

## Copolymer Characterization by Surface Tension

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### Synopsis

The use of surface tension measurements is proposed as a simple method for the determination of copolymerization ratios. The procedure depends on the parachor of the copolymer in the liquid state ( $\Pi$ ), which is defined by  $\Pi = \Pi_s + \Pi_0(w_p/w_s)(M_s/M_0)$  for solutions and  $\Pi = [DP]\Pi_0$  for liquid or molten polymers, where  $\Pi_s$  is the parachor of the solvent of molecular weight  $M_s$ ;  $w_p$  and  $w_s$  are the weights of the polymer and solvent in solution; while  $\Pi_0$  and  $M_0$  are the parachor and molecular weight of the repeating unit of the copolymer, respectively. The validity of this relationship is demonstrated by analysis of the surface tension properties of liquid silicone polymers, polystyrene-Decalin solutions, and molten polymers as well as by the calculation of the composition of some characterized tetrahydrofuran-propylene oxide copolymers. The application of surface tension measurement is also suggested as a means of estimating the degree of chain branching in a polymer.

The establishment of the ratio of the constituent units in a copolymer is a common problem often encountered in macromolecular research.<sup>1,2</sup> While the complete armamentarium of modern analytical chemistry can be brought to bear to resolve such questions, the procedures required may be cumbersome and tedious or they may involve the use of costly instrumentation not always readily accessible.<sup>3</sup>

The simple physical measurement of the surface tension<sup>4,5</sup> of a solution of the copolymer or the molten material is now proposed as a rapid, straightforward and inexpensive technique for securing this information without destruction of the sample. Thus, for example, rather precise ( $\pm 0.25\%$ ) determinations of surface tensions can be made using the ubiquitous analytical laboratory balance. The overall procedure ultimately depends on the evaluation of the parachor  $\Pi$  of the copolymer. The parachor was originally introduced as a physical constant by Sugden<sup>6</sup> nearly half a century ago and defined by eq. (1), in which  $\gamma$  is the surface tension of a substance of molecular weight  $M$  having a density of  $D_l$  and  $d_v$  for the liquid and vapor, respectively:

$$\Pi = \frac{M\gamma^{1/4}}{D_l - d_v} \quad (1)$$

If the density of the vapor  $d_v$  is neglected in comparison with that of the liquid, then eq. (1) can be simplified so that

$$\Pi = \frac{M\gamma^{1/4}}{D_l}$$

or

$$\Pi = V_m\gamma^{1/4}$$

where  $V_m$  is the molecular volume.

Furthermore, if the temperature is such that the surface tension is unity, then  $\Pi$  will be equal to  $V_m$ . This implies that the parachor may be regarded as the molar volume of a substance when its surface tension is unity.<sup>7-10</sup>

From an examination of isomeric substances, Sugden<sup>7</sup> was able to show that the parachor is an additive and also a constitutive property and to determine its value for a number of elements and various organic functional groups.<sup>8,9</sup>

Thus, in considering the development of a method of determining the composition of copolymers using the surface tension of liquid polymers or of polymer solutions, the parachor can be redefined as in eq. (2), where  $\Pi$  is the parachor of a mixture containing  $i$  components of mole fraction  $x_i$  and parachor  $\Pi_i$ :

$$\Pi = \sum_{i=1}^{\infty} x_i\Pi_i \quad (2)$$

Then, if the dissolved component is a copolymer consisting of monomer units  $A$  and  $B$  and the solvent is  $S$ , eq. (2) can be transformed into

$$\Pi = x_s\Pi_s + \sum_{i=1}^{\infty} x_i\Pi_i \quad (3)$$

in which  $\Pi_i$  is the parachor of the copolymer of molecular weight  $M_i$  and mole fraction  $x_i$  because the parachor of simple solutes obeys a straight-line mixture law in nonpolar solvents.<sup>11</sup> Since the summation  $\sum_{i=1}^{\infty} x_i\Pi_i$  can be replaced by  $x_{av}\Pi_{av}$ , if  $\Pi_{av}$  is the parachor based on the number-average molecular weight and  $x_{av}$  is the average mole fraction based on the same molecular weight average  $M_{av}$ , then

$$\Pi = x_s\Pi_s + x_{av}\Pi_{av} \quad (4)$$

Expressing eq. (4) in terms of weights instead of mole fractions affords eq. (5),

$$\Pi = \frac{(w_s/M_s) \Pi_s}{w_s/M_s + w_p/M_{av}} + \frac{(w_p/M_{av}) \Pi_{av}}{w_s/M_s + w_p/M_{av}} \quad (5)$$

where  $w_s$  and  $w_p$  are the total weights of solvent and copolymer, respectively, and  $M_s$  is the molecular weight of the solvent. If the molecular weight of

the copolymer is large and its concentration in solution is small, then the ratio  $w_s/M_s$  is very much greater than the ratio  $w_p/M_{av}$  and eq. (5) can be simplified to

$$\Pi = \Pi_s + (w_p/M_{av})(M_s/w_s) \Pi_{av}. \quad (6)$$

In addition,  $\Pi_{av}$  can be approximately related to the degree of polymerization ( $DP$ ) and composition of the copolymer by eq. (7) if the contribution of the polymer's end groups can be considered to be negligible. Thus

$$\Pi_{av} = DP \text{ [parachor of the polymer repeating unit]} \quad (7)$$

or

$$\Pi_{av} = DP [y_A \Pi_A + y_B \Pi_B] \quad (8)$$

where  $\Pi_A$  and  $\Pi_B$  are the parachors of the  $A$  and  $B$  constituent units and  $y_A$  and  $y_B$  are their mole fractions.

Moreover, the number-average molecular weight of the polymer  $M_{av}$  can be obtained from the product of the degree of polymerization and the molecular weight of the repeating unit, so that

$$M_{av} = DP \text{ [molecular weight of polymer repeating unit]} \quad (9)$$

or

$$M_{av} = DP [y_A M_A + y_B M_B] \quad (10)$$

where  $M_A$  and  $M_B$  are the molecular weights of the  $A$  and  $B$  constituent units, respectively. Recalling that the molecular weight of the constituent copolymer unit is

$$M_0 = y_A M_A + y_B M_B \quad (11)$$

and that the parachor of the same moiety is

$$\Pi_0 = y_A \Pi_A + y_B \Pi_B \quad (12)$$

allows eqs. (4), (8), (10), (11), and (12) to be combined to eliminate  $\Pi_{av}$  and  $M_{av}$  and thus afford

$$\Pi = \Pi_s + \Pi_0 (w_p/w_s)(M_s/M_0). \quad (13)$$

If  $M_{\text{solution}}$  is designated as the average molecular weight of the polymer solution, then

$$M_{\text{solution}} = x_s M_s + x_p M_p$$

or

$$M_{\text{solution}} = \frac{(w_s/M_s)M_s}{w_s/M_s + w_p/M_p} + \frac{(w_p/M_p)M_p}{w_s/M_s + w_p/M_p} \quad (14)$$

where  $x_p$  is the mole fraction of polymer of molecular weight  $M_p$  which is dissolved. However, it is clear from eq. (14) that  $M_{\text{solution}}$  will not change

appreciably with changes in  $M_p$  if the polymers used are of high molecular weight because  $M_{\text{solution}}$  can be written, by the same argument as before, as

$$M_{\text{solution}} = M_s + (w_p/w_s)M_s = M_s(1 + w_p/w_s)$$

This shows that  $M_{\text{solution}}$  is independent of  $M_p$  and depends only on  $w_p$  and  $w_s$ , provided  $M_p$  is large. Hence the surface tension of dilute solutions is also independent of the molecular weight of the dissolved polymer so long as  $M_p$  is large compared to  $M_s$ , as expressed by eq. (15):

$$\gamma^{1/4} = \Pi(D_t - d_v)/M = (D_t - d_v) [\Pi_s + (w_p/w_s)\Pi_0]/[M_s(1 + w_p/w_s)] \quad (15)$$

This conclusion is supported by the identity of the surface tensions<sup>12</sup> of dilute Decalin solutions (2%) of polystyrene of widely differing molecular weights (28,000 and 58,000), as shown in Table I.

TABLE I  
Surface Tension of Polystyrene in Decalin Solution (2%) at 50°C

Molecular weight	Surface tension, dynes/cm
28,000	28.3
58,000	28.3

For liquid or molten polymers, the parachor  $\Pi$  can be written as in eq. (2) so that

$$\Pi = \sum_{i=1}^{\infty} x_i \Pi_i$$

or

$$\Pi = (x_1 \Pi_1 + x_2 \Pi_2 + \dots \infty)$$

If the molecular weight of the polymer is high, then  $\Pi_i$  can be replaced by

$$\Pi_i = [DP]_i \Pi_0 \quad (16)$$

where  $[DP]_i$  is its degree of polymerization and  $\Pi_0$  is the parachor of the repeating unit; hence

$$\Pi = \sum_{i=1}^{\infty} x_i [DP]_i \Pi_0 = \Pi_0 \sum_{i=1}^{\infty} x_i [DP]_i \quad (17)$$

By definition,

$$\sum_{i=1}^{\infty} x_i [DP]_i = [DP] = \text{no.-average degree of polymerization}$$

so that

$$\Pi = [DP] \Pi_0 \quad (18)$$

Again

$$\Pi = M\gamma^{1/4}/(D_l - d_v) = [DP]M_0\gamma^{1/4}/(D_l - d_v)$$

so that

$$\gamma^{1/4}/(D_l - d_v) = \Pi/M_0[DP] = \Pi_0[DP]/M_0[DP] = \Pi_0/M_0 \quad (19)$$

Since by definition  $\Pi_0/M_0$  is a constant, and a characteristic of the monomer unit, eq. (19) therefore indicates that the specific parachor  $\gamma^{1/4}/(D_l - d_v)$  for a polymer in the liquid state is independent of the degree

TABLE II  
Surface Tension of Silicone Polymers of Differing Molecular Weights<sup>13,19</sup>

Viscosity at 25°C, centistokes	Densities, g/ml	Surface tension, dynes/cm	$\gamma^{1/4}/(D_l - d_v)$
65	0.7631	15.7	2.6084
1.0	0.8199	16.8	2.5953
1.5	0.8538	17.5	2.3955
3	0.8939	18.5	2.3811
5	0.9177	19.0	2.3733
10	0.9392	19.4	2.2344
35	0.9560	19.9	2.2083
56	0.9643	20.2	2.1927
70	0.9683	20.3	2.1920
10 <sup>2</sup>	0.970	20.5	2.1936
10 <sup>3</sup>	0.973	21.01	2.2003
10 <sup>4</sup>	0.974	21.25	2.2047
10 <sup>6</sup>	0.977	21.8	2.2117

TABLE III  
Specific Parachor of Molten Polymers

Polymer	Surface tension, <sup>a</sup> 150°C, dynes/cm	Densities ( $D_l$ ), 150°C, g/ml	$\gamma^{1/4}(D_l - d_v)$	$\Pi_0/M_0$
Poly(ethylene oxide)	33	1.0293	2.3284	2.2733
Linear polyethylene	28.1	0.7788	2.9563	2.8571
Polyisobutene	25.1	0.8464	2.6990	2.8572
Polypropylene	22.1	0.7790	2.7833	2.8571
Polydimethylsiloxane	13.6	0.8650	2.2260	2.1805

<sup>a</sup> From Roe.<sup>18</sup>

of polymerization, provided molecular weight and hence  $DP$  is high. Table II illustrates this with a series of silicone polymers of different molecular weights expressed as viscosity.<sup>13</sup> This shows that the specific parachor approaches a constant value as the molecular weight increases, and with sufficiently large molecules it is practically constant.

TABLE IV  
 Characterization of Tetrahydrofuran-Propylene  
 Oxide Copolymers by Surface Tension

Surface tension, 40°C, dynes/cm	Density, 40°C, g/ml	Molecular weight	Parachor	Mole fraction THF	
				Found	Calcd
38.43	1.0043	2300	176.0	0.9	0.893
37.38	1.0061	1000	171.1	0.80	0.780
37.38	1.0068	1500	171.5	0.80	0.792
35.35	1.0879	1700	151.2	0.65	0.159 <sup>a</sup>

<sup>a</sup> The poor agreement observed is attributed to the density value of 1.0879 g/ml for the copolymer of MW 1700, which seems to be in error when contrasted with the other densities reported. The calculated values for the parachor for the THF and PO homopolymers are also inaccurate in the translated version of the original publication.<sup>14</sup>

Table III shows the experimental and theoretical values of the specific parachors,  $\Pi_0/M_0$ , for molten poly(ethylene oxide), linear polyethylene, polyisobutene, polypropylene, and polydimethylsiloxane at 150°C, and shows a good agreement with the theoretical values.

These arguments can be extended to more complex situations which can be exemplified by a consideration of the surface tensions<sup>14</sup> of copolymers of tetrahydrofuran (THF) and propylene oxide (PO) which are collated in Table IV.

Conversion of these experimentally determined surface tensions to the corresponding parachors provides the means of determining the copolymerization of the THF/PO copolymer ratio since from eq. (12) the parachor of the copolymer is

$$\Pi_{\text{THF:PO}} = y_{\text{THF}}\Pi_{\text{THF}} + y_{\text{PO}}\Pi_{\text{PO}}$$

Using the experimentally derived values for  $\Pi_{\text{THF:PO}}$ , the calculated values for  $\Pi_{\text{THF}}$  (180) and  $\Pi_{\text{PO}}$  (140) and the relationship

$$y_{\text{THF}} + y_{\text{PO}} = 1$$

affords the copolymerization ratios collected in Table IV.

It is important to appreciate that this analysis would not be applicable to copolymers of isomeric monomers since the parachor values for isomers are almost identical.<sup>15,16</sup> The excellent concordance between the calculated composition and the reported analysis suggests that the characterization of polymers by surface tension measurements deserves wider attention than it has so far received.<sup>17,18</sup>

In this connection it is appropriate to point out that surface tension measurements may also be used to estimate the degree of chain branching in a polymer since, although straight chains have the highest parachor in most cases, there is a slight but definite decrease in the parachor due to branching.<sup>15,16</sup> The decrement varies somewhat, e.g., for hydrocarbons, according to the position and length of the branch. Nonetheless, within the limits of experimental error a mean value of  $\Delta\Pi$  of  $-3.0$  would appear

to be applicable to all branched groups of the  $-\text{CHR}_2$  type, while double this decrement should be invoked for  $-\text{CR}_3$  linkages and doubly branched moieties of the type  $-\text{CHR}_2-\text{CHR}_2$ . Thus, the difference between the specific parachors of linear (2.956) and branched (2.913) polyethylene is 1.45% of the former.

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