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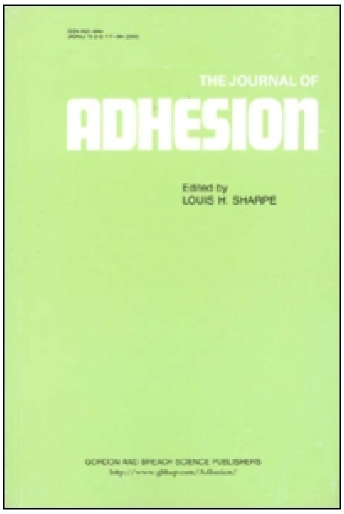

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Surface Tension for Some Aliphatic Polyesters

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Surface Tension for Some Aliphatic Polyesters

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Surface tensions of aliphatic polyesters having different lengths of the methylene sequence were measured by the sessile bubble method from 120 to 160°C. Surface tension decreased with an increase in the number (m) of carbon atoms in the methylene sequence. The linear relationship between γ and $1/(m+1)$ was derived from Sugden's equation which defined the parachor and the measured values fell on a single straight line. Surface tension of the ester group was also estimated as 56.6 dyn/cm.

Keywords: Surface tension; aliphatic polyesters; sessile bubble method; parachor; length of methylene sequence; ester group

1 INTRODUCTION

We [1] already reported that the molecular weight dependence of surface tension could be well explained by an equation derived from Sugden's equation [2], based on the additivity of the parachor and molar volume. In addition, we [3,4] also reported on the surface tension of some polymers whose molecular structure could be represented by $-\!\!\left[(CH_2)_m-X-\right]_n$, including poly(alkylene glycol)s, and poly (alkylene isophthalate)s. In this case, a linear relationship between surface tension and $1/m$ was derived from Sugden's equation. In general, aliphatic polyesters are also represented by the above molecular structure. In this paper, we study aliphatic polyesters having different lengths of the methylene sequence and report on the surface tension of these polymers.

Recently, aliphatic polyesters have been high-lighted as biodegradable polymers. The surface chemical properties for these polymers, such as surface tension, wetting and so on, are very important, since the degradation at first begins at the surface of polymer. The wetting property in environmental media significantly affects the polymer's biodegradability. Therefore, surface tension data will be a useful tool to investigate the biodegradability of these polymers.

2 EXPERIMENTAL

2.1 Materials

Aliphatic polyesters were prepared by the condensation polymerization of alkane diols with alkane dimethylesters, both alkanes having the same number of carbon atoms. The stoichiometric amount of commercially-available alkane diol and alkane dimethylester were mixed with di-tert-butylhydroquinone and PbO. The mixture was heated at 172°C for 2 hours and then for 4 hours at a pressure of 0.05 mm Hg. The synthesized polymers were purified by precipitation of a chloroform solution into methanol three times. The molecular structure of the synthesized polymers were represented as shown in Scheme 1.

$$-\!\!\!\left[(CH_2)_mOOC(CH_2)_mCOO\right]\!\!\!-_n$$

SCHEME 1

As the direction of head to tail of the ester group could be neglected in the analysis shown later, the structure shown in Scheme 1 could be represented by $-\!\!\!\left[(CH_2)_m\!-\!X\right]\!\!\!-_n$.

2.2 Surface Tension Measurement

Surface tension (γ) was measured from 120 to 160°C by the sessile bubble method. The maximum radius (r) of the bubble and the height (h) from the plane including the maximum circle of the bubble to the top of the meniscus were measured. γ was calculated from these two values and the density using Porter's equation. We have already reported this method in detail elsewhere [4].

2.3 Dilatometry

Temperature dependence of the density (specific volume) and melting temperature for sample polymers were determined *via* dilatometry. Standard densities of polymers which were used to calculate densities at certain temperatures from the dilatometric data were measured with a density gradient tube at 25°C.

3 RESULTS

3.1 Temperature Dependence of Surface Tension

In general, surface tension (γ) linearly decreased with an increase in temperature (T). The relationship of γ to T could be described as follows:

$$\gamma = E^s - S^s T \qquad (1).$$

where E^s is surface energy and S^s is surface entropy. Figure 1 shows this relationship for aliphatic polyesters and it is clear that good linear

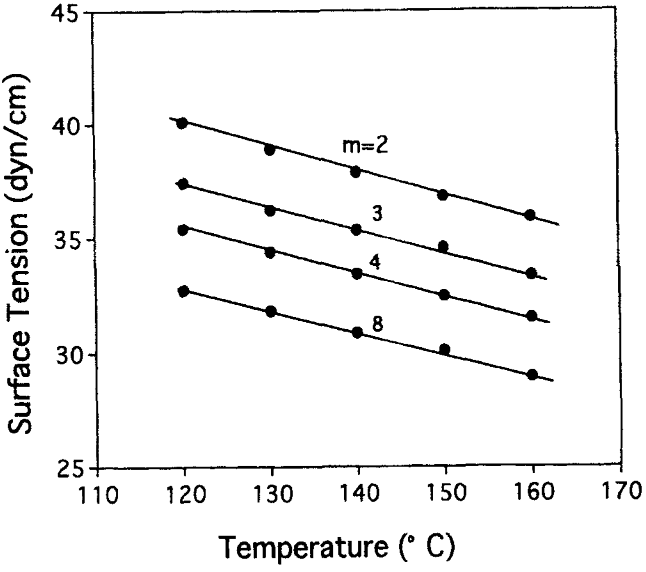

FIGURE 1 Temperature dependence of surface tension for aliphatic polyesters.

relationships were obtained. We could obtain E^s *via* the extrapolated value of the straight line to $T=0$ and S^s *via* this temperature dependence of γ. These values are listed in Table I.

3.2 Relationship of Surface Tension to the Length of the Methylene Sequence (*m*)

Figure 2 shows the relationship of γ to the number (m) of methylene groups in a repeating unit of the aliphatic polyesters at 150°C. γ decreased with an increase in m. This is due to the reduction of the volume fraction and, therefore, of the contribution of the ester group, which had a larger surface tension than methylene group, to γ.

3.3 Relationship of Specific Volume to the Length of the Methylene Sequence (*m*)

Density of aliphatic polyesters obtained *via* dilatometry are listed in Table I. Specific volume (v) is described as follows:

$$v=\frac{V}{M} \tag{2}$$

where V is molar volume and M is molecular weight.

For $-\!\![(CH_2)_m-X-]\!\!-_n$ type polymer, the following equation can be derived, based on the additivity of molar volume (V) and molecular

TABLE I Aliphatic polyesters used and their surface tension, density and melting temperature

Aliphatic polyesters	*Abbr.*	*m*	γ^1	E^{S2}	S^{S3}	ρ^4	*m.p.*[5]
Poly(ethylene succinate)	PES	2	36.8	80.2	0.102	1.193	110
Poly(*n*-propylene glutarate)	PPG	3	34.6	75.4	0.097	1.101	55
Poly(butylene adipate)	PBA	4	32.5	72.6	0.094	1.037	65
Poly(octylene sebacate)	POS	8	30.1	69.7	0.094	0.933	75
Polyethylene	PE	∞	27.3	53.4	0.062	0.780	127

[1] Surface tension(dyn/cm) at 150°C,
[2] Surface energy(erg/cm^2),
[3] Surface entropy(erg/cm°C),
[4] Density(g/cm^3) at 150°C,
[5] Melting temperature.

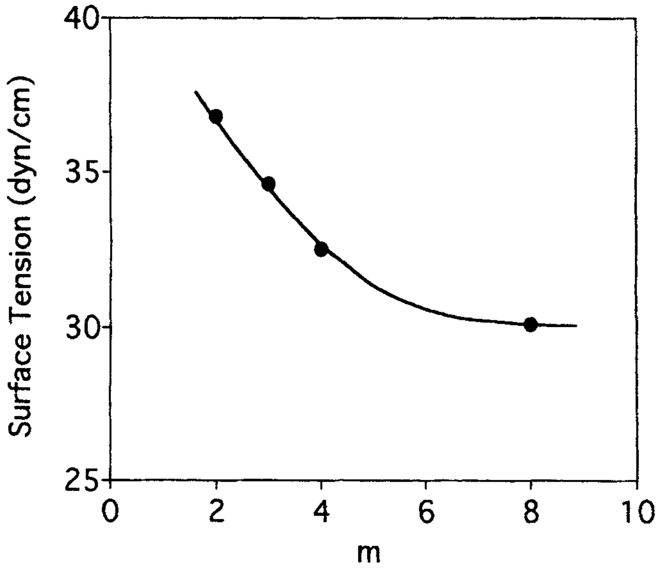

FIGURE 2 Surface tension for aliphatic polyesters at 150°C plotted against the number (*m*) of carbon atoms in the methylene sequence.

weight (M).

$$v = \frac{n(mV_{\mathrm{CH_2}} + V_X)}{n(mM_{\mathrm{CH_2}} + M_X)} \tag{3}$$

where $V_{\mathrm{CH_2}}$ and V_X are the molar volume of $\mathrm{CH_2}$ and X, respectively, and $M_{\mathrm{CH_2}}$ and M_X are the molecular weight of $\mathrm{CH_2}$ and X, respectively. From this equation, the following equation can be derived, using $v_{\mathrm{CH_2}} = V_{\mathrm{CH_2}}/M_{\mathrm{CH_2}}$, $v_X = V_X/M_X$ and $k' = M_X/M_{\mathrm{CH_2}}$:

$$v = v_{\mathrm{CH_2}} + \frac{k'}{m + k'}(v_X - v_{\mathrm{CH_2}}) \tag{4}$$

This equation tells us that a linear relationship between v and $k'/(m + k')$ exists. In Figure 3, v is plotted against $k'/(m + k)'$ for aliphatic polyesters. All data fall on a single straight line and the extrapolated value of the line to $k'/(m + k') = 0$ coincides with that of polyethylene. From this

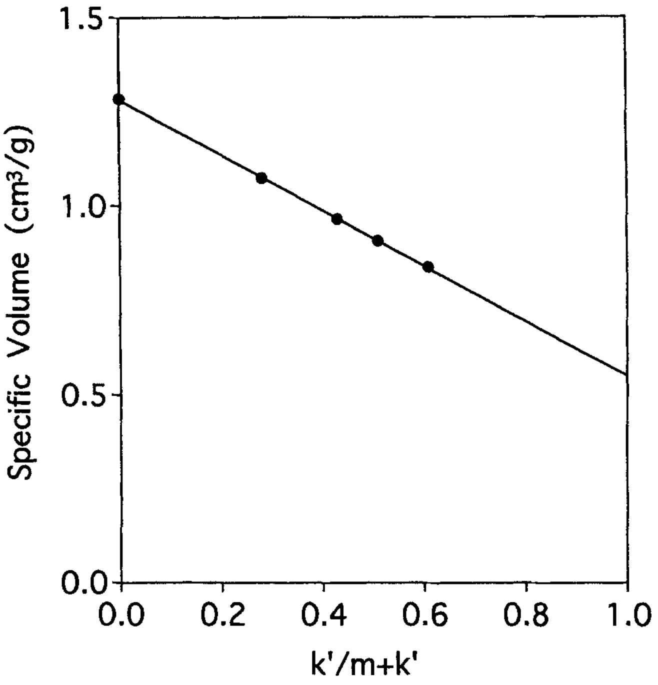

FIGURE 3 Specific volume *vs* $k'/(m+k')$ for aliphatic polyesters.

value, we could obtain $V_{\mathrm{CH_2}}$ as 17.9 cm^3. In addition, the molar volume of the ester group (V_X) could be obtained from the slope of this line as 24.4 cm^3 at 150°C.

3.4 Macleord's Exponent and Thermal Expansion Coefficient

Sugden [2] defined the parachor (P) by following equation:

$$\gamma=\left\{\frac{(\rho_L-\rho_G)P}{M}\right\}^4=\left(\frac{\rho P}{M}\right)^4=\left(\frac{P}{V}\right)^4 \tag{5}$$

where ρ_L and ρ_G are densities of the polymer in the liquid and gas states, respectively, M is molecular weight and V is molar volume. As the exponent 4 varied with molecular weight of the polymer, it was replaced by β and was called Macleord's exponent.

The logarithm of this equation is as follows:

$$\ln\gamma = \beta \ln\rho + A \tag{6}$$

where A is a constant value independent of temperature. The relationships between $\ln\gamma$ and $-\ln\rho$ for various m have shown in Figure 4. Linear relationships are observed. The values of β were obtained from the slope of the straight lines and are listed in Table II. β increased with an increase in the number of methylene group in the repeating units of the aliphatic polyesters. The following equation was obtained

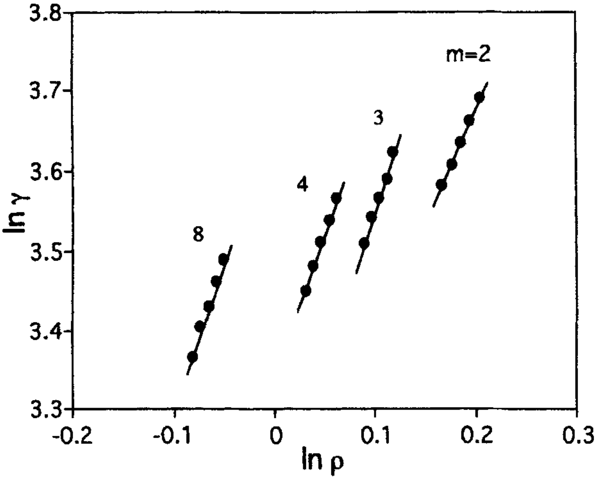

FIGURE 4 $\ln\gamma$ *vs* $\ln\rho$ for aliphatic polyesters.

TABLE II Thermal expansion coefficient (α), and Macleord's exponent (β) for aliphatic polyesters

Aliphatic polyesters	$\alpha \times 10^{-4}$	β	$\alpha\beta \times 10^{-3}$	$d\ln\gamma/dT \times 10^{-3}$
PES	7.81	2.9	2.3	2.7
PPG	6.68	3.6	2.4	2.7
PBA	7.32	3.7	2.7	2.8
POS	8.10	3.8	3.1	3.1
PE	8.0	3.0	2.4	2.4

by differentiation of Equation (6) with respect to temperature

$$\frac{d\ln\gamma}{dT} = \beta\frac{d\ln\rho}{dT} = \beta\alpha \tag{7}$$

where α is the thermal expansion coefficient of the polymers. This equation tells us that the product of Macleord's exponent and thermal expansion coefficient is $d\ln\gamma/dT$. In Table II, the measured values of α, β, $\alpha\beta$ and $d\ln\gamma/dT$ for aliphatic polyesters are listed. It can be seen that the values of $\alpha\beta$ approximately coincide with those of $d\ln\gamma/dT$.

4 DISCUSSION

4.1 Relationship of Surface Tension to Length of Methylene Sequence

For polymers whose molecular structure could be represented by $-[(CH_2)_m-X]_n$, surface tension could be described based on the additivity of the parachor and molar volume, using Sugden's equations as follows:

$$\gamma = \left\{\frac{n(mP_{CH_2} + P_X)}{n(mV_{CH_2} + V_X)}\right\}^{\beta} \tag{8}$$

where P_{CH_2} and P_X are the parachors of CH_2 and X, respectively, and V_{CH_2} and V_X are their respective molar volumes. This equation can be rewritten as follows:

$$\gamma = \left(\frac{P_{CH_2}}{V_{CH_2}}\right)^{\beta}\left(1 + \frac{1}{m+1}\frac{P_X - P_{CH_2}}{P_{CH_2}}\right)^{\beta}\left(1 + \frac{1}{m+1}\frac{V_X - V_{CH_2}}{V_{CH_2}}\right)^{-\beta} \tag{9}$$

As $(P_X - P_{CH_2})/P_{CH_2}$ and $(V_X - V_{CH_2})/V_{CH_2}$ are very much smaller than 1, Equation (9) can be expanded and, as higher power terms can be neglected, we can obtain following equation.

$$\gamma = \gamma_{\mathrm{CH}_2}\left[1 + \frac{\beta k}{m+1}\left\{\left(\frac{\gamma_X}{\gamma_{\mathrm{CH}_2}}\right)^{1/\beta} - 1\right\}\right]$$

$$= \gamma_{\mathrm{CH}_2} + \frac{k\gamma_{\mathrm{CH}_2}}{m+1}C \tag{10}$$

$$C = \beta\left\{\left(\frac{\gamma_X}{\gamma_{\mathrm{CH}_2}}\right)^{1/\beta} - 1\right\} \tag{11}$$

where γ_{CH_2} is $(P_{\mathrm{CH}_2}/V_{\mathrm{CH}_2})^{\beta}$, γ_X is $(P_X/V_X)^{\beta}$ and k is the ratio of V_X to V_{CH_2}. As shown Table II, β varies from 3 to 4 with an increase in the length of the methylene sequence (m) for the aliphatic polyesters studied. However, the coefficient C is approximately constant because the contributions of the coefficient β and exponent $1/\beta$ cancelled each other. For example, in the case of $\gamma_{\mathrm{CH}_2} = 27.3$ dyn/cm ($= \gamma$ of polyethylene at 150°C) and $\gamma_X = 54.6$, $\gamma_X/\gamma_{\mathrm{CH}_2} = 2$; if $\beta = 3$, C is 0.780 and if $\beta = 4, C$ is 0.757. The difference between these two values is only 3%. Therefore, we can look upon C as a constant coefficient. In addition, as k and γ_{CH_2} are also constant, Equation (10) tells us that a linear relationship exists between γ and $1/(m+1)$. The γ_s for the aliphatic polyesters are plotted against $1/(m+1)$ in Figure 5. A good linear relationship between γ and $1/(m+1)$ is observed and the extrapolated value of γ to $1/(m+1) = 0$ coincides with that of polyethylene. In addition, we could obtain γ_X (surface tension of the ester group) from the value of the slope of the line as 55.6 dyn/cm, using $\gamma_{\mathrm{CH}_2} = 27.3$ dyn/cm, $\beta = 4$ and $k(= V_X/V_{\mathrm{CH}_2}) = 1.363$, where we used 24.4 and 17.9 cm^3 for V_X and V_{CH_2}, respectively, as shown above.

On the other hand, we could obtain the surface tension of the ester group from Sugden's Equation (5). As the parachors of H, C, O and the double bond are given as 17.1, 4.8, 20, and 23.3, respectively, γ_{COO} could be calculated as 60.6 dyn/cm.

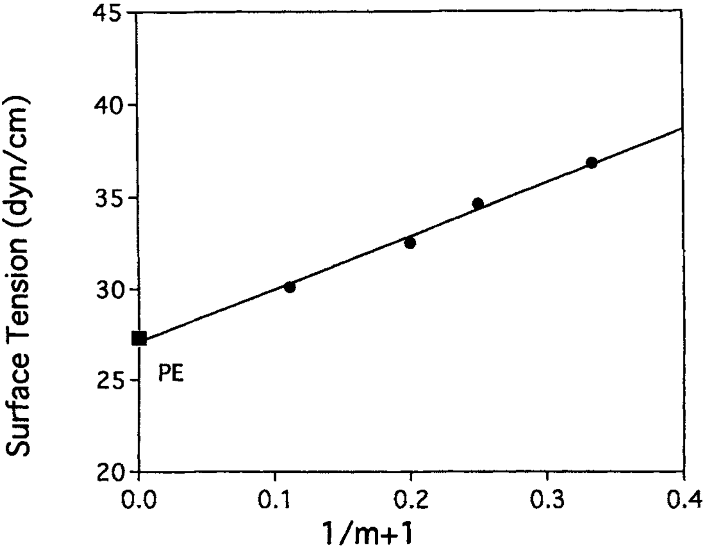

FIGURE 5 Surface tension for aliphatic polyesters at 150°C plotted against $1/(m+1)$.

5 CONCLUSION

The surface tensions of aliphatic polyesters having different lengths of the methylene sequence were measured by the sessile bubble method from 120 to 160°C. Surface tension decreased with an increase in the number (m) of carbon atoms in the methylene sequence. The linear relationship between γ and $1/(m+1)$ was derived from Sugden's equation which defined the parachor and the measured values fell on a single straight line. The surface tension of the ester group was also estimated from the slope of the line as 56.6 dyn/cm. This value is smaller than that calculated from Sugden's equation.

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