

Equilibrium Swelling of Polystyrene by Alkanes and Carboxylic Acids: A Simple Quantitative Correlation Model

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ABSTRACT: In this study, we show that the equilibrium saturation swelling of polystyrene by linear alkanes and linear carboxylic acids, as reported earlier (Bernardo and Vesely, *Eur Polym J* 2007, 43, 4983, Bernardo and Vesely, *J Appl Polym Sci* 2008, 110, 2393) can be correlated quantitatively using a model where only the alkyl-chain lengths and the saturated vapor pressures of the organic liquids are considered. According to this model, at very low vapor pressures, the number of polystyrene

monomer units per solvent molecule is directly proportional to the alkyl chain length of the solvent molecule under consideration. At higher vapor pressures, the number of polystyrene monomer units per solvent molecule tends to become independent of its alkyl chain length. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1348–1356, 2010

Key words: miscibility; modeling; polystyrene; swelling

INTRODUCTION

It is known that when a solvent, in the liquid state, miscible with a polymer diffuses into a matrix of that polymer sorption occurs until an equilibrium saturation plateau is attained.^{1–7} Saturation is reached when the osmotic pressure of the solvent is counter-balanced by the elastic energy penalty upon stretching of the entangled polymer chains. This constant saturated swelling is, for the same polymer-solvent system and temperature (at atmospheric pressure), a highly reproducible and measurable physical quantity. Several different techniques have been used so far to detect this constant saturation plateau including gravimetry,^{1–3,5} FTIR,⁶ and neutron and x-ray analysis.⁷

The authors have recently measured the equilibrium swelling of polystyrene along the homologous series of carboxylic acids¹ and alkanes,² at different temperatures. Our results show that in all the studied systems, solubility diagrams of the upper critical solubility temperature type have been obtained.

The measurement, usually at 25°C, of the sorption of homologous series of organic compounds into polymer matrices has long been a standard method used to determine polymer solubility parameters.⁸ The solubility parameter of a polymer is usually considered as equal to the solubility parameter of the strongest solvent, producing the largest swelling.⁸ The solubility parameter approaches either in the form of total solubility parameter, as originally developed by Hildebrand and Scott⁹ or in the form of partial solubility parameters, as later developed by Hansen,¹⁰ have played during the last 60 years a central role in the interpretation and qualitative prediction of polymer solubility.

However, despite their irrefutable qualitative value, the solubility parameter approaches have several problems associated with them, as it was recently emphasized by several different authors.^{11–20} The correlation between polymer swelling and solubility parameters are often not precise enough to allow the quantitative prediction of the swelling of a polymer in a given liquid.^{11,12,17} The determination of polymer solubility parameter depends on the class of solvents used²⁰ and quite often severe deviations are observed and some data do not correlate even qualitatively. Furthermore, in certain cases, the criterion for differentiating “good” from “bad” solvents has a strong influence on the values obtained for the polymer Hansen solubility parameters (HSP).¹² In addition, the absence of a theoretically justified and experimentally

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observed linear relationship between the affinity and the mutual solubility of solvents with a given polymer throws doubt on the reliability of the HSP for polymers.¹² Finally, the calculated HSP values are highly dependant on the presence or the absence of a few critical solvents,¹² and the list of these critical solvents varies for each different polymer.

As the solubility parameter concepts do not appear to be sufficient to explain the swelling of polymers by solvents, new approaches have been recently proposed and tested by several authors.^{13–19} Jonquières et al.¹³ have attempted to correlate, with moderate success, polymer swelling with the empirical solvent polarity parameters $E_T(30)$ of Dimroth and Reichardt.²¹ Nakaie and coworkers^{14,15} found that polymer swelling can be best correlated with the composite parameter (AN + DN) where AN and DN are the solvent acceptor number and the solvent donor number, respectively. Makitra et al.^{16–18} have suggested the use of linear polyparameter relationships between the logarithm of the polymer swelling and the physicochemical characteristics of the organic solvents including the refractive index, the electric permittivity, Palm's basicity, Reichardt's electrophilicity, Hildebrand's solubility parameters, and molar volume. Another different approach was recently suggested by Nohilé et al.¹⁹ who have shown that in the swelling of butyl rubber by solvents, when solvents are grouped by chemical class, strong correlations between polymer swelling and both solvent molar volume and solvent saturation vapor pressure are obtained.

Despite all these efforts, no satisfactory solution allowing the prediction of polymer swelling from the physicochemical characteristics of the solvent-polymer system has been obtained yet.

It is known that the physical and chemical properties of compounds of different homologous series ("X-linear alkyl chain" where X is a functional group) converge between them when the size of the linear alkyl chain attached to the functional group increases.^{22–25} This happens due to the "dilution" of the effect of the functional group.²² In the hypothetical situation of two different functional groups, A and B, attached to linear alkyl chains of infinite size, i.e., "A-linear alkyl chain of infinite size" and "B-linear alkyl chain of infinite size" the physical and chemical properties of both compounds of different classes (like alkanes and carboxylic acids) will be very similar. Therefore, considering that liquid sorption into a particular polymer is dictated by the physical and chemical properties of the organic liquids, as has been previously suggested by many authors,^{13–19} when the alkyl chain-length in solvents of different classes increases, the swelling of a polymer on those liquids should converge and in the hypothetical limit of solvent infinite chain length, should become identical.

On the basis of this simple principle, in this study, we show that polystyrene swelling in linear carboxylic acids¹ and in linear alkanes² can be correlated quantitatively, using a very simple model where only the alkyl chain lengths and the liquid saturation vapor pressures are considered.

RESULTS AND DISCUSSION

In this study, we have correlated polystyrene swelling in two different classes of homologous organic liquids (alkanes and carboxylic acids) with the alkyl chain lengths and the saturated vapor pressures of those liquids. In the rest of this section, we introduce this correlation model, which is based on the simple principle mentioned earlier.

Vapor pressure

To avoid ambiguities with the possible use of different units to express the vapor pressure of organic liquids, in this study, instead of using absolute pressures we use relative vapor pressures (RVP), expressed as the coefficient of the absolute saturated vapor pressure of the liquid at the temperature under consideration to the normal atmospheric pressure (101325 Pa):

$$\frac{\text{Vapor pressure (Pa) at temperature } T}{101325 \text{ Pa}} = \text{Relative Vapour Pressure (RVP)} \quad (1)$$

At the normal boiling point of the liquid, this coefficient is always equal to 1. For convenience of presentation, the values of RVP are plotted on a natural logarithmic scale, as they span several different orders of magnitude. So, in the following discussion, we will be expressing the relative vapor pressure of each organic liquid as $\ln(\text{RVP})$. By representing vapor pressures in this way, their values are always negative and increase with increasing temperature, until they reach zero at the corresponding boiling points.

Saturated vapor pressures of the organic liquids at different temperatures can be calculated using eq. (2) and parameters A , B , C , D , and E taken from one of the most authoritative data compilations in the field of physical and thermodynamic properties of organic liquids²³ (Table I):

$$\text{VP} = \exp \left[A + \frac{B}{T} + C \ln T + DT^E \right] \quad (2)$$

In this equation, the temperature T is expressed in Kelvin and the calculated saturated vapor pressures are expressed in Pa. In Table I, the temperature

TABLE I
Values of the Fitting Parameters A , B , C , D , and E for eq. (2) on the Vapor Pressure of the Alkanes and Carboxylic Acids Used in this Work (Reproduced from Ref 23)

Name	A	B	C	D	E	Temperature range ($^{\circ}\text{C}$)	% Error
Vapor pressure of alkanes and carboxylic acids							
Octane (C_8)	9.6084E+01	-7.9002E+03	-1.1003E+01	7.1802E-06	2.0000E+00	-56 to 295	<3%
Iso-Octane ($i\text{-C}_8$)	1.2081E+02	-7.5500E+03	-1.6111E+01	1.7099E-02	1.0000E+00	-107 to 270	<3%
Decane (C_{10})	1.1273E+02	-9.7496E+03	-1.3245E+01	7.1266E-06	2.0000E+00	-29 to 344	<3%
Dodecane (C_{12})	1.3747E+02	-1.1976E+04	-1.6698E+01	8.0906E-06	2.0000E+00	-9 to 384	<3%
Tetradecane (C_{14})	1.4047E+02	-1.3231E+04	-1.6859E+01	6.5877E-06	2.0000E+00	6 to 419	<3%
Hexadecane (C_{16})	1.5606E+02	-1.5015E+04	-1.8941E+01	6.8172E-06	2.0000E+00	19 to 450	<3%
Hexanoic acid (C_6)	1.3863E+02	-1.3776E+04	-1.5953E+01	1.0131E-17	6.0000E+00	-3 to 386	<3%
Heptanoic acid (C_7)	1.5280E+02	-1.5046E+04	-1.7901E+01	1.0680E-17	6.0000E+00	-7 to 404	<5%
Octanoic acid (C_8)	1.4016E+02	-1.4813E+04	-1.6004E+01	6.4239E-18	6.0000E+00	17 to 421	<5%
Decanoic acid (C_{10})	1.2336E+02	-1.4680E+04	-1.3474E+01	1.9491E-18	6.0000E+00	32 to 448	<5%
Lauric acid (C_{12})	2.0156E+02	-2.0484E+04	-2.4334E+01	8.0558E-18	6.0000E+00	44 to 469	<5%
Myristic acid (C_{14})	2.0948E+02	-2.1776E+04	-2.5321E+01	7.2474E-18	6.0000E+00	55 to 491	<5%
Palmitic acid (C_{16})	6.3503E+02	-4.5621E+04	-8.7646E+01	3.5199E-05	2.0000E+00	63 to 502	<3%

The temperature range of applicability of these parameters is shown in the next to the last column and the reliability of the correlation is shown in the last column.

range of applicability of those parameters (in Celsius $^{\circ}\text{C}$) as well as the estimated error involved, as taken from Daubert et al. are indicated.²³

The saturated vapor pressures of alkanes and carboxylic acids, as calculated using eq. (2) and the parameters on Table I, are represented graphically on a logarithmic scale in Figure 1, together with some discrete saturation vapor pressure data values taken from another authoritative literature source.²⁵ As Figure 1(a) illustrates, in the case of alkanes there is an excellent agreement between the values from both literature sources. In the case of carboxylic acids, as shown in Figure 1(b), there is also an excel-

lent agreement between both literature sources except for a very small deviation observed at the lowest vapor pressures, $\ln(\text{RVP})$ less than -9 . This gives us a strong confidence about the high reliability of the parameters in Table I.

Concentration

In this study, we express the solvent concentration inside the polymer as the ratio of the number of monomer units of PS per liquid molecule. A straightforward calculation shows that this quantity can be obtained from the solubility values X_L (i.e.,

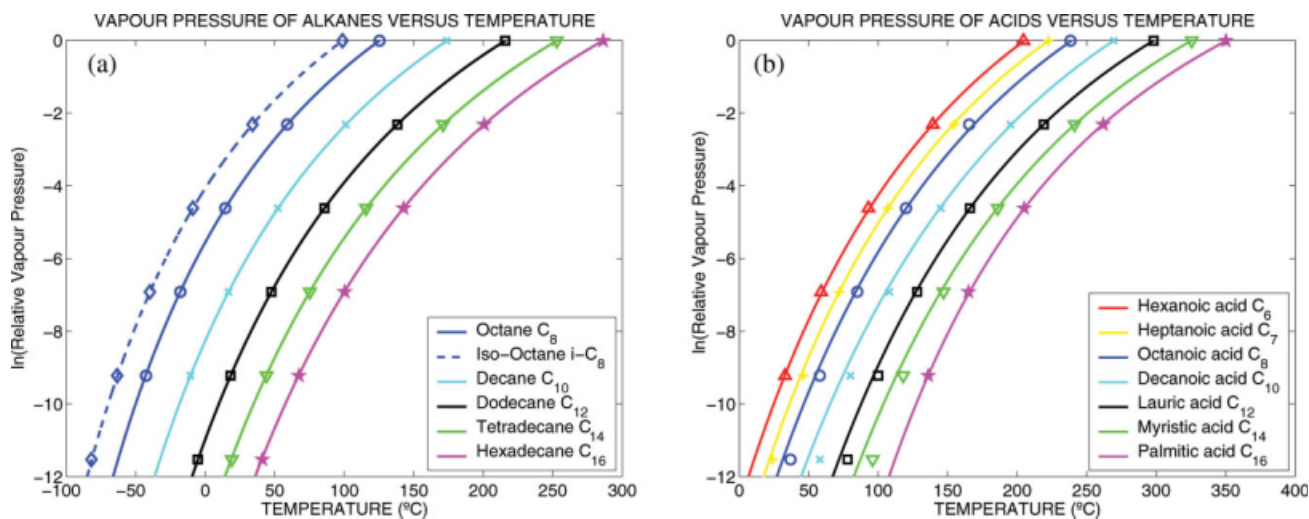


Figure 1 Vapor pressure of organic liquids as a function of temperature, as taken from Daubert et al.²³ (continuous lines) and from Lide²⁵ (discrete data). (a) Alkanes: (\circ) octane (C_8); (\diamond) isooctane ($i\text{-C}_8$); (\times) decane (C_{10}); (\square) dodecane (C_{12}); (∇) tetradecane (C_{14}); (five-pointed star) hexadecane (C_{16}). (b) Carboxylic acids: (Δ) Hexanoic acid (C_6); (+) Heptanoic acid (C_7); (\circ) Octanoic acid (C_8); (\times) Decanoic acid (C_{10}); (\square) Lauric acid (C_{12}); (∇) Myristic acid (C_{14}); (five-pointed star) Palmitic acid (C_{16}). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

TABLE II
Relative Vapor Pressure, as Defined in eq. (1), and Solubility of Alkanes at Different Temperatures

Liquid	Temperature (°C)	Relative vapor pressure (RVP)	ln(RVP)	Monomer units of PS/molecules of L
Octane (C ₈)	75	1.9009 e-1	-1.6602 e0	1/0.224
	95	3.9093 e-1	-9.3923 e-1	1/0.259
	125	9.8097 e-1	-1.9213 e-2	1/0.329
Decane (C ₁₀)	95	7.6472 e-2	-2.5708 e0	1/0.189
	125	2.3476 e-1	-1.4492 e0	1/0.252
	145	4.4453 e-1	-8.1074 e-1	1/0.314
Dodecane (C ₁₂)	95	1.5768 e-2	-4.1498 e0	1/0.134
	125	5.9563 e-2	-2.8207 e0	1/0.188
	145	1.2639 e-1	-2.0684 e0	1/0.244
Tetradecane (C ₁₄)	95	3.3007 e-3	-5.7136 e0	1/0.0941
	125	1.5376 e-2	-4.1749 e0	1/0.142
	145	3.6728 e-2	-3.3042 e0	1/0.188
	165	7.9283 e-2	-2.5347 e0	1/0.226
Hexadecane (C ₁₆)	95	7.1742 e-4	-7.2398 e0	1/0.0669
	125	4.1120 e-3	-5.4938 e0	1/0.105
	145	1.1030 e-2	-4.5071 e0	1/0.139
	165	2.6351 e-2	-3.6362 e0	1/0.177
Iso-octane (i-C ₈)	65	3.3836 e-1	-1.0836 e0	1/0.169
	75	4.4668 e-1	-8.0591 e-1	1/0.180
	95	8.8628 e-1	-1.2072 e-1	1/0.193

percentage mass of solvent in total mass), previously reported,¹⁻² using the following equation:

$$\frac{\text{Monomer units of PS}}{\text{Molecules of L}} = \frac{(100 - X_L)M_{wL}}{104.149X_L} \quad (3)$$

where M_{wL} is the molecular weight of the liquid and 104.149 g/mol is the molar mass of the monomer unit of PS.

This way of representing concentration is the one that gives us the clearest picture of the microscopic details of the system. If we assume that the liquid molecules are homogeneously distributed inside the polymer and if the ratio in eq. (3) has, for example, the value 5 then we can consider our system as one where each liquid molecule has, at least, five benzene rings surrounding (solvating) it. In the previous sentence, we say "at least" because, assuming a system of homogeneously distributed solvent molecules and PS monomer units, the solvation numbers obtained with eq. (3) are not real solvation (coordination) numbers of the liquid molecules (calculated by considering nearest benzene rings to one solvent molecule) but just apparent solvation numbers (calculated from the bulk composition). The real solvation number of each organic liquid molecule is higher than that obtained with eq. (3) because each benzene ring of the polystyrene matrix may be solvating simultaneously (i.e., adjacent to) more than one liquid molecule.

Our proposed model

The values of the RVP, as given by eq. (1), and ln(RVP) are presented in Table II for alkanes. The

values of the saturated concentrations of the liquid inside polystyrene, expressed in "Number of PS monomer units per liquid molecule" [eq. (3)] are also included. The results from Table II are plotted in Figure 2.

Figure 2 shows that the experimental points that correspond to the linear alkanes all follow a trend along an average continuous line. The experimental points of isooctane (2,2,4-trimethylpentane), the only branched alkane used in this study, are clearly further apart and do not follow the same trend. This seems to suggest that there exists a relationship

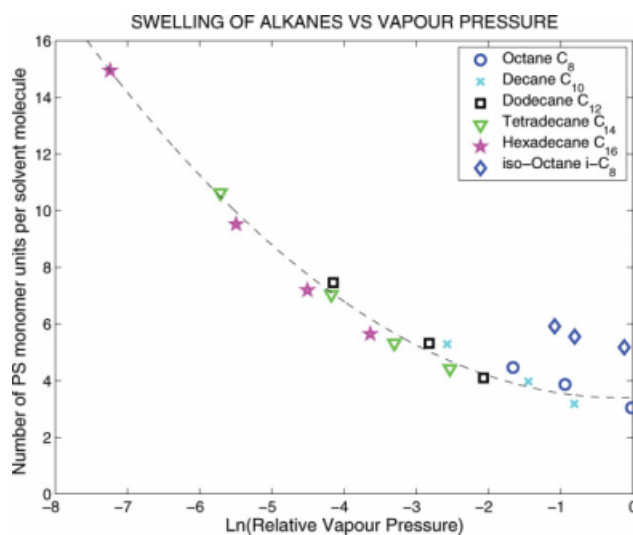


Figure 2 Equilibrium saturated sorption of alkanes: "Number of PS monomer units per solvent molecule" versus "ln(Relative vapor pressure)." [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

TABLE III
Relative Vapor Pressure, as Defined in eq. (1), and Solubility of Carboxylic Acids at Different Temperatures

Liquid	Temperature (°C)	Relative vapor pressure (RVP)	ln(RVP)	Monomer units of PS/molecules of L
Hexanoic acid (C ₆)	35	1.2182 <i>e</i> -4	-9.0130 <i>e</i> 0	1/0.573
	55	6.8405 <i>e</i> -4	-7.2875 <i>e</i> 0	1/0.734
	75	2.9847 <i>e</i> -3	-5.8143 <i>e</i> 0	1/0.897
Heptanoic acid (C ₇)	45	1.0494 <i>e</i> -4	-9.1621 <i>e</i> 0	1/0.425
	55	2.5541 <i>e</i> -4	-8.2726 <i>e</i> 0	1/0.476
	75	1.2407 <i>e</i> -3	-6.6921 <i>e</i> 0	1/0.579
Octanoic acid (C ₈)	55	9.9266 <i>e</i> -5	-9.2177 <i>e</i> 0	1/0.281
	75	5.1675 <i>e</i> -4	-7.5680 <i>e</i> 0	1/0.341
	105	4.0542 <i>e</i> -3	-5.5080 <i>e</i> 0	1/0.502
Decanoic acid (C ₁₀)	125	1.2800 <i>e</i> -2	-4.3583 <i>e</i> 0	1/0.640
	65	4.3551 <i>e</i> -5	-10.0416 <i>e</i> 0	1/0.156
	75	1.0239 <i>e</i> -4	-9.1867 <i>e</i> 0	1/0.177
Lauric acid (C ₁₂)	95	4.7734 <i>e</i> -4	-7.6473 <i>e</i> 0	1/0.221
	105	9.5570 <i>e</i> -4	-6.9531 <i>e</i> 0	1/0.247
	115	1.8296 <i>e</i> -3	-6.3037 <i>e</i> 0	1/0.278
Myristic acid (C ₁₄)	125	3.3614 <i>e</i> -3	-5.6954 <i>e</i> 0	1/0.311
	145	1.0157 <i>e</i> -2	-4.5896 <i>e</i> 0	1/0.403
	85	3.5354 <i>e</i> -5	-10.2501 <i>e</i> 0	1/0.0998
Palmitic acid (C ₁₆)	95	8.5791 <i>e</i> -5	-9.3636 <i>e</i> 0	1/0.112
	105	1.9532 <i>e</i> -4	-8.5409 <i>e</i> 0	1/0.131
	125	8.5412 <i>e</i> -4	-7.0654 <i>e</i> 0	1/0.167
Myristic acid (C ₁₄)	135	1.6559 <i>e</i> -3	-6.4034 <i>e</i> 0	1/0.187
	145	3.0691 <i>e</i> -3	-5.7864 <i>e</i> 0	1/0.218
	165	9.3418 <i>e</i> -3	-4.6733 <i>e</i> 0	1/0.292
Myristic acid (C ₁₄)	105	5.0275 <i>e</i> -5	-9.8980 <i>e</i> 0	1/0.0798
	125	2.4786 <i>e</i> -4	-8.3026 <i>e</i> 0	1/0.0994
	135	5.0745 <i>e</i> -4	-7.5861 <i>e</i> 0	1/0.114
Palmitic acid (C ₁₆)	145	9.8995 <i>e</i> -4	-6.9179 <i>e</i> 0	1/0.132
	165	3.3087 <i>e</i> -3	-5.7112 <i>e</i> 0	1/0.173
	185	9.5036 <i>e</i> -3	-4.6561 <i>e</i> 0	1/0.235
Palmitic acid (C ₁₆)	125	3.6425 <i>e</i> -5	-10.2203 <i>e</i> 0	1/0.0656
	145	2.1161 <i>e</i> -4	-8.4608 <i>e</i> 0	1/0.0832
	165	9.3704 <i>e</i> -4	-6.9728 <i>e</i> 0	1/0.105
	185	3.3174 <i>e</i> -3	-5.7086 <i>e</i> 0	1/0.135

between the solubility of the alkane molecules inside polystyrene matrices, their saturated vapor pressures, and their structural shape.

We have also plotted in Figure 2 the average line (dashed line) to which all the solubility results of the linear alkanes seem to fit. The small scatter observed, around the average line, is well within the experimental error associated with the alkanes sorption measurements.² As was clearly mentioned in our previous publication,² due to the occurrence of some microvoiding in the measurement of polystyrene swelling in alkanes, the corresponding experimental error associated is higher than in the measurement of polystyrene swelling in carboxylic acids.

By studying the swelling of polystyrene in alkanes,² it was our aim to have a system of reference. Alkanes are the simplest class of organic compounds as they only contain -CH₂- and -CH₃ units ("functional groups"). As they do not contain any functional group with oxygen or other electronegative atoms, their molecules interact with each other

and with other molecules (e.g., PS chains) simply by London dispersion interaction forces. Therefore, in our model, they constitute our "ideal" system of reference, against which the solubility of carboxylic acids can be compared.

In Table III, the data for carboxylic acids are shown. The values of their saturated sorption concentrations are expressed in "Number of PS monomer units per liquid molecule" and also shown are the values of their relative vapor pressures at particular temperatures. In Figure 3, we have plotted the "Number of PS monomer units per liquid molecule" versus "ln (RVP)" for carboxylic acids. We also show in the same graph, just for reference, as black filled squares and a dashed line the results previously shown for linear alkanes. In Figure 4, we represent the same data as in Figure 3 but with the y-axis inverted, i.e., in the y-axis we represent "Number of solvent molecules per PS monomer unit" instead of "Number of PS monomer units per solvent molecule."

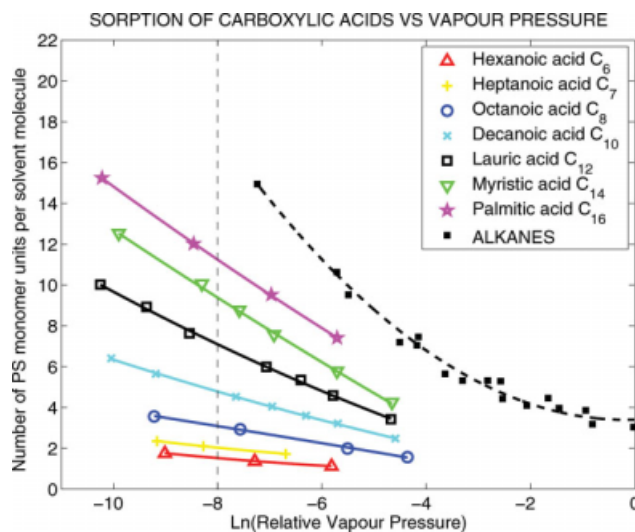


Figure 3 Equilibrium saturated sorption of carboxylic acids: "Number of PS monomer units per solvent molecule" versus "ln(Relative vapor pressure)." [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

As we can see in Figure 3 and more clearly in Figure 4, when the alkyl chain length of a carboxylic acid increases, the corresponding line gradually approaches the line of the alkanes. This correlation is due to the reduction in concentration of the $-\text{COOH}$ functional groups and consequently to the "dilution" of their effect. We may consider, as a good approximation, that a molecule with a terminal $-\text{COOH}$ group connected to a linear alkyl chain of infinite length behaves in the same way as a linear

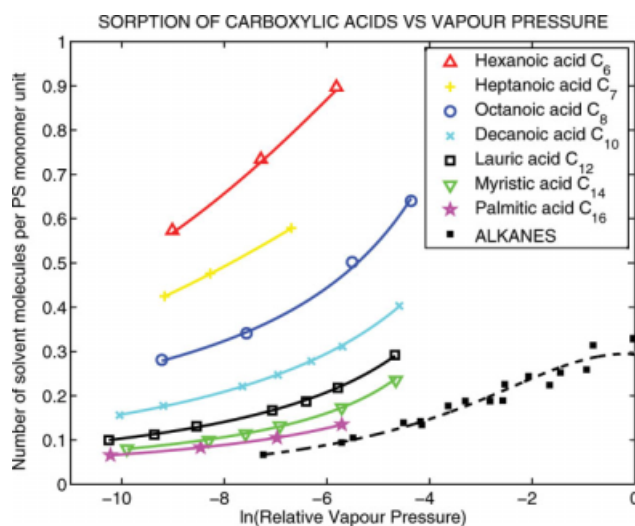


Figure 4 Equilibrium saturated sorption of carboxylic acids: "Number of solvent molecules per PS monomer unit" versus "ln(Relative vapor pressure)." [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

TABLE IV
Values of the Parameters A , B , and C that Give the Best Fit of the Polynomial $y = Ax^2 + Bx + C$ to the Experimental Results

	A	B	C
Hexanoic acid (C_6)	0.01682	0.05232	0.8504
Heptanoic acid (C_7)	0.01901	0.04804	1.197
Octanoic acid (C_8)	-0.003012	-0.4586	-0.3998
Decanoic acid (C_{10})	0.01977	-0.4225	0.1440
Lauric acid (C_{12})	0.03598	-0.6416	-0.3298
Myristic acid (C_{14})	0.01971	-1.309	-2.309
Palmitic acid (C_{16})	0.02909	-1.269	-0.7721

alkane of infinite length, i.e., the influence of a functional group in a molecule, decreases continuously as the alkyl chain length of that molecule increases.²²

For each system in Figure 3, we have determined, using the least squares method, the values of the parameters A , B , and C of the quadratic polynomial function $y = Ax^2 + Bx + C$ that give the best fit to the experimental points, where y is the "Number of PS monomer units per solvent molecule" and x is the "ln(RVP)." The values obtained for each carboxylic acid are shown in Table IV. In Figure 3, we also show for each system the corresponding line, calculated using the parameters in Table IV, connecting the first and the last points of interest. In doing this fitting of experimental points to polynomials, our aim is solely to facilitate the quantitative analysis of our data and to make that analysis as accurate as possible using continuous analytical functions.

As we can see in Figure 3, for the same ln(RVP), the number of PS monomer units per solvent molecule increases proportionally to the size of the alkyl chain of that molecule. To make this clearer, we have drawn a vertical black dashed line at $\ln(\text{RVP}) = -8$. By measuring the interception points of this vertical line with the oblique lines in the graph, we can determine for that particular value of ln(RVP) what is the number of PS monomer units, $-(\text{C}_6\text{H}_5-\text{CH}-\text{CH}_2)-$, solvating the several different carboxylic acids. To test more precisely this type of relationship, we have also performed this calculation analytically. We have calculated for each carboxylic acid (using the predetermined polynomial functions), the number of PS monomer units per solvent molecule at the values of ln(RVP) of -10 , -9 , -8 , -7 , -6 , and -5 . In this calculation, we have only considered interpolation points because extrapolations would have no physical support. The results are shown in Table V. In Figure 5, we have plotted for each different value of ln(RVP), using the values in Table V, the "Number of PS monomer units per solvent molecule" versus "Number of C atoms in the alkyl chain of that molecule." As shown in

TABLE V
Number of Monomer Units per Carboxylic Acid Molecule at
Different Vapor Pressures

	ln(RVP)					
	-10	-9	-8	-7	-6	-5
Hexanoic acid (C ₆)		1.742	1.508	1.308	1.142	
Heptanoic acid (C ₇)		2.304	2.029	1.792		
Octanoic acid (C ₈)		3.484	3.076	2.663	2.243	1.818
Decanoic acid (C ₁₀)	6.346	5.548	4.789	4.070	3.391	2.751
Lauric acid (C ₁₂)	9.684	8.359	7.106	5.924	4.815	3.778
Myristic acid (C ₁₄)	12.752	11.069	9.424	7.820	6.255	4.729
Palmitic acid (C ₁₆)	14.827	13.005	11.242	9.536	7.889	

Figure 5, for carboxylic acid molecules with seven or more C atoms (i.e., from heptanoic to palmitic acid), the number of PS monomer units solvating each acid molecule is directly proportional to the length of that molecule. We have also plotted straight lines ($y = Ax + B$) in Figure 5, obtained using regression analysis, to stress the linear relationship. The values of the parameters A and B that give the best fit of each straight line to the experimental results and the values of the corresponding correlation coefficients R are given in Table VI. The excellent correlation coefficients obtained ($R \cong 1$) emphasizes the nearly perfect linearity of the graphs. This linear relationship is logical considering that a long solvent molecule (e.g., palmitic acid) needs proportionally more benzene rings to solvate it, than a shorter solvent molecule (e.g., heptanoic acid).

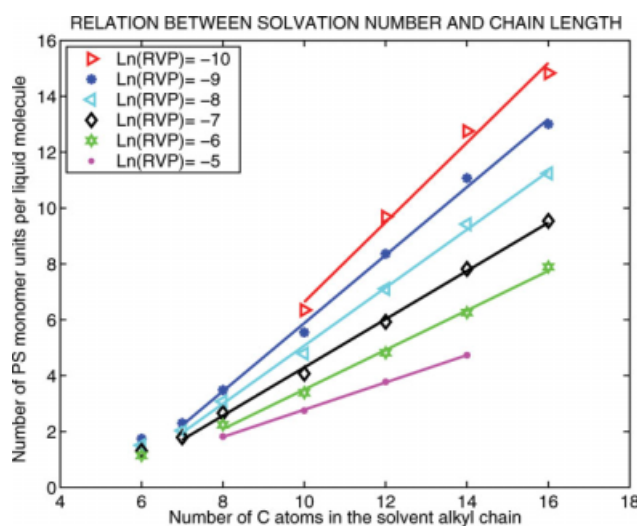


Figure 5 The relationship between the size of the alkyl chain in the carboxylic acid molecules and the number of PS monomer units solvating it. As clearly shown, the dependency on the solvent alkyl chain length (slope of the lines) decreases when the vapor pressure increases. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

In Figure 5, the points corresponding to hexanoic acid deviate from linearity. This deviation may be due to experimental errors, as was mentioned in our previous study,¹ samples saturated with hexanoic acid are very much swollen and are very soft and sticky (even after cooling) and consequently very difficult to handle. Their weighing is, therefore, more prone to experimental error than the weighing of the other samples. Alternatively, the observed deviation may be caused by the proximity of the $-\text{COOH}$ group, i.e., it may be the case that the solvation of the $-\text{CH}_2-$ units closest to the $-\text{COOH}$, may be affected by the proximity of the $-\text{COOH}$ group.

We can see in Figure 3 that with the increasing vapor pressure, the lines of individual carboxylic acids converge. Therefore, in Figure 5, the slope of the lines decreases as vapor pressure increases, i.e., for example the line corresponding to $\ln(\text{RVP}) = -5$ is much less steep than the line corresponding to $\ln(\text{RVP}) = -10$. This means that at higher vapor pressures, the number of monomer units per solvent molecule is much less dependent on the size of the alkyl chain. This behavior of carboxylic acids is compatible with the behavior of the alkanes in Figure 1. At higher vapor pressures, the number of PS monomer units per alkane molecule seems to depend solely on the vapor pressure and not on the alkyl

TABLE VI
Values of the Parameters A and B that Give the Best Fit of the Straight Line ($y = Ax + B$) to the Experimental Results and Values of the Corresponding Correlation Coefficients, as Determined by Regression Analysis

ln(RVP)	A	B	R
-10	1.426	-7.623	0.9948
-9	1.218	-6.303	0.9986
-8	1.039	-5.319	0.9990
-7	0.8636	-4.343	0.9991
-6	0.7078	-3.575	0.9982
-5	0.4880	-2.099	0.9998

chain length (for example points corresponding to octane and decane appear very close to each other in Fig. 1). At such high vapor pressures, we may consider that a line in Figure 5 would have a slope approximately equal to zero.

One possible explanation for this is that solvent molecules inside the polymer matrix at lower vapor pressures, due to their lower rotational energies, adopt preferentially linear conformations. On the other hand, at higher vapor pressures the solvent molecules have higher rotational energies (higher entropy), and therefore, may adopt many different nonlinear conformations inside the polymer matrix.

According to this model, the $-\text{COOH}$ group has a very favorable interaction with polystyrene and the $-\text{CH}_2-$ and $-\text{CH}_3$ groups have a very weak interaction. Therefore, when the alkyl chain length increases, the very favorable interaction of the $-\text{COOH}$ group becomes progressively diluted by the weak interactions of the $-\text{CH}_2-$ and $-\text{CH}_3$ groups. This model is, however, unable to explain the very anomalous sorption behavior of acetic acid reported in our previous study.¹ As mentioned before,¹ such an anomalous behavior of acetic acid is probably due to the fact that acetic acid exists mainly in the form of dimers. In our previous study,¹ we were unable to obtain reliable values for the swelling of polystyrene in butyric and propionic acids. Therefore, those acids could not be considered in the present study.

The extension of this model to other homologous series, is still in progress. However, we anticipate that homologous series ("X-linear alkyl chain") containing a functional group (X) that interacts favorably with polystyrene (as $-\text{COOH}$ does) will behave in a way similar to carboxylic acids. On the other hand, for homologous series ("Y-linear alkyl chain") containing a functional group (Y) that has a repulsive interaction with polystyrene, we expect that when the alkyl chain length increases the corresponding lines will approach the line of the alkanes from the opposite side, i.e., "top \rightarrow line of alkanes" in Figure 3 and "bottom \rightarrow line of alkanes" in Figure 4.

Although the values obtained with eq. (3) are apparent solvation numbers, it can be easily shown that in a system where solvent molecules and monomer units are homogeneously distributed the apparent solvation number should increase linearly with the solvent molecule chain length. Consider a cube with $1000 \times 1000 \times 1000$ small cubic cells and suppose that there is a small solvent molecule per cell and there is a benzene ring in each face of a cell. In such a system, there are $1\text{E}9$ solvent molecules and $3\text{E}9$ benzene rings, and therefore, the apparent solvation number is $3\text{E}9/1\text{E}9 = 3$ and the real solvation number is 6 (one benzene ring in each face of the small cube). Let us consider the same large cubic system

but let us now suppose that each solvent molecule occupies two cubic cells instead of just one. In such a system, there are $0.5\text{E}9$ solvent molecules and just $2.5\text{E}9$ benzene rings (a benzene ring cannot pass through the middle of a solvent molecule). Therefore, in such a system, the apparent solvation number is $2.5\text{E}9/0.5\text{E}9 = 5$ and the real solvation number is 10. A continuation of this reasoning rapidly lead us to the conclusion that if n is the number of cells occupied by each solvent molecule, then the apparent solvation number is always equal to $2n+1$ and the real solvation number is always twice that value, i.e., $4n + 2$. Therefore, the apparent solvation number should increase linearly with the alkyl chain length, as we observed.

Finally, we must emphasize that in this study, we have used polynomials only as a way of giving more rigor to our presentation and to the final conclusions presented in Figure 5.

CONCLUSIONS

In the present study, we show that the equilibrium swelling of polystyrene along the series of linear 1-carboxylic acids can be correlated quantitatively using a model where only the alkyl chain lengths and the saturated vapor pressures of the liquids are considered. We also show that those equilibrium swelling values can be correlated qualitatively with the equilibrium swelling values of polystyrene in linear alkanes. Our results corroborate recent results and conclusions obtained by Nohil  et al.¹⁹ in the study of the swelling of butyl rubber by solvents.

The model presented here is still in an embryonic state and will obviously need to be tested with many other homologous series of compounds. This will require a very meticulous, accurate, and time consuming study of polystyrene swelling in other homologous series of organic liquids, at several different temperatures.

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