A test of the applicability of small-molecule group additivity parameters in the estimation of fusion entropies of macromolecules

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Abstract

The applicability of using a group method for estimating the total phase change entropy of small molecules is tested on a series of macromolecules. The total phase change entropies of 64 polymers are calculated and compared to experimental data. The correlation of the experimental and calculated fusion entropies and enthalpies for 63 of these polymers resulted in standard errors of 12.5 J mol^{-1} K^{-1} and 5.15 kJ mol^{-1}, respectively. These errors are similar in magnitude to those observed with small molecules. The errors associated with these estimations suggest that estimations using the group values generated from small molecules are applicable in estimating similar properties in more complex systems.

1. Introduction

The fusion enthalpy is a thermodynamic property that plays an important role in a variety of thermodynamic studies. Aqueous solubility data are becoming increasingly important as a result of environmental concerns and thermodynamic models used to predict the solubility of crystalline non-electrolytes require information regarding a solute's melting point and molar enthalpy of fusion [1]. Studies of new energy storage materials [2] can benefit from reliable fusion entropy and enthalpy estimates, as can

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estimations of sublimation enthalpies [3] and more fundamental studies of side-chain conformational flexibility of proteins [4].

Recently we reported a simple group additivity method that could be used to estimate the total phase change entropies (ΔS_{tpce}) associated with the solid state in going from 0 K to the liquid at the melting point [5]. For the many solids that do not show any discernible phase changes in the solid state, the total phase change entropy is numerically equivalent to the fusion entropy. Other compounds which are solids at room temperature exhibit phase transitions close to the melting point. For some applications at 298 K or near room temperature, such as in estimating solubility [1] and sublimation enthalpies [3], the use of the total phase change entropy to estimate the fusion enthalpy of these types of compounds is reasonably successful and does not usually result in significant errors.

2. Results and discussion

The total phase change entropy of a molecule can be estimated as the sum of three components: the contribution of the hydrocarbon portion of the molecule, the contribution of the carbon(s) bearing the functional group(s), and the contribution of the functional group(s) as summarized by the three terms of Eq. (1). The subscript i identifies the hydrocarbon components and the carbons bearing the functional group, and the subscript k identifies the functional groups. The terms n, C and G refer to the number of each group present, its group coefficient and group value, respectively. Values for a number of these terms reported previously [5] are reproduced in Table 1. The terms in parentheses in Table 1 following the group values and coefficients are included for identification purposes. Eq. (2) evaluates the total number of functional groups (K) present and identifies the appropriate C_K value to use. The contribution of a functional group to the total fusion or total phase change entropy depends on the nature of the functional group, G_K, and the group coefficient, C_K, which is determined by the total number of functional groups present in the molecule. A complete list of group values and coefficients is available in Ref. [5].

$$\Delta_{tpce}S_m = \sum_i n_i G_i + \sum_i n_i C_i G_i + \sum_k n_k C_K G_k \qquad (1)$$

where

$$K = \sum_k n_k \qquad (2)$$

The empirical observation that group values used in evaluating the contribution of certain functional groups were not solely additive but could depend on the total number of functional groups in the molecule complicates the estimation of $\Delta_{tpce}S_m$. It becomes unclear how to evaluate the contribution of a functional group to the total phase change entropy in cases where a C_K value is unavailable. In effect, this brings into question the applicability of using group values derived from total phase change and

Table 1
Group values ($J\,mol^{-1}\,K^{-1}$) used in the estimation of fusion entropies of polymers

Hydrocarbon group	Group value G_i	Group coeff. C_i
Acyclic hydrocarbon groups		
Primary sp3 carbon atom	18.33 (A_1)	1
Secondary sp3 carbon atom	9.41 (B_1)	1
Tertiary sp3 carbon atom	-16.2 (C_1)	0.69 (C_2)
Quaternary sp3 carbon atom	-38.7 (D_1)	0.67 (D_2)
Acyclic olefinic		
Secondary sp2 carbon	14.56 (E_1)	1
Tertiary sp2 carbon	4.85 (F_1)	3.23 (F_2)
Quaternary sp2 carbon	-11.38 (G_1)	1
Aromatic groups		
Tertiary sp2 carbon	6.44 (H_1)	1
Quaternary sp2 carbon adjacent to an sp3 carbon	-10.33 (I_1)	1
Peripheral quaternary sp2 carbon adj. to sp2 carbon	-4.27 (J_1)	1

Functional group	Group value G_k	Group coefficient [a] C_k			
		C_1	C_2	C_3	C_4
Acyclic groups					
Chlorine	8.37 (O_1)	1	2.0 (O_2)	2.0 (O_3)	1.93 (O_4)
Fluorine on sp3 carbon	14.73 (P_1	1	1.0	1.0	1.0
Hydroxyl group on alcohols	1.13 (Q_1)	1	12.6 (Q_2)	18.9 (Q_3)	26.4 (Q_4)
Nitrile	9.62 (R_1)	1	1.4 (R_2)	[1.4] (R_3)	[1.4] (R_4)
Ester	3.68 (S_1)	1	1.0	1.0	1.0
Ether	1.09 (T_1)	1	[1.0]	1.0	[1.0]
Amides secondary	-0.40 (U_1)	1	1.0	[1.0]	[1.0]
Sulfide	7.20 (V_1)	1	[1.0]	[1.0]	0.38 (V_4)
Ketone	3.14 (W_1)	1	1.0	1.0	1.0

[a] Values in brackets are tentative assignments.

fusion entropies of small molecules to estimate similar properties in highly complex molecules [4].

In order to address the question of whether group properties of small molecules can be used successfully to model similar properties in molecules with numerous functional groups in instances where C_K values are not available, we decided to examine how successfully these group values could be used to estimate fusion properties in linear organic polymers. In particular, we addressed the suitability of using group values and group coefficients derived from molecules containing only a few functional groups to evaluate similar properties of molecules containing numerous ones. We felt that the quality of the correlation observed with polymers would be a good diagnostic test of the

reliability of similar estimations in more complex molecules and in particular, would test whether the group coefficients would tend to vary randomly with increased substitution or to approach some limiting value asymptotically. The results of such a test are important in assessing the reliability of estimates in molecules containing functional groups that did or did not show synergistic effects upon successive substitution.

The fusion entropies (and enthalpies) of polymers are important thermodynamic properties that are more difficult to access than similar properties in homogeneous systems. Many polymers consist of both crystalline and amorphous domains and it is necessary to correct fusion enthalpy measurements for the degree of crystallinity [6]. Since molecular weights can vary depending on sample preparation, fusion entropies and enthalpies are usually reported as a function of the repeating unit. Fusion transitions in polymers are generally less well-defined since polymers are more heterogeneous. The melting point is taken as the point at which crystallinity disappears although the melting process may take place over a range of temperatures. As a result, fusion entropies and enthalpies are less well known and uncertainties associated with these measurements tend to be larger than those of more homogeneous systems. Despite the experimental obstacles associated with obtaining reliable data, these measurements assess some important physical properties and knowledge of the magnitude of these properties is necessary for a number of important practical reasons [7, 8]. This has resulted in a collection of critically reviewed data [8].

We have tested the applicability of using the group values and group coefficients generated from the fusion entropies of small molecules in two ways. We have used these values to model the fusion entropies of polymers and have compared our estimates to experimental data. In addition, we have compared our estimates to a group additivity method developed by Van Krevelen [7] from polymer data to estimate fusion entropies and enthalpies directly. The limited amount of fusion data currently available on polymers has restricted the number of group values that have been evaluated and this in turn has precluded our use of the Van Krevelen group values to estimate fusion properties of some polymers. Unless otherwise noted, all experimental data on polymers were obtained from the 'Advanced Thermal Analysis System Table of Thermal Properties of Linear Macromolecules' [8].

As noted above, the protocol developed for estimating fusion entropies actually estimates the total phase change entropy from 0 K to the liquid at the melting point [5], $\Delta_{tpce}S_m$. Table 1 lists the group values that were used in the estimation of $\Delta_{tpce}S_m$. Application of the group additivity scheme to evaluate fusion entropies depends on the structure and complexity of the repeating unit in the polymer in question. Eqs. (1) and (2) were used for estimating the total phase change entropy of the repeat unit in polymers containing acyclic and aromatic components. Non-aromatic cyclic molecules are treated separately. Since all the polymer estimations were evaluated using Eqs. (1) and (2), the estimation of cyclic molecules is not discussed any further here. Consequently, it has not been possible to test the group values and group coefficients for cyclic molecules in this study. As noted above, the contributions of some functional groups to the total phase change entropy are not strictly additive but depend on the total number of functional groups in the molecule [5]. This fact is reflected by the magnitude of a few of the group coefficients (C_K) in Table 1. The entropy contribution of

each functional group in the polymer has been modeled in one of two ways. In one approach, we have considered the functional groups present only in the repeating unit of the polymer and have chosen the value of C_K accordingly. In a second approach, we have approximated the cumulative effect of multiple functional group substitution by using the nearest-neighbor approximation. The group coefficient, C_K, in the latter case was chosen on the basis of the total number of functional groups on the repeat unit and on the two adjacent repeating units. If the appropriate C_K value was not available, the value closest to the appropriate one was used as a replacement. For example, the number of functional groups in poly(ethylene oxalate) using the nearest-neighbor approximation is 6, two on the repeat unit and two on each neighbor. The group coefficient for six functional groups, C_6, is not presently available. In this case the nearest available coefficient, C_4, was used as a substitute. It is not included in the formula used for the calculations in Table 2 (column 8) because its value is one. Fluorine atom substitution represents an exception to the use of Eq. (2) in choosing the appropriate group coefficient (C_K). Fluorine atom substitution is considered as a single functional group, regardless of the number of fluorine atoms attached [5]. Thus in a polymer such as poly(chlorotrifluoroethylene), the total number of functional groups using the nearest-neighbor approach is 4 with chlorine contributing 3 (1 on each repeat unit and 1 from each neighbor) and fluorine contributing 1 to the total.

Table 2 summarizes the results of the two sets of calculations for the polymers with available experimental data. The first column in the table identifies the molecular formula of the repeating unit. Experimental and calculated values are based on this repeat unit. Columns 2–5 contain the experimental data. Column 2 lists the experimental fusion or phase transition temperature, column 3 lists phase transition enthalpies, column 4 the corresponding fusion enthalpy and column 5 the total phase change entropy associated with these enthalpic transitions. Column 6 contains the fusion entropies calculated by using the group values provided by the Van Krevelen tables and are included to illustrate the correlation available using group values generated from experimental polymer data. The seventh column contains the results calculated from Table 1 using the two protocols summarized above. The values in parentheses are the results of choosing C_K values based on the number of functional groups on the repeat unit only; the number just preceding the parentheses is the result using the nearest-neighbor approximation. The last column characterizes the formula used for the estimation in column 7. The formulae included are those using nearest-neighbor corrections for the appropriate functional groups. C_K values are included in these formulae only if they differed numerically from one.

The applicability of using group values derived from small molecules to model fusion properties in macromolecules is shown in Fig. 1. This figure illustrates the correlation observed between experimental and calculated total phase change entropies (tpce) calculated using the nearest-neighbor approximation. A very similar correlation was obtained using the repeat unit approximation for C_K (graph not shown). The results of correlating experimental fusion entropies with the Van Krevelen estimates and estimates of total phase change entropy using the repeat unit and nearest-neighbor approximations are summarized in Table 3. Correlation of all the experimental data in Table 2 with the results estimated by the group values in Table 1 by least squares

Table 2
Estimation of fusion entropies of polymers [a]

Repeat unit	Fusion or transition temp. T/K	$\Delta_t H^d$ (J mol^{-1}) repeat unit	$\Delta_{fus}H_m$ (J mol^{-1} K^{-1}) repeat unit	$\Delta_{tpce}S_m$ (J mol^{-1} K^{-1}) repeat unit	$\Delta_{fus}S_m$ calc. Van Krevelen [b]	$\Delta_{tpce}S_m$ calc. (this work)	Formula used for calculation [c]
CF$_2$	Poly(tetrafluoroethylene) 297	850					
	605		4100	9.64	4.8	3.53 (3.53)	$D_1D_2 + 2P_1$
CH$_2$	Poly(ethylene) 414.6		4110	9.91	8.4	9.41 (9.41)	B_1
CH$_2$O	Poly(oxymethylene) 457.5		9790	21.4	15.9	10.5 (10.5)	$B_1 + T_1$
C$_2$ClF$_3$	Poly(chlorotrifluoroethylene) 493		5020	10.2	14.0	8.5 (9.1)	$2D_1D_2 + O_1O_4 + 3P_1$
C$_2$HF$_3$	Poly(trifluoroethylene) 495.2		5440	11.0	12.4	7.1 (7.1)	$C_1C_2 + D_1D_2 + 3P_1$
C$_2$H$_2$F$_2$	Poly(vinylidene flouride) 483		6700	13.2	13.2	12.9 (12.9)	$B_1 + D_1D_2 + 2P_1$
C$_2$H$_2$O$_2$	Poly(glycolic acid) 501		9740	19.4	8.4	13.0 (13.0)	$B_1 + S_1$
C$_2$H$_3$Cl	Poly(vinylchloride) 546		11000	20.1	20.0	15.0 (6.6)	$B_1 + C_1C_2 + O_1O_3$
C$_2$H$_3$F	Poly(vinylfluoride) 473		7540	15.0	16.0	13.0 (13.0)	$B_1 + C_1C_2 + P_1$
C$_2$H$_4$O	Poly(oxyethylene) 342		8660	25.3	23.8	19.9 (19.9)	$2B_1 + T_1$
C$_2$H$_4$O	Poly(vinyl alcohol) 538		7110	13.2	13.0	19.6 (−0.6)	$B_1 + C_1C_2 + Q_1Q_3$
C$_3$H$_3$N	Poly(arcylonitrile) 590		5000 [b]	8.4	8.46	11.7 (7.85)	$B_1 + C_1C_2 + R_1R_3$
C$_3$H$_4$O$_2$	Poly(ß-propiolactone) 366		10900	29.8	24.3	22.5 (22.5)	$2B_1 + S_1 + T_1$

C_3H_6	Poly(propylene) 460.7	18.9	22.0	8700	11.5 (11.5)	$A_1 + B_1 + C_1$
C_3H_6O	Poly(propyleneoxide) 348	24.1	29.0	8400	17.7 (17.7)	$A_1 + B_1 + C_1C_2 + T_1$
C_3H_6O	Poly(trimethyleneoxide) 308	30.6	32.8	9440	29.3 (29.3)	$3B_1 + T_1$
$C_3H_6O_2$	Poly(oxymethylenoxyethylene) 328	50.9	39.2	16700	30.4 (30.4)	$3B_1 + 2T_1$
$C_4H_3F_3O_2$	Poly(vinyl trifluoroacetate) 448	16.7	NA[e]	7500[b]	20.2 (20.2)	$B_1 + C_1C_2 + D_1D_2 + 3P_1 + S_1$
$C_4H_4O_4$	Poly(ethylene oxalate) 450	51.1	16.8	23000	26.2 (26.1)	$2B_1 + 2S_1$
$C_4H_4O_4$	Poly(γ-butyrolactone) 337.5	41.5	25.2	14000	31.9 (31.9)	$3B_1 + S_1$
C_4H_5Cl	trans-Poly(chloroprene) 368	22.8	26.4	8400[b]	29.0 (20.6)	$2B_1 + F_1 + G_1 + O_1O_3$
C_4H_6	cis-Poly(1,4-butadiene) 284.7	32.3	NA[e]	9200	28.5 (28.5)	$2B_1 + 2F_1$
C_4H_6	trans-Poly(1,4-butadiene) 356 437 7800	30.4	NA[e]	3730	28.5 (28.5)	$2B_1 + 2F_1$
C_4H_8	Poly(1-butene) 411	17.0	NA[e]	7000	21.0 (21.0)	$A_1 + 2B_1 + C_1$
C_4H_8	Poly(isobutylene) 317	37.9	18.4	12000	7.4 (7.4)	$2A_1 + B_1 + D_1$
C_4H_8O	Poly(oxytetramethylene) 330	43.6	40.6	14400	38.7 (38.7)	$4B_1 + T_1$
C_5H_8	cis-Poly(isoprene) 301.2	14.4	38.5	4350	30.6 (30.6)	$A_1 + 2B_1 + F_1 + G_1$
C_5H_8	trans-Poly(isoprene) 347	36.9	38.5	12800[b]	30.6 (30.6)	$A_1 + 2B_1 + F_1 + G_1$
$C_5H_8Cl_2O$	Poly(2,2-bis(chloromethyl)trimethylene-3-oxide) 463	69.1	NA[e]	32000	32.3 (33.5)	$4B_1 + D_1 + 2O_1O_4 + T_1$

Table 2 (*continued*)

Repeat unit	Fusion or transition temp. T/K	$\Delta_t H^d$ (J mol^{-1}) repeat unit	$\Delta_{fus} H_m$ (J mol^{-1} K^{-1}) repeat unit	$\Delta_{tpce} S_m$ (J mol^{-1} K^{-1}) repeat unit	$\Delta_{fus} S_m$ calc. Van Krevelen[b]	$\Delta_{tpce} S_m$ calc. (this work)	Formula used for calculation[c]
$C_5H_8O_2$	Poly(methyl methacrylate) 450	9500	21.1	NA[e]	23.8 (23.8)	$A_1 + B_1 + D_1D_2 + S_1$
$C_5H_8O_2$	Poly(2,2-dimethylpropiolactone) 513	14900	29.0	18.4	23.8 (23.8)	$2A_1 + B_1 + D_1D_2 + S_1$
C_5H_{10}	Poly(1-pentene) 403.2	6300	15.6	NA[e]	30.4 (30.4)	$A_1 + 3B_1 + C_1$
$C_5H_{10}O_2$	Poly(oxymethyleneoxytetramethylene) 296	14300	48.3	57.0	49.2 (49.2)	$5B_1 + 2T_1$
C_6H_4O	Poly(oxy-1,4-phenylene) 535	7820	14.6	36.8	18.3 (18.3)	$4H_1 + 2J_1 + T_1$
C_6H_4S	Poly(thio-1,4-phenylene) 593	8650	14.6	NA[e]	19.8 (24.4)	$4H_1 + 2J_1 + V_1V_4$
$C_6H_{10}O_2$	Poly(ε-caprolactone) 342.2	17900	52.3	42.0	50.8 (50.8)	$5B_1 + S_1$
$C_6H_{10}O_2$	Poly(isopropyl acrylate) 421	5900	14.0	NA[e]	27.4 (27.4)	$2A_1 + B_1 + 2C_1C_2 + S_1$
$C_6H_{11}NO$	Nylon-6poly(6-aminohexanoic acid) 533	26000	48.8	42.0	46.7 (46.7)	$5B_1 + U_1$
C_6H_{12}	Poly(4-methyl-1-pentene) 523	9960	19.0	NA[e]	23.1 (23.1)	$2A_1 + 2B_1 + 2C_1$
C_8H_8	Poly(styrene) 516.2	10000	19.4	18.0	15.1 (15.1)	$2B_1 + 5H_1 + I_1$
C_8H_8	Poly(xylylene) 504 / 560 / 700	5000 / 1500 / 10000	26.6	42.8	23.9 (23.9)	$2B_1 + 4H_1 + 2I_1$

Formula	Polymer					Groups
C_8H_8O	Poly(2,6-dimethyl-1,4-diphenylene oxide) 580	5950	10.3	NAᵉ	21.4 (21.4)	$2A_1 + 2H_1 + 2I_1 + 2J_1 + T_1$
$C_8H_{12}O_4$	Polyester-2,6poly(ethylene adipate) 320 / 338	15900ᵇ / 21000ᵇ	49.7ᵍ / 62.1ᵍ	50.4	63.8 (63.8)	$6B_1 + 2S_1$
$C_8H_{16}O$	Poly(oxyoctamethylene) 347	29300	84.4	74.2	76.4 (76.4)	$8B_1 + 2T_1$
$C_{10}H_8O_4$	Poly(ethylene terephthalate) 553	26900	48.6	42.8	43.4 (43.4)	$2B_1 + 4H_1 + 2J_1 + 2S_1$
$C_{11}H_{20}O_2$	Poly(undecanolactone) 365	39500	108.2	84.0	97.8 (97.8)	$10B_1 + S_1$
$C_{11}H_{21}NO$	Nylon-11 poly(11-aminoundecanoic acid) 493	44700	90.7	84.0	93.7 (93.7)	$10B_1 + U_1$
$C_{12}H_{12}O_4$	Poly(tetramethylene terephthalate) 518	32000	61.8	59.6	62.2 (62.2)	$4B_1 + 2S_1 + 4H_1 + 2J_1$
$C_{12}H_{20}O_4$	Polyester-2,10 poly(ethylene decanedioate) 356.2	31900	89.6	84.0	101.5 (101.5)	$10B_1 + 2S_1$
$C_{12}H_{22}N_2O_2$	Nylon-6,6,αpoly(hexamethylene hexanediamide) 574	57800	100.6	84.0	93.3 (93.3)	$10B_1 + 2U_1$
$C_{12}H_{23}NO$	Poly(12-aminododecanoic acid) 500	48400	96.8	92.4	103.1 (103.1)	$11B_1 + U_1$
$C_{13}H_{24}O_2$	Poly(tridecanolactone) 368	50600	137.5	100.8	116.6 (116.6)	$12B_1 + S_1$
$C_{14}H_{10}O_4$	Poly(ethylene naphthalene-2,6-dicarboxylate) 610	25000	40.9	NAᵉ	47.7 (47.7)	$2B_1 + 6H_1 + 4J_1 + 2S_1$
$C_{14}H_{16}O_4$	Poly(hexamethylene terephthalate) 434	35000	80.6	76.4	81.1 (81.1)	$6B_1 + 4H_1 + 2J_1 + 2S_1$
$C_{15}H_{28}N_2O_2$	Nylon-6,9 poly(hexamethylene nonanediamide) 500	69000	138.0	109.2	121.5 (121.5)	$13B_1 + 2U_1$
$C_{15}H_{28}O_2$	Poly(pentadecanolactone) 370.5	63400	171.1	117.6	135.4 (135.4)	$14B_1 + 2S_1$
$C_{16}H_{28}O_4$	Poly(decamethylene adipate) 343	42676	124.4	117.6	139.1 (139.1)	$14B_1 + 2S_1$

Table 2 (continued)

Repeat unit	Fusion or transition temp. T/K	$\Delta_t H^d$ (J mol^{-1}) repeat unit	$\Delta_{fus}H_m$ (J mol^{-1} K^{-1}) repeat unit	$\Delta_{tpce}S_m$ (J mol^{-1} K^{-1}) repeat unit	$\Delta_{fus}S_m$ calc. Van Krevelen[b]	$\Delta_{tpce}S_m$ calc. (this work)	Formula used for calculation[c]
$C_{16}H_{30}N_2O_2$	Nylon-6,10 Poly(hexamethylene decanediamide)						
	506	71700		141.6	117.6	130.9 (130.9)	$14B_1 + 2U_1$
$C_{18}H_{12}O$	Poly(oxy-2,6-diphenyl-1,4-diphenylene)						
	753	12200		16.2	NA[e]	52.8 (52.8)	$12H_1 + 6J_1 + T_1$
	770	87000[b,f]		113.0			
$C_{18}H_{32}O_4$	Polyster-9,9 poly(nonamethylene nonanedioate)						
	338	43200[b]		127.8	134	157.9 (157.9)	$16B_1 + 2S_1$
$C_{18}H_{24}O_4$	Poly(decamethylene terephthalate)						
	411	46100		112.1	110.0	118.7 (118.7)	$10B_1 + 4H_1 + 2J_1 + 2S_1$
$C_{18}H_{32}N_2O_2$	Nylon-6,12 Poly(hexamethylene dodecanediamide)						
	520	80100		154.0	134.4	149.7 (149.7)	$16B_1 + 2U_1$
$C_{19}H_{12}O_3$	Poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene)						
	668.2	37400		56.0	NA[e]	57.0 (57.0)	$12H_1 + 6J_1 + 2T_1 + W_1$
$C_{20}H_{36}O_4$	Poly(decamethylene-sebacate)						
	353	50208[b]		142.2[g]	151.2	176.8 (176.8)	$18B_1 + 2S_1$
	344	50300[b]		146.2[g]			

[a] All data from Ref. [8] unless otherwise noted.
[b] Data from Ref. [7].
[c] Only group coefficients differing from unity are included.
[d] Enthalpy of transition.
[e] Not available.
[f] Not used in correlation.
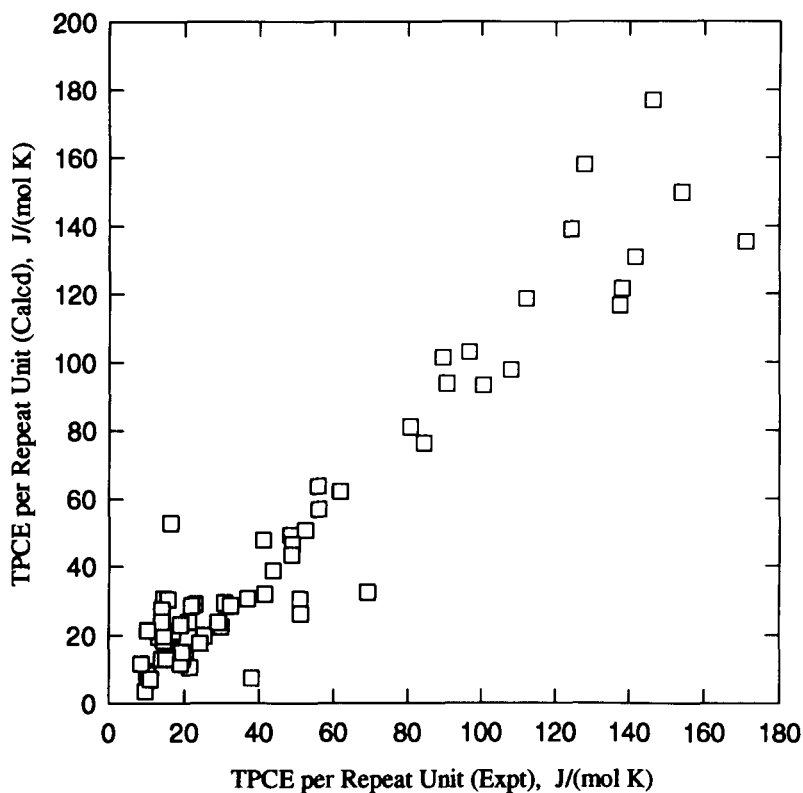[g] A mean value was used in least squares analysis.

Calculated and Experimental Total Phase Change Entropies of Polymers

Fig. 1. A comparison of the calculated and experimental fusion entropies (J mol^{-1} K^{-1}) of 64 polymers.

resulted in a standard deviation of approximately 13.2 J mol^{-1} K^{-1} using both the repeat unit and nearest-neighbor approximation. One entry, the results for poly(oxy-2,6-diphenyl-1,4-diphenylene), was characterized with an error in excess of 3 standard deviations. Excluding this datum from both approximations resulted in a standard deviation of 12.4 J mol^{-1} K^{-1} for $\Delta_{tpce}S_m$.

The uncertainty of 12.4 J mol^{-1} K^{-1} for $\Delta_{tpce}S_m$ obtained in this study is clearly in line with the uncertainty observed in studies of smaller multi-substituted molecules (10.5 J mol^{-1} K^{-1} [5]). Given the larger uncertainties likely to be associated with experimental measurements on polymers, this correlation suggests that the group values evaluated from small molecules are applicable to larger molecules. Functional groups whose group coefficients are not very sensitive to increased substitution in small molecules appear to remain so in large molecules. An examination of the individual entries in column 7 of Table 2 shows that the calculation for most repeat units is not affected by the approximations used. The correlation of those calculations affected (7 out of 64) varied, increasing in some cases and decreasing in others. There appears to be

Table 3

A summary of the correlation parameters using the Van Krevelen parameters and the parameters of Table 1

A. Comparison of linear regression results for $\Delta_{tpce}S_m$ using the nearest-neighbor and repeat unit approximation for C_K

	All data	Data within 3 std. deviations
Linear regression results for $\Delta_{tpce}S_m$ using the nearest-neighbor approximation		
Intercept	0	0
Standard error of $\Delta_{tpce}S_m$ (calc.)	13.2	12.4 J mol^{-1} K^{-1}
Correlation coefficient	0.954	0.960
Number of data points	64	63
Slope	0.969	0.967
Linear regression results for $\Delta_{tpce}S_m$ using the repeat unit approximation		
Intercept	0	0
Standard error of $\Delta_{tpce}S_m$(calc.)	13.3	12.5 J mol^{-1} K^{-1}
Correlation coefficient	0.954	0.960
Number of data points	64	63
Slope	0.967	0.965

B. Comparison of linear regression results for ΔS using the Van Krevelen parameters and the nearest-neighbor approximation for C_K

Linear regression results for $\Delta_{fus}S_m$ using the Van Krevelen parameters	
Intercept	0
Standard error of $\Delta_{fus}S_m$ (calc.)	12.0 J mol^{-1} K^{-1}
Correlation coefficient	0.959
Number of data points	50
Slope	0.869
Number of parameters used	16
Linear regression results for $\Delta_{tpce}S_m$ using the nearest-neighbor approximation	
Intercept	0
Standard error of $\Delta_{tpce}S_m$ (calc.)	12.3 J mol^{-1} K^{-1}
Correlation coefficient	0.966
Number of data points	50
Slope	0.969
Number of parameters used	18

C. Comparison of experimental and calculated fusion enthalpies

	All data	Data within 3 std. deviations
Intercept	0	0
Standard error of $\Delta_{fus}H_m$ (calc.)	6.32	5.15 kJ mol^{-1}
Correlation coefficient	0.942	0.962
Number of data points	64	63
Slope	0.935	0.962

some improvement in correlation using the nearest-neighbor approximation although there are not enough data available in this study to reach any definite conclusion.

Correlation parameters of experimental and calculated results are also included in Table 3 for the data estimated by the group additivity parameters reported by Van Krevelen. The fusion enthalpies of a total of 50 of the 64 polymers in Table 2 could be estimated by the Van Krevelen group method using available parameters (16 in all) [7]. A comparison of the correlation between experimental and calculated total phase change entropies using the same data base is also included in Table 3 (B). Since only two of the fifty polymers show additional phase changes, fusion entropy results from the Van Krevelen estimates and $\Delta_{tpce} S_m$ estimates obtained using the parameters of Table 1 (a total of 18 in all) can be compared directly. The similarity in results suggest that the parameters of Table 1 are capable of giving predictions comparable to those derived directly from polymers. This suggests that these parameters can also be applied with some degree of confidence to assess similar properties in other large complex molecules [4].

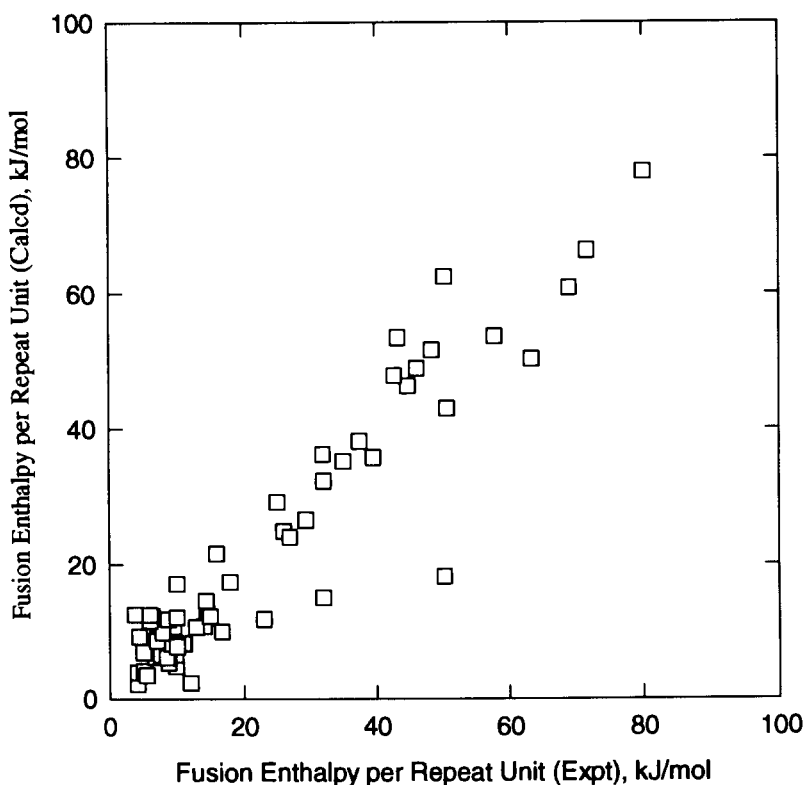## Calculated and Experimental Fusion Enthalpies of Polymers

Fig. 2. A comparison of the calculated and experimental fusion enthalpies (kJ mol^{-1}) of 64 polymers.

The application of the group values in Table 1 to model fusion enthalpies is illustrated in Fig. 2. Fusion enthalpies of the 64 polymers of Table 2 are compared to the values calculated by multiplying calculated $\Delta_{\text{tpce}}S_m$ values (column 7) by the experimental fusion temperature (column 2, Table 2). The correlation parameters reported in Table 3 (C) are those using the nearest-neighbor approximation for ΔS_{tpce}. The standard deviation of 5.15 kJ mol^{-1} can be compared with the value of approximately 4.0 kJ mol^{-1} obtained from a similar estimation of fusion enthalpies of small molecules.

3. Summary

In conclusion, we find that the experimental fusion entropies and enthalpies of polymers can be successfully estimated from group parameters derived from small molecules. This success is important because it suggests that contributions of many functional groups are fixed and do not depend on the degree of substitution. The results observed for chlorine, a functional group that shows some dependence on substitution, are encouraging. Most experimental $\Delta_{\text{tpce}}S_m$ values for chlorine-containing polymers are modeled reasonably well (within 1 standard deviation) with existing C_K values. This suggests that the dependence of C_K values on substitution observed for some groups such as nitrile, hydroxyl, and carboxylic acid, may be confined by the present parameters and will not vary widely or randomly with increasing substitution. This is a significant finding in assessing the applicability of the group values previously reported [5] to modeling entropy and enthalpy changes in other highly functionalized molecules [4].

Acknowledgements

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