithms, we obtain

$$\log \eta = \log A_\eta + 0.4343\ b v_s \left[v_f(1) - K v_1 \log (L + P)/L \right]^{-1} \qquad (10)$$

where $v_f(1)$ is the free volume when no pressure is applied, v_1 is the corresponding specific volume, and K and L are the constants in the Tait equation. Inverting and substituting the value of $v_f(1)/bv_s$ from equation (1) and (9), we have

$$\frac{1}{\log(\eta/A_\eta)} = \frac{T-T_0}{B_\eta} - \frac{2.303\,K v_1}{b v_s} \log \frac{L+P}{L} \qquad (11)$$

K is known to be independent of temperature, and in fact equals 0.2058(30) for all liquids for which it has been determined. It is evident from the manner in which equation (11) was derived that A, B and T_0 are independent of pressure. The change in viscosity with pressure is therefore predicted by means of only two adjustable parameters: (bv_s) and L. In accordance with the finding that equation (1) is obeyed more closely by kinematic than absolute viscosities, equation (11) has been applied to the kinematic viscosities calculated from the data reported by Lowitz(31) et al. It was found that the plots of $1/\log(\eta/A)$ were linear in $\log(L+P)/L$ for every liquid examined, for the proper choice of L.

The free volume $v_f(1)$, occupied volume v_s and Doolittle constant b can be calculated from the slope and intercept of the latter plot. These are shown in Table 7 along with the constants A, B and T_0 and the Tait equation parameter L. The temperature-dependent values were obtained at 37.78°, except for n-octane at 30°.

Table 7

FREE VOLUME PARAMETERS FOR EFFECT OF PRESSURE ON VISCOSITY

Liquid	n-Octane	9-(2-cyclohexylethyl)-heptadecane	Perhydro-chrysene	Dodeca-hydrochrysene
T_0 (°K.)	62.9	155	203	250
B_η (°K.)	256.7	370.7	240.5	215.7
log A_η	-1.634	-1.3053	-0.815	-0.8616
L (atm)	745	700	1200	1200
$v_f(1)$ (cc/gr)	0.5259	0.4413	0.1261	0.1003
v_s (cc/gr)	0.9140	0.7758	0.9056	0.8633
v_1 (cc/gr)	1.4399	1.2171	1.0317	0.9636
b	1.751	3.229	0.6180	0.9530
bv_s (cc/gr)	1.6008	2.505	0.5597	0.8227
η_1 (cp)	0.483	12.1	25.6	514

There are some consistent trends in these results. In order of increasing T_0: $v_f(1)$ decreases, v_1 decreases and η_1 increases. These parameters will be calculated for those liquids for which viscosity-pressure data are available. It is hoped that the data will fit into either a corresponding states relationship or a direct correlation with molecular structure.

Cutler, et al.(30) reported the values of L for compressibilities of some of their compounds. They found L = 1275 atm. for 9-(2-cyclohexylethyl)-heptadecane at 37.78°, whereas the viscosity data fits equation (11) only for L = 700 atm. The use of absolute instead of kinematic viscosity in equation (11) does not change this value of L appreciably. The L values for viscosities and compressibilities will be compared for various liquids, to see if this situation is general.

REFERENCES

1. W. Kauzmann, Chem. Revs. 43, 219 (1948).

2. G. S. Fulcher, J. Am. Ceram. Soc. 8, 339 (1925).

3. G. Tammann and W. Hesse, Z. Anorg. Chem. 156, 245 (1926).

4. A. A. Miller, J. Phys. Chem. 67, 1031 (1963); J. Polymer Sci. 1A, 1857 (1963).

5. J D. Ferry "Viscoelastic Properties of Polymers", Wiley, N.Y., 1961, p. 216.

6. M. Hoffmann and K. Rother, Rheologica Acta 2, 164 (1962).

7. Document No. 4597, ADI Auxiliary Publications Project, Library of Congress.

8. F. Gutmann and L. M. Simmons, J. Appl. Phys. 23, 977 (1952).

9. S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, N.Y., 1941.

10. M. Souders, Jr., J. Am. Chem. Soc. 60, 154 (1938).

11. A. K. Doolittle, J. Appl. Phys. 22, 1032 (1951).

12. "Selected Values of Properties of Hydrocarbons and Related Compounds", Am. Pet. Inst. Res. Project 44, Carnegie Inst. of Tech.

13. P. A. Small, J. Appl. Chem. 3, 71 (1953).

14. C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, J. Res. Natl. Bur. Standards 35, 219 (1945).

15. L. H. Tung, J. Polymer Sci. 46, 409 (1960).

16. S. L. Aggarwal, L. Marker and M. J. Carrano, J. Appl. Polymer Sci. 3, 77 (1960).

17. L. Marker, R. Early and S. L. Aggarawal, J. Polymer Sci. 38, 381 (1959).

18. M. Kh. Karapet'yants and K. H. Yan, Zh. Fiz. Khim. 37, 2041 (1963).

19. T. G. Fox and P. J. Flory, J. Appl. Phys. 21, 581 (1950).

20. M. L. Williams, J. Appl. Phys. 29, 1395 (1958).

21. R. R. Dreisbach, "Phys. Propr. of Chem. Cpds." III, Adv. in Chem. Series, Am. Chem. Soc., Washington, D. C., 1961.

22. J. H. Gibbs and E. A. DiMarzio, J. Chem. Phys. 28, 373 (1958).

23. D. J. Millen, Ch. 4, p. 160 in "Progress in Stereochemistry", Vol. 3, Butterworths, Washington, 1962.

24. S. Lifson, J. Chem. Phys. 30, 964 (1959).

25. K. Nagai and T. Ishikawa, J. Chem. Phys. 37, 496 (1962).

26. C. A. J. Hoeve, J. Chem. Phys. 35, 1266 (1961).

27. H. W. Starkweather, Jr. and R. H. Boyd, J. Phys. Chem. 64, 410 (1960).

28. W. J. Taylor, J. Chem. Phys. 16, 257 (1948).

29. B. Wunderlich, J. Chem. Phys. 37, 1203 (1962).

30. W. G. Cutler, R. H. McMickle, W. Webb and R. W. Schiessler, J. Chem. Phys. 29, 727 (1958).

31. D. A. Lowitz, J. W. Spencer, W. Webb and R. W. Schiessler, J. Chem. Phys. 30, 73 (1959).