# Surface Tensions of Liquid Polyisobutylenes

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## Synopsis

Measurements of surface tensions were carried out in the temperature range 25–120°C on seven different liquid polyisobutylenes with molecular weights ranging from 100 to 80,000. Relationships between the surface tension of polyisobutylene and other properties, such as the parachor, cohesive-energy density, and molecular weight are discussed.

## INTRODUCTION

Measurement of the surface tensions of polyisobutylenes was required as part of the study of their spreading on solid surfaces. The surface tensions of ordinary organic liquids can be easily measured, but those of viscous materials, such as polyisobutylene, are much more difficult to measure because of the high viscous forces involved, which can mask the true value of the surface tension forces.

Studies of viscous molten glasses with a variety of methods[1] have been reported in the past. Those which also have been used with organic polymers include the pendant drop,[2] maximum bubble pressure,[3,4] ring,[5] and capillary rise[6] methods. Two methods were used for this study, a modification by Bradley[7] of Jaeger's maximum bubble pressure method and the differential capillary rise method.

## MATERIALS

All materials in this investigation were used as received from the manufacturer. The characteristics of the polyisobutylenes are listed in Table I. The B grades of polyisobutylene were supplied by Badische Anilin-and-Soda-Fabrik A.G., the Vistac by Advanced Solvent and Chemical Corporation, and the Vistanex LM-MH by Enjoy Chemical Company.

The viscosities were determined by the falling-sphere method,[8] and the temperature coefficients of viscosity were calculated from

$$\theta = (\log \eta_2 - \log \eta_1)/(1/T_2 - 1/T_1) \qquad (1)$$

where $T_2 - T_1 \leq 10°C$. For the grades of polyisobutylene B10 and Vistanex LM-MH the relationship between $\log \eta_2 - \log \eta_1$ and $1/T_2 -$

TABLE I
Characteristics of the Polyisobutylenes

| Material | Viscy. at 25°C, P | Temp.[a] coeff. of viscy. | Intr. viscy. $[\eta]$, ml/g | Mol. wt. $\bar{M}_v$ | $\bar{M}_n$ | $\bar{M}_v/\bar{M}_n$ | Density at 25°C, g/ml |
|---|---|---|---|---|---|---|---|
| B1 | 0.253 | 1590 | 1.26 | 140 | 140 | 1 | 0.820 |
| B2 | 71.7 | 3130 | 3.54 | 790 | | | 0.876 |
| B3 | 227 | 3160 | 4.04 | 1560 | $820 \pm 20\%$ | 1.75 | 0.885 |
| Vistac | 1030 | 3670 | 5.18 | 2340 | 1000 | 2.34 | 0.889 |
| B8 | $90 \times 10^4$ | 3130 | 14.0 | 17100 | | | 0.911 |
| B10 | $2.7 \times 10^5$ | 3280 | 20.9 | 38200 | $900 \pm 20\%$ | 4.25 | 0.911 |
| Vistanex LM-MH | $1.5 \times 10^6$ | 3090 | 29.8 | 77500 | | | 0.911 |

[a] Over the temperature range of 25–60°C.

$1/T_1$ was found by experiment to be linear for the temperature range $-40$ to $80°C$. For the other grades the temperature coefficients of viscosity were determined only for the temperature range $25–60°C$. Linear relationships were again found.

The viscosity-average molecular weights $\bar{M}_v$ of the polyisobutylenes were derived from their intrinsic viscosities measured in benzene at $24°C$ by the equation

$$[\eta] = K\bar{M}_v{}^\alpha \tag{2}$$

where $[\eta]$ is the intrinsic viscosity, and $K$ and $\alpha$ have the values $1.07 \times 10^{-1}$ and $0.5$ as given by Meyerhoff.[9] The values for the number-average molecular weight $M_n$ quoted for B3, B10, and Vistac were given by the manufacturers; that for B1 was assumed to be equal to $\bar{M}_v$.

The density/temperature relationship was determined for all grades of polyisobutylene for the temperature range $25–100°C$ by using a 100-ml S.G. bottle. The relationship is given by the linear equation

$$\rho_2 = \rho_1(1 - \beta t) \tag{3}$$

where $\beta = 0.005$ g/ml-C°.

## EXPERIMENTAL

### Method A: Maximum Bubble Pressure

Jaeger's method of measuring surface tension involves measuring the excess pressure above the atmospheric necessary to cause a bubble to break from the end of a capillary tube immersed in the liquid.

If the end of the capillary tube rests exactly in the surface of the liquid, the pressure observed is entirely that necessary to overcome the surface tension forces, and no correction due to hydrostatic pressure is required.

The theory of the method has been worked out by Schrödinger[10] and Vershaffelt,[11] and the expression derived is

$$\gamma = pr(1 - 2r/3h - r^2/6h^2)/2 \tag{4}$$

where $\gamma$ is the surface tension (dyn/cm), $r$ the radius of the capillary (cm), $p$ the maximum excess pressure observed (dyn/cm²), and $h$ equal to $p/(\rho_1 - \rho_2)g$, where $\rho_1$ is the density of the liquid, $\rho_2$ the density of the gas in the bubbles, and $g$ the acceleration due to gravity. In this work the third term in parentheses is omitted as insignificant.

With mobile liquids the method is easily used, but for viscous materials the maximum pressure is a measure of the combined effect of surface tension and viscosity and depends upon the rate at which the pressure is applied. To overcome this difficulty Bradley[7] developed a technique based on the condition that at any pressure below the maximum that can be counterbalanced by surface tension only the bubble will be stable, whereas at any pressure above this "true maximum" the bubble will be unstable and will break. How quickly the bubble breaks will depend on
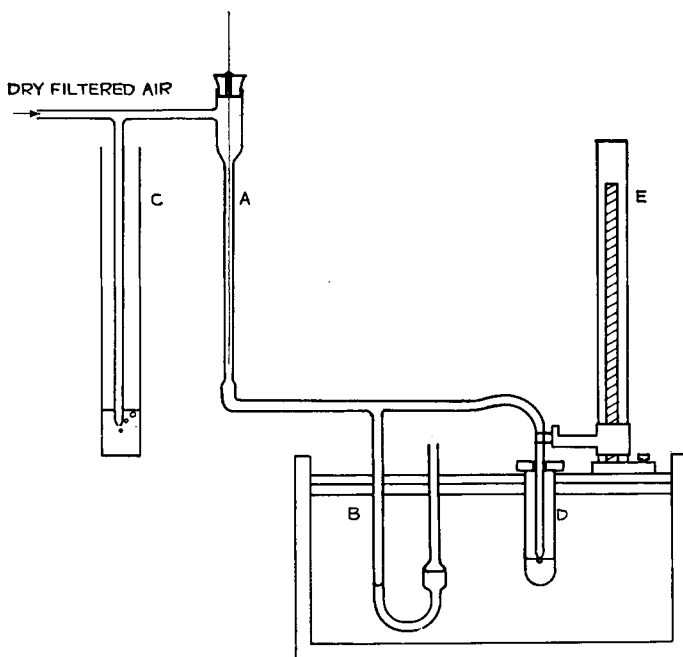
Figure 1.

the viscosity of the liquid and on the pressure above the true maximum. Thus, if a pressure is applied such that the bubble will break, it is known that the true maximum pressure is smaller. If further bubbles are blown at successively reduced pressures, the maximum pressure at which the bubble will not break can ultimately be found. The length of time between the application of the pressure and the breaking of the bubble will increase as the true maximum is approached, and as the excess pressure decreases to zero.

The bubble-pressure apparatus is shown diagrammatically in Figure 1. The flow regulator A consists of a length of capillary tube, the bore of which was partly filled with a steel rod of diameter fractionally less than that of the tube. The length of rod inserted in the capillary and, hence, the flow rate of the air could be varied by sliding it through a rubber seal. The manometer fluid was deaerated di-$n$-butyl phthalate, and the radii of the arms of the manometer B were in the ratio 10:1. Pressure was determined by measuring the height of the liquid, to ±0.001 cm, in the small-bore arm by means of a cathetometer and subtracting the value from that corresponding to atmospheric pressure.

The pressure stabilizer C was a glass T-piece supported in a container of di-$n$-butyl phthalate. The T-piece was attached to the arm of a mechanical device, not shown in Figure 1, which enabled it to be raised or lowered quickly and its final position to be adjusted precisely by means of a fine control, the smallest movement being 0.001 cm. With this arrange-

TABLE II
Surface Tension (dyn/cm) of PIB in the Temperature Range of 25–120°C

| Temp., °C | Maximum bubble pressure method | | | | | | | Capillary rise method | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | B1 | B2 | B3 | V.ᵃ | B8 | B10 | V. L.ᵇ | B1 | B2 | B3 | V.ᵃ | B8 | B10 | V. L.ᵇ |
| 25 | 26.3 | 29.2 | 29.3 | 29.8 | — | — | — | 26.9 | 30.1 | 31.1 | 30.8 | — | — | — |
| 40 | 25.0 | 28.0 | 28.6 | 28.9 | — | — | — | 25.6 | 29.1 | 30.3 | 30.3 | — | — | — |
| 60 | 23.1 | 26.9 | 26.7 | 27.3 | — | — | — | 24.1 | 27.8 | 28.9 | 28.8 | — | — | — |
| 80 | 21.7 | 25.0 | 25.5 | 25.8 | — | — | — | 22.7 | 26.4 | 27.6 | 27.8 | — | — | — |
| 100 | 20.5 | 23.1 | 24.1 | 24.5 | 26.3 | 27.7 | 28.1 | 21.2 | 25.2 | 26.3 | 26.5 | 27.9 | 28.0 | — |
| 120 | 19.0 | 22.2 | 23.3 | 23.5 | 25.2 | 26.6 | 27.1 | 20.0 | 24.1 | 25.3 | 25.4 | 26.8 | 27.1 | 27.3 |

ᵃ Vistac.
ᵇ Vistanex LM-MH.

ment the glass T-piece was used as a pressure regulator for the system, and the final pressure adjustments were always made with this regulator.

The capillary tubes used in these experiments were made from 6-mm bore glass tubing.  One end of a piece of tubing was tapered to a capillary, which was cut to give an orifice with diameter about 0.130 cm.  The end was ground with Carborundum to give a flat surface.  Only tubes with orifices having an inner circumference free from chips and fissures were retained.  The chosen capillary tube D was supported by an arm of a mechanical device E similar to that supporting the glass T-piece of the pressure regulator.  The capillary and manometer were connected by a flexible tube.

For the determination of surface tension of each polyisobutylene about 20 cm³ of material were poured into a tube and centrifuged until all air bubbles had been removed.  Initial heating prior to centrifuging was required for the more highly viscous materials.

The samples, together with the manometer, were supported in an oil bath at the required temperature controlled to $\pm 0.01\,°C$.

The apparatus was flushed out with dry air, and then the capillary tube was lowered so as to touch the surface of the polyisobutylene.  A bubble was formed and allowed to burst.  It was found from preliminary experiments with various rates of bubble formation that for polyisobutylenes of viscosities about 100 P or less this breaking pressure would be only a few millimeters of di-*n*-butyl phthalate above the true maximum value. The pressure was then lowered, usually by 0.2 mm of dibutyl phthalate, and another bubble was blown and allowed to burst.  This procedure was repeated until a pressure was reached at which the bubble would not break in 10 or 15 min but would burst when the pressure was then increased slightly.  With the more viscous polyisobutylenes pressure differences of 0.5 mm of dibutyl phthalate were used, and the pressure was held constant for 30 min or more.

The surface tensions of the polyisobutylenes listed in Table I were measured in the temperature range of 25–120°C, and the results of these experiments are given in Table II.  The results are the means of three determinations.  The difference between each of the three determinations and the respective mean was no greater than $\pm 0.3$ dyn/cm.

The measured surface tensions at 25°C of distilled water, benzene, glycerol (viscosity 7 P) and silicone oil (viscosity 1000 P) as compared to the accepted values (given in brackets) were, in dynes per centimeter, 71.6 (71.97),[12] 28.59 (28.24),[12] 63.37 (63.0),[12] and 20.5 (20.5),[13] respectively.

## Method B: Differential Capillary Rise

In this method two capillary tubes of different bore were used to avoid the difficulties, described by Findley,[14] encountered in the elementary technique of capillary rise.  The elementary theory, assuming a zero angle of contact, equates the upward pull of surface tension, $2\pi r\gamma$ (where $r$ is the internal radius) with the weight of the column of liquid (density $\rho$),

$\pi r^2 h \rho$. Thus $\gamma = r h \rho g / 2$. Hence for two tubes $r_1 h_1 = r_2 h_2$, and the difference in level is

$$h = h_1 - h_2 = 2\gamma(1/r_1 - 1/r_2)/\rho g \tag{5}$$

from which $\gamma$ can be found. This simple theory gives results accurate to about 1%.

The two capillary tubes for the differential capillary rise experiments had internal diameters of about 0.3–0.4 mm and 1.5–2 mm, respectively. They were mounted, as close together as possible, in a centrifuge tube through a plastic lid so that they could be viewed simultaneously in the telescope of a vernier cathetometer reading to 0.001 cm. The lid provided a sliding fit, so that the tubes could be raised or lowered. When the apparatus was at the required temperature the capillary tubes were immersed in the liquid polyisobutylene. The capillary rise in each tube was measured at intervals with the cathetometer until a steady reading was achieved. This was taken as the equilibrium height. At all times during the final reading the contact angle of the meniscus in the capillary was zero. The results are given in Table II. The drawback with this method is the time needed. For the higher viscosity samples, B8 and above, at least 4 wk were required for the meniscus to come to a constant height. Moreover, the higher molecular weight materials, which have to stand at 100 and 120°C for 4 wk, tend to degrade during the experiment; this was particularly true of B8 and B10, which become brown in color. The value for Vistanex LM-MH at 100°C by this method was the same as that at 120°C even after a period of 4 wk, and it seems that with material of such high viscosity the equilibrium height cannot be obtained in any reasonable period of time.

## RESULTS

The least-squares plots of surface tension measured by the two methods as a function of temperature, Figures 2 and 3, show a linear relationship for B1, B2, B3, and Vistac. The agreement between the respective surface tensions by each method is within 1 dyn/cm. Surface tension increases

### TABLE III
Temperature Coefficients[a] of Surface Tension of PIB

| Material | Max. bubble press. method | Capillary rise method |
|---|---|---|
| B1 | 0.0760 | 0.0726 |
| B2 | 0.0765 | 0.0638 |
| B3 | 0.0662 | 0.0627 |
| Vistac | 0.0684 | 0.0585 |
| B8 | 0.0550 | 0.0550 |
| B10 | 0.0550 | 0.0450 |
| Vistanex LM-MH | 0.0500 | — |

[a] In $- d\gamma/dt$ dyn/cm-°C.

slightly with increasing molecular weight, whereas the temperature coeffi-
cient of the surface tension decreases, as shown in Table III.

Assuming a linear relationship exists between surface tension and tem-
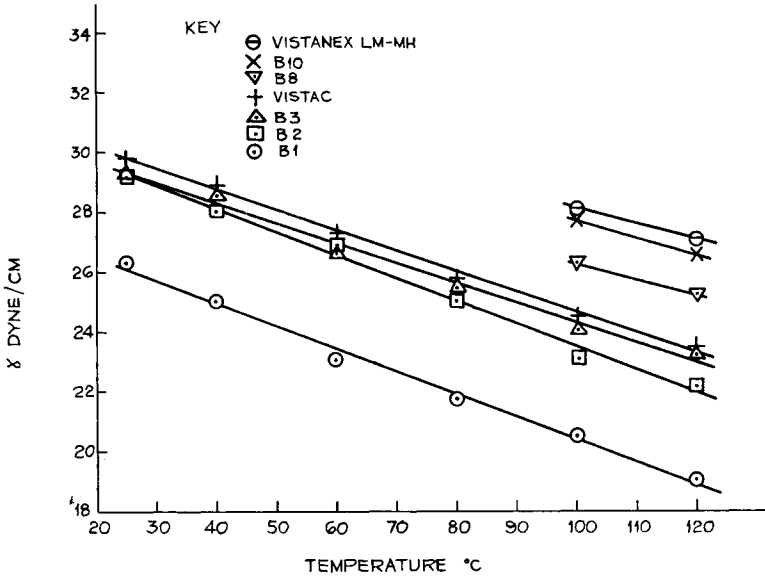perature for all grades of polyisobutylene, the values obtained for B8,
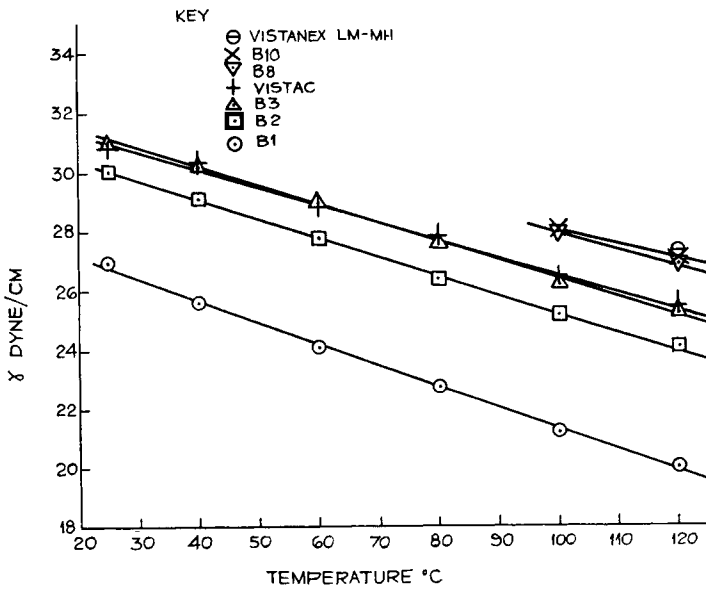


Figure 2.



Figure 3.

B10, and Vistanex LM-MH at 100 and 120°C were extrapolated to 25°C. These values are given in Table IV.

TABLE IV
Extrapolated Surface Tensions[a] of PIB at 25°C

| Max. bubble press. method | | | Capillary rise method | | |
|---|---|---|---|---|---|
| B8 | B10 | Vistanex LM-MH | B8 | B10 | Vistanex LM-MH |
| 30.4 | 31.8 | 31.9 | 32.0 | 31.4 | — |

[a] In dyn/cm.

## Theoretical Relationships

Theoretical relationships between the surface tension and other properties, such as the parachor, cohesive-energy density, and molecular weight, have been proposed by other authors. These will now be examined in terms of the results obtained for polyisobutylene.

## Parachor

Ryon-Joo Roe[15] suggested the parachor to be a useful means of estimating the surface tensions of low molecular weight polymers, and he calculated the surface tensions of a few polymers and compared them with measurements with a refined pendant-drop method. The calculated values were within ±3 dyn/cm of the measured values.

Table V compares the relationship between the surface tensions of the

TABLE V
Comparison of $\gamma$ Observed and $\gamma$ Calculated from the Parachor

| Material | $\gamma$, dyn/cm | | | |
|---|---|---|---|---|
| | 100°C | | 120°C | |
| | Exptl. | Calcd. | Exptl. | Calcd. |
| B1 | 20.5 | 19.8 | 19.0 | 18.7 |
| B2 | 23.1 | 26.9 | 22.2 | 25.5 |
| B3 | 24.1 | 28.1 | 23.3 | 26.6 |
| Vistac | 24.5 | 28.4 | 23.5 | 26.8 |
| B8 | 26.3 | 32.0 | 25.2 | 31.0 |
| B10 | 27.7 | 32.0 | 26.6 | 31.0 |
| Vistanex LM-MH | 28.1 | 32.0 | 27.1 | 31.0 |

polyisobutylenes used in this investigation, as calculated from the parachor, with the measured values. The value of the parachor $P$ taken was that of the repeat unit and was computed by use of the atomic parachor values recommended by Quayle:[16]  9.0 for C, 15.5 for H, and $-3.7$ for a branching point. The surface tension $\gamma$ (dyn/cm) was calculated from the parachor by means of Sugden's[17] equation:

$$\gamma = (P\rho/M)^4 \tag{6}$$

where $M$ is the molecular weight of the repeat unit and $\rho$ is the bulk density of the polyisobutylene.

Correlation between the calculated and measured values is only achieved with the low molecular weight sample B1; this is understandable when it is remembered that the parachor is only an empirical relationship derived for ideal liquids. It must be concluded that the parachor is useful only for calculating approximate surface tension values.

## Cohesive-Energy Density (CED)

Recently Schonhorn[18] derived an expression that relates the surface tension of nonpolar polymeric liquids to the cohesive-energy density by applying the rigid-sphere theory of liquids to polymers. He arrives at the expression

$$\gamma = 0.310m(V_L/nN)^{1/3} (\Delta E_v/V_L) \tag{7}$$

where $m$ is the ratio of the internal pressure to CED, $V_L$ the molar volume of the polymer, $N$ Avogadro's number, $n$ the number of carbon atoms in the chain, and $\Delta E_v$ the molar energy of vaporization. The values of $m$ and CED ($\Delta E_v/V_L$) for polyisobutylene in the literature is given as 1.2[19] and 63 cal/cm$^3$,[20,21] respectively. Substituting these figures into eq. (7) the surface tensions of B1, B3, and B10 at 25°C were 38.8, 36.9, and 36.4 dyn/cm, respectively. The values are higher than the observed and also decrease with increase of molecular weight, contrary to experimental results. For these calculations it was assumed that the CED and $m$ remain constant with change in molecular weight, but workers[19] in this field have suggested that the CED increases with molecular weight. At the present moment this cannot be proved, because accurate data are not available. The CED used in the calculations above was that of polyisobutylene of a molecular weight 20 times that of B10. Therefore the discrepancy in the calculated and measured surface tensions may be due simply to wrong values for the CED and $m$, which would explain why the calculated surface tension approaches the measured value as the molecular weight increases.

## Molecular Weight (Chain Length)

Because of the difficulties of direct experimental measurement of the surface tension of high molecular weight polymers Starkweather[22] investigated the possibility of deducing the surface properties of polyethylene by extrapolation from data relating to compounds of low molecular weight. The surface tension $\gamma$ at 150°C of normal alkanes containing 9–16 carbon atoms, and $C_{26}$ and $C_{60}$ compounds, obtained from the literature, were plotted against the reciprocal of the number of carbon atoms in the chain backbone. Extrapolating the linear plot to an infinitely long chain gave a value of 26 dyn/cm, and linear extrapolation of the temperature

coefficient $-d\gamma/dT$ also against the reciprocal of the chain length gave a value of 0.0585 dyn/cm-deg for the temperature coefficient. These agree quite closely with the measured values for high molecular weight linear polyethylene, which are 28 dyn/cm at 150°C and 0.06 dyn/cm-deg.[22] Similar treatment of the results obtained for the polyisobutylene did not yield a straight-line relationship. Figure 4 illustrates the shape of the curve found for polyisobutylenes.
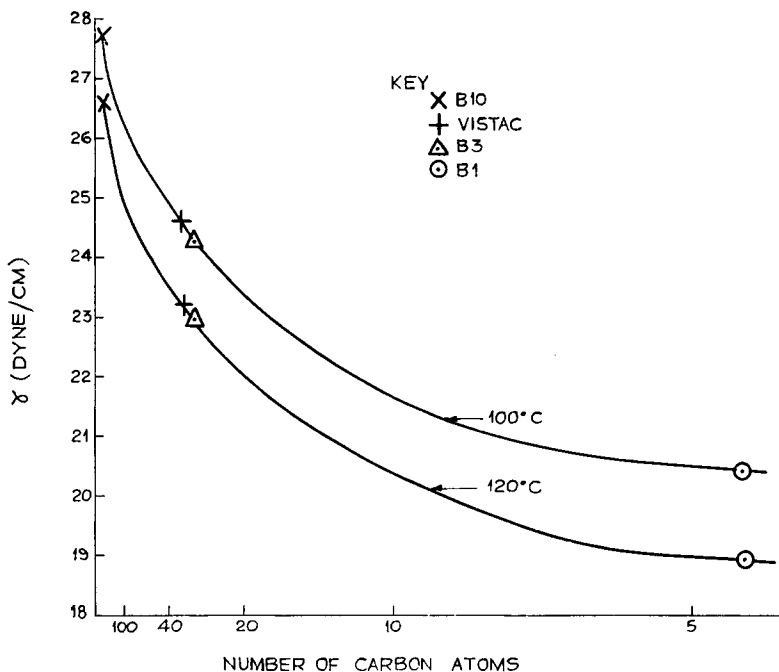


Figure 4.

Starkweather also discusses the "total surface energy," which is equal to

$$E = \gamma - Td\gamma/dt \qquad (8)$$

His plots show that this quantity is about 51 dyn/cm for a high molecular weight polyethylene and that it is much less dependent on chain length than on surface tension. He infers that the increase of surface tension with increasing chain length is associated largely with decreasing surface entropy. The total surface energies of B10, B3, and B1 at 120°C, computed from the surface tensions plotted in Figure 2 and measured by the maximum bubble pressure method, are 49.0, 46.7, and 46.7 dyn/cm, respectively, and at 25°C they are 47.2, 47.3, and 47.1 dyn/cm. These figures uphold Starkweather's statement that the total surface energies of the members of a homologous series of liquid polymers are almost constant and independent of molecular weight.

## CONCLUSION

No satisfactory theoretical expression exists from which the surface tension of liquid polymers can be calculated accurately.

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