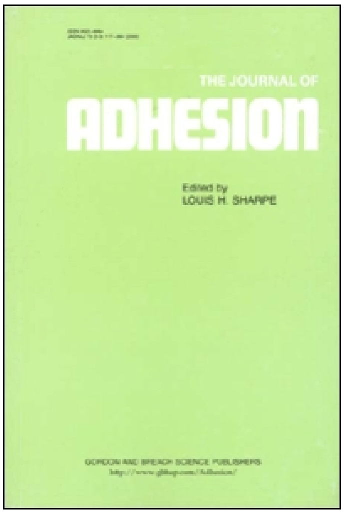

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Simple Methods for the Prediction of Surface Free Energy and Its Components. Application to Polymers*

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The surface free energy of a polymer can be easily calculated by the Group Contribution Method developed by the authors. After having briefly recalled the method and illustrated it with new examples, the latest developments including the Weighted Group Contribution Method and the study of the molecular weight dependence of surface free energy are also expounded.

Finally, very simple means to determine the dispersive contribution to the surface energy are described. The dispersive component values calculated from the Lifshitz theory, and from the solubility parameters, are in good agreement with those obtained from wettability measurements.

KEY WORDS polymers; surface free energy; dispersive component; group contribution; solubility parameter; refractive index.

I INTRODUCTION

The surface free energy, γ, is an important parameter for understanding, interpreting or predicting surface phenomena of great importance such as wetting and adhesion. Poor mobility of molecules in a solid polymer does not allow one to determine directly its surface energy. Therefore, indirect methods of determination based on wettability phenomena have been widely developed during the last few decades.

In previous papers,[1-3] it has been demonstrated that the surface free energy, γ_n, of a compound containing n carbonated groups can be written as

$$\gamma_n = \frac{1}{n}[x\gamma_x + y\gamma_y + z\gamma_z + \ldots] \tag{1}$$

where x, y, z are, respectively, the number of groups X, Y, Z forming the molecule and γ_x, γ_y, γ_z are the corresponding contribution of each group to γ_n.

If we consider a homologous series containing N CH_2 groups and m other groups $(N + m = n)$, we can write $(N = x, m = y + z + \ldots)$:

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$$n\gamma_n = N\gamma_{CH_2} + y\gamma_y + z\gamma_z + \ldots \qquad (2)$$

The linear relationship (2), plotted as a function of N for different experimental γ_n values, has a slope equal to γ_{CH_2} and $y\gamma_y + z\gamma_z + \ldots$ is the Y-axis intercept. This generalized Group Contribution Method (GCM) can be applied to any series of carbonated compounds in order to obtain the contribution of groups other than CH_2. Then, equation (1) permits one to calculate the surface energy of polymers from their chemical structure.

This calculation constitutes the simplest route to obtain the surface free energy with a group contribution method. In this paper, we propose a new and more accurate approach, the Weighted Group Contribution Method, which takes into account the size of the different carbonated groups. The study of the molecular weight dependence of polymer surface free energy is also undertaken.

II SURFACE FREE ENERGY OF POLYMERS FROM THE GCM

II.1. Contribution of Carbonated Groups

Figures 1 and 2 illustrate the GCM to obtain the contribution to surface free energy of carbonated groups, γ_g. For example, the alkane series (Figure 1) leads to γ_{CH_2}

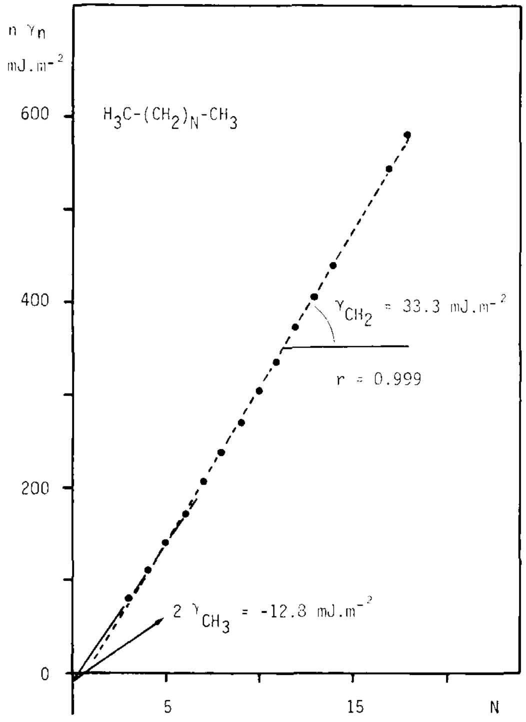

FIGURE 1 Determination of γ_{CH_2} and γ_{CH_3} by GCM, applied to the alkane series.

(n from 5 to 20) and to γ_{CH_3} (n from 5 to 8). The nitrile compound series allows one to evaluate the nitrile group contribution, γ_{CN} (n from 2 to 10, Figure 2). The comprehensive paper by Jasper[4] provides the γ_n values necessary for the calculations.

In Table I are summarized the γ_g values of twelve carbonated groups. It can be noticed that γ_{CH_2} does not depend significantly on the nature of the homologous

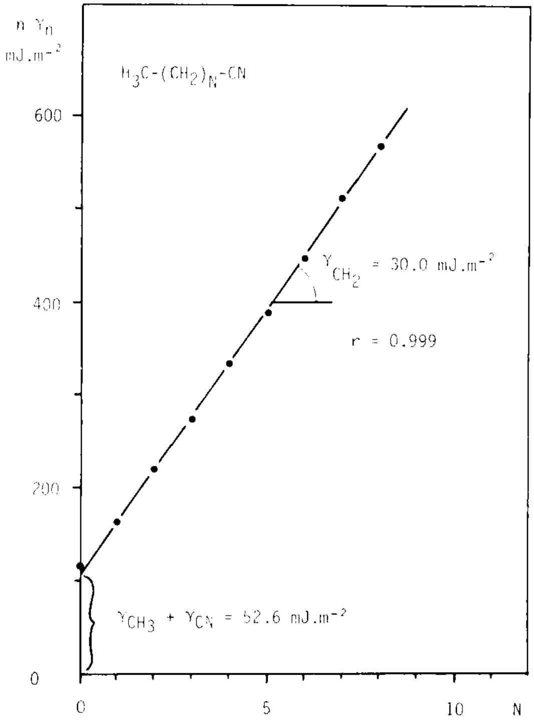

FIGURE 2 Determination of γ_{CH_2} and γ_{CN} by the GCM, applied to the nitrile series.

TABLE I
Group contribution values, γ_g, of carbonated groups at 20°C (mJ·m^{-2})

Group	γ_g	Group	γ_g
—CH_3	−6.4	—CF_3	−7.3
—CH_2—	33.3 (olefins) 30.5 (others)	—CF_2— —CH_2OH	21.4 47.5
>CH—	63.3	>CH OH	72.0
>C<	94.0	>C— │ OH	104.0
—COO— —CHCl—	74.8 70.8	—C≡N	59.0

series used. The negative values of the contribution of CH_3 and CF_3 groups at 20°C must be related to the fact that ethane C_2H_6 and hexafluoroethane C_2F_6 are gases and have no surface tension at 20°C. As $d\gamma/dT$ is negative for most of organic compounds, there exists a lower temperature at which the sign of γ_{CH_3} and γ_{CF_3} is positive.

II.2. Surface Free Energy of Polymers with the Simple GCM

In a macromolecular material, the contribution of the end groups of the chain to the surface free energy is negligible due to the polymer's high molecular weight. For a homopolymer, γ is equal to the contribution of the simplest repetitive pattern obtainable with equation (1). The surface free energy of a dozen common polymers has been evaluated with the GCM by using equation (1). The results are presented in Table II. In comparison with the surface energies deduced from wettability measurements,[5] the agreement is generally good, with the exception of polyvinyl chloride. This may be so because the liquid probes used for the wetting measurements are not necessarily able to reveal the acidity of this solid.

II.3. The Weighted Group Contribution Method

Although the correlation coefficients of linear regressions of relationship (2) are very close to 1 for many series of homologous liquids[1-3] (in this paper, $r = 0.999$ for the n-alkane and nitrile series), a very small deviation from linearity is often noticeable with the first terms of a series (Figure 1).

This observation points out one limitation of the simple Group Contribution Method. In fact, the decomposition of a molecule into several carbonated groups having the same importance or "weight" in the calculation, without taking into con-

TABLE II
Surface energies, γ, and dispersive components, γ^D, of polymers at 20°C (mJ·m^{-2}). Comparison between theoretical and experimental results

Polymer	γ GCM	γ Ref. 5	γ^D Eq. (13)	γ^D Eq. (14)	γ^D Eq. (14)+(15)	γ^D Ref. 5
Polytetrafluoroethylene	21.4[+]	20.0	18.9	—	20.6	18.4
Polyvinylidene fluoride	27.4	30.3	25.3	—	26.6	23.3
Polypropylene	30.1	30.1	31.2	30.5	31.7	30.1
Polyethylene	33.3[++]	35.3	35.4	—	35.0	35.3
Polyisobutylene	28.6	33.6	35.2	24.8	34.8	33.6
Polyethyl methacrylate	36.2	35.9	32.5	32.4	32.7	26.9
Polymethyl methacrylate	37.3	41.1	33.0	37.2	33.1	29.6
Polyethyl acrylate	38.5	37.0	30.7	—	31.2	30.7
Polymethyl acrylate	40.6	41.0	31.5	—	31.8	29.7
Polyvinyl acetate	40.6	36.5	30.5	39.1	31.0	24.5
Polyvinyl chloride	50.7	41.5	40.2	37.2	38.8	39.5
Polyvinyl alcohol	51.3	—	37.8	—	36.9	—
Polyacrylonitrile	50.9	—	36.6	35.3	36.0	—

[+] 20.5 mJ·m^{-2} from the Weighted Group Contribution Method.

[++] 34.9 mJ·m^{-2} from the Weighted Group Contribution Method (this paper).

sideration the group size or its local density, is not very satisfactory if we need the finest analysis.

To approach this problem, we have considered the variation of the density, d_n, of a term of a homologous series containing $(n-2)$ X groups and 2 Y end groups (chemical formula: $Y-(X)_{n-2}-Y$).

Observing that molecular weight, M_n, and molar volume, V_n, of the members of the series are additive, we have

$$M_n = 2M_y + (n-2)\,M_x \tag{3}$$

and:

$$V_n = 2V_y + (n-2)\,V_x\,. \tag{4}$$

If $d_n = M_n/V_n$, $d_x = M_x/V_x$ and $d_y = M_y/V_y$, it is easily deduced that

$$d_n = 2\frac{V_y}{V_n}\,d_y + (n-2)\,\frac{V_x}{V_n}\,d_x \tag{5}$$

or:

$$d_n = \frac{1}{2\dfrac{V_y}{V_x} + n - 2}\left[2\frac{V_y}{V_x}\,d_y + (n-2)\,d_x\right]. \tag{6}$$

When n→∞, $d_n \to d_x$ so that equation (6) can be written as:

$$d_n = \frac{1}{2\dfrac{V_y}{V_x} + n - 2}\left[2\frac{V_y}{V_x}\,d_y + (n-2)\,d_\infty\right]. \tag{7}$$

It can be seen that this relationship has the same mathematical form as equation (1) when $V_y/V_x = 1$. Conversely, the surface free energy being also a function of density,[1,6] if we admit that a more accurate expression of equation (1) has the same empirical mathematical form as equation (7), one "weighted" expression of equation (1) can be written

$$\gamma_n = \frac{1}{2\dfrac{V_y}{V_x} + n - 2}\left[2\frac{V_y}{V_x}\,\gamma_y + (n-2)\,\gamma_\infty\right] \tag{8}$$

that is equivalent to equation (1) when $V_y/V_x = 1$.

This Weighted Group Contribution Method has been applied to the alkane and perfluoroalkane series. The data necessary for the calculations are given in Tables III and IV. Figure 3 presents the perfect linear regression ($r = 0.999996$) obtained from equation (8) with the alkane series. The different values of γ_{CH_2}, γ_{CH_3}, γ_{CF_2} and γ_{CF_3} determined by using the simple and the weighted GCM are presented in Table V. The surface free energies of pentane and perfluoropentane have also been calculated and compared with the experimental values to evaluate the accuracy of the two methods of calculation (GCM and WGCM).

TABLE III

Data necessary for the application of the Weighted Group Contribution Method to the n-alkane series, C_nH_{2n+2} (T = 20°C)

n	γ_n $mJ \cdot m^{-2}$	M_n	d_n	V_n cm^3
5	16.05	72.15	0.6262	115.22
6	18.40	86.18	0.6603	130.52
7	20.14	100.20	0.6837	146.56
8	21.62	114.23	0.7025	162.60
9	22.85	128.26	0.7176	178.74
10	23.83	142.28	0.7300	194.90
11	24.66	156.31	0.7402	211.17
12	25.35	170.34	0.7487	227.51
13	25.99	184.37	0.7564	243.75
14	26.56	198.39	0.7628	260.08
15	27.07	212.42	0.7685	276.41
16	27.47	226.45	0.7733	292.84
19	28.59	268.53	0.7885	340.56
20	28.87	282.55	0.7886	358.29

$V_{CH_3} = 32.79$ cm^3, $V_{CH_2} = 16.21$ cm^3 (Eq. 4)
$V_{CH_3}/V_{CH_2} = 2.02$

TABLE IV

Data necessary for the application of the Weighted Group Contribution Method to the perfluoroalkane series, C_nF_{2n+2} (T = 20°C)

n	γ_n $mJ \cdot m^{-2}$	M_n	d_n	V_n cm^3
5	9.89	288.04	1.7326	166.25
6	11.91	338.04	1.6995	198.91
7	13.19	388.05	1.7333	223.88

$V_{CF_3} = 40.54$ cm^3, $V_{CF_2} = 28.82$ cm^3 (Eq. 4)
$V_{CF_3}/V_{CF_2} = 1.41$

Clearly, it appears that the WGCM leads to the more reliable values, especially for pentane in which the ratio V_{CH_3}/V_{CH_2} (2.02) is much greater than 1. Nevertheless, the simple GCM allows one to obtain very easily the surface free energy of polymers with an acceptable accuracy (Table II).

II.4. Molecular Weight Dependence of Polymer Surface Energy

The values of polymer surface free energies reported in Table II are calculated on the basis of an infinite molecular weight.

The variation of γ with the molecular weight can be deduced from the simple or Weighted Group Contribution Method. As an example, if we consider a series of polyethylenes of different molecular weight, M_n, n referring to the number of carbon atoms in a chain, the relationship between n and M_n is given by equation (3), y and x representing the CH_3 and CH_2 groups, respectively, and is written as:

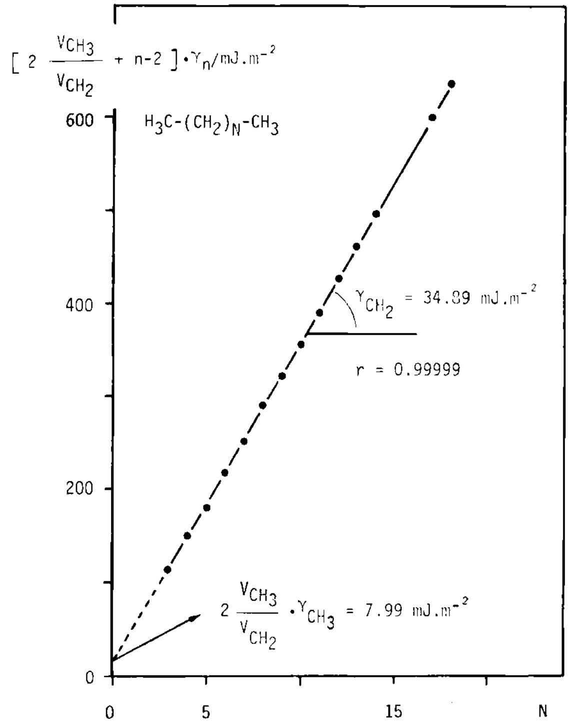

FIGURE 3 Application of the Weighted GCM to the alkane series.

TABLE V

Comparison between the weighted (W) and the simple Group Contribution Method (GCM) with the alkane and perfluoroalkane series (unit: mJ·m^{-2})

Method	γ_{CH_2}	γ_{CH_3}	γ_{CF_2}	γ_{CF_3}	γ_{C5H12}	γ_{C5F12}
GCM	33.28	−6.39	21.44	−7.34	17.41 (16.05)$^+$	9.93 (9.89)$^+$
WGCM	34.89	1.98	20.46	−6.29	15.98 (16.05)$^+$	9.92 (9.89)$^+$

$^+$Experimental values at 20°C.

$$n=\frac{M_n-2M_y}{M_x}+2 \tag{9}$$

Replacing n by this function of M_n in equations (1) or (8) leads, after some elementary calculations, to

$$\gamma_n=\gamma_\infty-\frac{2(\gamma_\infty-\gamma_y)M_x}{M_n+2(M_x-M_y)} \tag{10}$$

from the simple GCM, and to

$$\gamma_n=\frac{M_n}{M_n+2\ (\lambda M_x-M_y)}\gamma_\infty-\frac{2\ (M_y\gamma_\infty-\lambda M_x\gamma_y)}{M_n+2\ (\lambda M_x-M_y)} \tag{11}$$

TABLE VI
Experimental and theoretical values of γ ($mJ \cdot m^{-2}$) for polyethylenes of different molecular weight, M_n (T = 20°C)

M_n	Experimental γ	γ from GCM (Eq. 10)	γ from WGCM (Eq. 11)
>50,000	35.3	33.3	34.9
2,100	34.4	32.8	34.0
1,100	33.4	32.3	33.2
339	30.5	30.1	29.8
226.4	27.5	28.4	27.5

from the weighted GCM, where $\lambda = V_y/V_x$. For polyethylene, $\lambda = V_{CH_3}/V_{CH_2} = 2.02$, $M_x = M_{CH_2} = 14$ and $M_y = M_{CH_3} = 15$.

The experimental[6] and theoretical values of γ_n for several polyethylenes of molecular weight M_n are presented in Table VI. A very good agreement is obtained between the measured and calculated values of γ, especially for those deduced from the Weighted Group Contribution Method.

It is also interesting to notice that equations (10) and (11) are simplified to

$$\gamma_n = \gamma_\infty - \frac{\alpha}{M_n} \tag{12}$$

for high values of M_n ($\geq$10,000), α being a constant. This relationship has been recently proposed by Dee and Sauer[6] using a different approach. It is also deducible from Fox and Flory's work.[7]

III DISPERSIVE COMPONENT OF THE SURFACE FREE ENERGY

III.1. From Refractive Index

The London dispersion forces between molecules depend on their polarizability, so that a relationship exists between the dispersive component of the surface energy of a liquid or a solid and its refractive index, n_D. On the basis of the Lifshitz theory, the dispersive contribution, γ^D, to the surface energy can be quantified by using the next equation:[8,9]

$$\gamma^D = 128.39 \frac{(n_D^2 - 1)^2}{(n_D^2 + 1)^{1.5}} \quad (\gamma^D \text{ in } mJ \cdot m^{-2}) \tag{13}$$

As shown in Figure 4 with the nitrile series, equation (1) and the GCM apply perfectly to the dispersive components (calculated γ_n^D in Table VII) of a series of homologous compounds and lead to values of γ_g^D ($\gamma_{CN}^D = 37.2$ $mJ \cdot m^{-2}$). Nevertheless, the refractive indexes of most polymers usually being known, it is obviously easier to use equation (13) with the refractive index of the polymer to obtain its γ^D directly. Thus, the dispersive contribution, γ^D, of the polymers considered have been evaluated in Table II from their respective n_D (listed in Table VIII). A very good agreement is found between the calculated (Eq. 13) and measured[5] dispersive components of polymers.

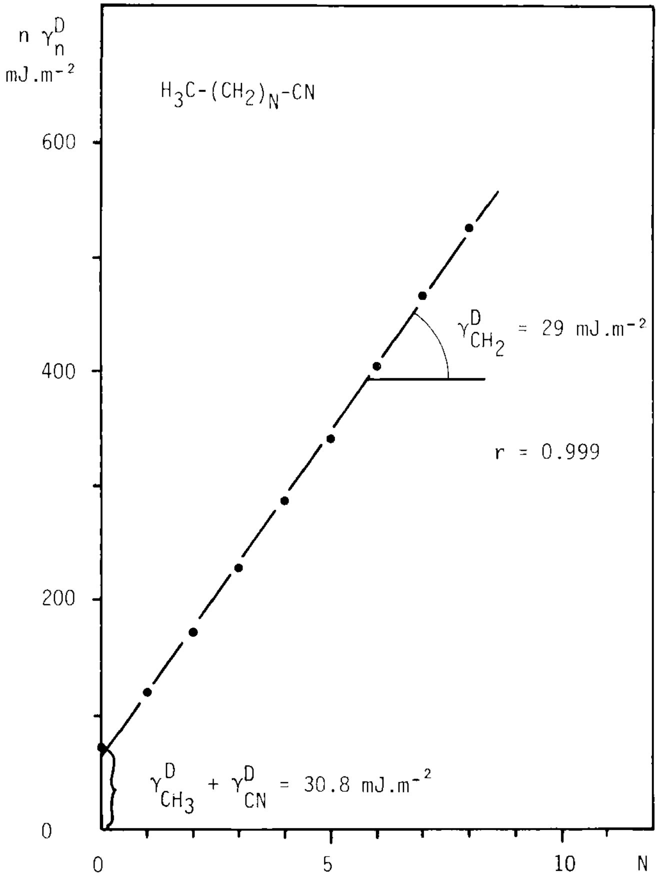

FIGURE 4 Determination of γ^D_{CN} by the GCM, applied to the nitrile series, by using γ^D_n values.

TABLE VII
Surface free energies, γ_n, and dispersive components, γ_n^D, of the nitrile compounds $H_3C—(CH_2)_N—CN$ at 20°C (mJ·m^{-2}). γ_n^D is calculated from the refractive index, n_D, with Eq. (13)

n	N	γ_n Ref. 4	n_D	γ_n^D Eq. (13)
2	0	29.29	1.3442	17.77
3	1	27.32	1.3655	19.80
4	2	27.44	1.3842	21.63
5	3	27.41	1.3971	22.94
6	4	27.83	1.4068	23.94
7	5	27.75	1.4104	24.31
8	6	28.01	1.4203	25.35
9	7	28.50	1.4255	25.90
10	8	29.36	1.4296	26.34

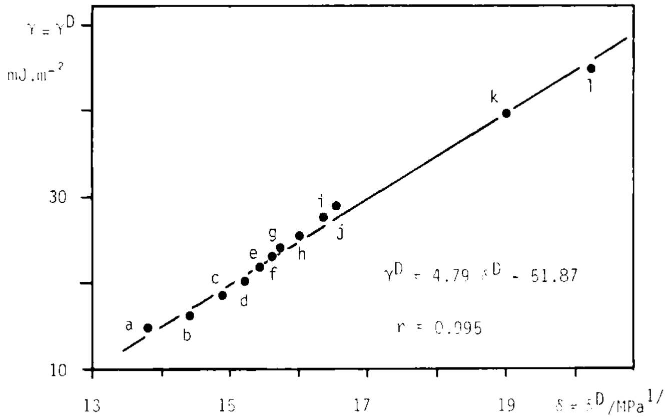

FIGURE 5 Linear relationship between the surface energy, γ, and the solubility parameters, δ, of nonpolar liquids. a: isopentane, b: pentane, c: hexane, d: heptane, e: octane, f: nonane, g: decane, h: dodecane, i: hexadecane, j: eicosane, k: tricresylphosphate, l: α-bromonaphthalene.

III.2. From Cohesion Parameters

Since surface free energy results from intermolecular forces, it is also closely related to cohesion parameters and, in particular, to solubility parameters, δ. Figure 5 demonstrates that an empirical relationship exists between γ and δ for nonpolar liquids. In assuming that this relation is valid for the dispersive components of polar liquids, we obtain

$$\gamma^D = 4.79\,\delta^D - 51.87 \tag{14}$$

δ^D being the dispersive component of the Hansen solubility parameter in $\mathrm{MPa}^{1/2}$ and γ^D being in $\mathrm{mJ{\cdot}m^{-2}}$. As explained for equation (13), the Group Contribution Method with homologous series of compounds having components deduced from equation (14) is also valid, but the direct calculation of γ^D is faster by using the δ^D of the polymer considered.

Experimental δ^D are given in Table VIII,[10,11] allowing one to determine the γ^D values of the polymers listed in Table II.

Since γ^D is related to n_D (Eq. (13)) and γ^D to δ^D (Eq. (14)), there is a relationship between δ^D and n^D. If δ^D is expressed in $\mathrm{MPa}^{1/2}$, this relationship is written:[12]

$$\delta^D = 19.53\,n_D - 11.35\,. \tag{15}$$

As a third possibility of evaluation, the dispersive components of polymers, γ^D, have been obtained by combining equations (14) and (15) and are given in Table II.

In most cases, it is observed that the theoretical γ^D are very close to the experimental results derived from wetting measurements.

IV DISCUSSION AND CONCLUSION

Although the GCM considers only the chemical structure of polymers and, therefore, neglects effects arising from the physical state of the polymers (amorphous or

TABLE VIII
Refractive indexes, n_D, and dispersive contributions to solubility parameters, δ^D ($MPa^{1/2}$), of polymers

Polymer	n_D	δ^D Ref. 8, 9	δ^D Eq. (15)
Polytetrafluoroethylene	1.356	—	15.1
Polyvinylidene fluoride	1.420	—	16.4
Polypropylene	1.474	17.2	17.4
Polyethylene	1.510	—	18.1
Polyisobutylene	1.508	16.0	18.1
Polyethyl methacrylate	1.485	17.6	17.7
Polymethyl methacrylate	1.489	18.6	17.7
Polyethyl acrylate	1.469	—	17.3
Polymethyl acrylate	1.476	—	17.5
Polyvinyl acetate	1.467	19.0	17.3
Polyvinyl chloride	1.550	18.6	18.9
Polyvinyl alcohol	1.530	—	18.5
Polyacrylonitrile	1.520	18.2	18.3

crystalline) and from possible segregation at the surface, it provides reliable values of the polymer surface free energies, γ.

This approach is essentially empirical but it is widely and successfully used for many other polymer properties such as density, rheological properties, transition temperature, etc.[11]

Concerning the effect of orientation phenomena on the surface free energy, the GCM considers implicitly that the orientation of a given group at a liquid/air interface will correspond to a comparable orientation at the polymer/air interface. This assumption is acceptable, in particular, for amorphous polymers which can be considered as highly viscous fluids. In the case of semicrystalline polymers, an amorphous surface is also usually formed when a polymer melt cools and solidifies, fractions of polymer not accommodated in the crystalline structure being rejected to the surface,[13] so that our calculations are not much changed by molecular orientation at the polymer/air interface, as a first approximation.

A more rigorous and sophisticated approach which takes into account the respective size of each carbonated group has been also considered. Although this Weighted Group Contribution Method appears very promising as a matter of accuracy, the simple Group Contribution Method permits a rapid and simple evaluation of γ.

The molecular weight dependence of surface free energy of polymers has been also considered in the case of polyethylene.

Several simple methods of estimation of the dispersive components of the polymers, γ^D, either from their optical or cohesive properties on the basis of Lifshitz theory, or empirical relationships, have been also described.

From our results, it is verified that $\gamma \approx \gamma^D$ for polymers having a saturated and nonpolar chemical structure and that $\gamma > \gamma^D$ for acrylic, vinylic or nitrile polymers. The difference $\gamma - \gamma^D$ can be attributed to polar or acid-base intermolecular interactions.

All the results obtained in this study are very similar to those deduced from wetting measurements. This good agreement justifies the validity of our different approaches.

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