

Use of Empirical Polarity Parameters to Describe Polymer/Liquid Interactions: Correlation of Polymer Swelling with Solvent Polarity in Binary and Ternary Systems

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SYNOPSIS

Dimroth and Reichardt polarity parameters $E_T(30)$ have been used, in a new approach, to quantitatively describe the swelling features due to polymer liquid interactions in binary and ternary systems. With the help of a polyurethaneimide (PUI) synthesized from polytetramethyleneglycol 650, sorption of pure liquids was first examined, and it was shown that a linear relationship between the molar swelling G_m and the $E_T(30)$ values well fits the experimental data of each of the two series studied, i.e., aliphatic alcohols and linear ethers: $G_m = a + b E_T(30)$. The slope value b , regarded as the sensitivity of the polymer to the liquid polarity, is 3 times higher for the aprotic series. The proposed correlation was further proved valid from the study of published results concerning nine binary systems polymer-liquid, whatever the polarity of the liquids in a given family (alcohols, esters, ketones, hydrocarbons) and the nature of the polymer. Finally, that method was tested on two types of PUI-alcohol-ether ternary systems, and it was found for each case that the partial molar swelling due to an homologous set of solvents can also be described by a similar law. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Lots of work have been devoted to study polymer-liquid interactions in order to allow their modelization and find relationships leading to the quantitative prediction of their intensity.

One of the common approach consists of expressing the amount of sorbed liquid against its activity in the swollen polymer. This thermodynamic approach can be applied to binary (polymer-liquid 1) or ternary (polymer-liquid 1-liquid 2) systems, but the corresponding laws often remain complex, like in the case of the Flory-Huggins model¹ or its extension to crosslinked polymers.² However, even in the simplest case of a pure liquid, very numerous reported results have only led to very general con-

siderations about influence of size, polarity, or chemical nature of the penetrative molecule on its ability to interact with a given polymer.³⁻⁶

The correlation attempts, mainly those using the Hildebrand solubility parameters,⁷ have revealed interesting tendency relationships that, unfortunately, are often not precise enough to allow the quantitative prediction of the swelling of a polymer in a given liquid.⁸⁻¹¹

We report here the first results of a different approach using the solvent polarity parameters. These parameters, widely used in physical organic chemistry, are a relative measurement of the local interactions (i.e., interactions at a molecular scale) between solute and solvent. The most famous ones are measurements of solvatochromic effects, the first series of values being due to Kosower (Z value).¹² In the present study, the $E_T(30)$ values of Dimroth and Reichardt¹³ have been used. For a given solvent, the $E_T(30)$ polarity parameter is defined as the

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transition energy (related to solvation energy and measured in kcal/mol) for the longest wavelength Vis absorption band of the pyridinium-*N*-phenoxide betaine called Reichardt's dye. The characteristic wavelength of this dye decreases as solvent polarity increases, allowing the definition of the most comprehensive polarity scale so far known which, thus, remains the reference one.

In the first part of this study, the sorption of two types of polar pure liquids (i.e., activity = 1), alcohols, and ethers, has been examined in the case of a polar polymer. The chosen reference polymer is a polyurethaneimide (PUI) block copolymer in which alternate oligomeric flexible segment and very hard polar blocks. The flexible segment of moderate polarity and suitable size (oligoether PTMG of 650 daltons) are strongly physically crosslinked by the pyromellitimide hard blocks. Thus, the solvation effects mainly affect the flexible segments endowed with high but limited swelling properties which avoid to be too close to the solubility conditions.

Then the investigations have been extended to several other typical cases of binary systems already reported in the literature which are different in the polarity of the polymers and liquids used.

At last, the case of real ternary systems (and not pseudobinary ones) was also able to be considered due to the ability of the reference PUI to give relatively high swelling values in both pure liquids, alcohols, and ethers, leading to only moderate sorption selectivities in mixture of these solvents.

EXPERIMENTAL

Material

The used polyurethaneimide was prepared by modifying the procedure of Masiulani,¹⁴ which allows the obtention of an imide function by reaction of a cyclic anhydride with an isocyanate. An α - ω diisocyanate block was first prepared by reaction of 4,4'-methylenebis-phenylisocyanate (MDI, from Tokyo KASEI, previously distilled under vacuum) with polytetramethyleneglycol (PTMG 650, Polysciences). The resulting macrodiisocyanate was then chain extended by reaction with pyromellitic dianhydride (AP, Aldrich 99%, previously bisublimed under vacuum) to give the final copolymer with 75–80% yield. η (C_o) = 1,2 dL/g measured in dimethylacetamide (C_o = 1 mg/mL) at 25°C—IR (film on KBr disc): ν (cm^{-1}): ether: 1110, urethane: 3290, AMIDE I: 1725, AMIDE II: 1530, AMIDE III: 1220, imide: 1780, 1725, 1510, 715.

Thick films ($e = 600 \mu m$, $\phi \simeq 13$ cm) were casted on a teflon plate from a polymer solution in dimethylformamide (DMF, 10 wt %). After solvent evaporation in a thermally controlled oven at 40°C, the films were thermally cured under vacuum (10°C/h from 50 to 100°C and 130°C during 15 h) to complete the formation of imide rings. Before sorption measurements, the films were washed carefully with anhydrous ethanol in order to extract unreacted starting reagents and then dried under vacuum at 70°C to constant weight.

Reagents

All the solvents used for the sorption experiments were of analytical grade, their water content exceeding not 0.1 wt %, except in the case of the most polar MeOH and EtOH (up to 0.2 wt %) according to GC analysis.

Concerning the E_T determinations (see below), all the investigated ethers were subjected to drastic purifications in order to eliminate the most polar impurities responsible for large errors on the E_T values.^{15,16} Methyl *t*-butyl ether (MTBE, Solvant Documentation Synthese, analytical grade anhydrous) and Ethyl *t*-butyl ether (ETBE, provided by Institut Français du Pétrole) were distilled successively from Na (twice for ETBE) and from Li Al H₄ just before use. Methyl butyl ether (MeOBu, Aldrich 99%, first dried on Na) and dibutylether (BuOBu, Aldrich analytical grade) were distilled from CaH₂ just before use, whereas *n*-Butyl acetate (Aldrich anhydrous 99+ %) was used as received.

The liposoluble Reichardt dye,¹⁷ stored under argon in the dark, was kindly provided by C. Reichardt at request of C. Laurence (Laboratoire de Spectrochimie Moléculaire de l'Université de Nantes 2, France) and used without further purification.

Swelling Measurements in Pure Liquids

The PUI swellings in pure liquids were measured by the well-known gravimetric method.^{3,4,6} Polymer samples cut from the previous prepared thick films were weighed (m_o) and immersed in the solvent in a tightly closed bottle. The amount of polymer was calculated to provide at least 0.5 g of sorbed liquid. After standing 24 h at 30°C \pm 0.5°C, the polymer pieces were blotted very quickly with filter paper to remove the superficial liquid and weighed in an other tightly closed bottle (accuracy = 0.1 mg). This procedure was then repeated with the same sample until the obtention of a stable swelling value. The thermodynamic equilibrium was generally attained after

2 or 3 days. The mass m of the swollen polymer allows the definition of:

the weight swelling G_w

$$= \frac{m - m_0}{m_0} \text{ (g solvent/g dry polymer)}$$

the molar swelling G_m

$$= \frac{G_w \times 1000}{M} \text{ (mmol solvent/g dry) polymer) with}$$

M = solvent molecular weight.

Swelling Measurements in Binary Mixture of Liquids

Analogous measurements of the total sorption G_w were carried out with binary alcohol/ether solutions. Mixture composition was kept constant (error less than 1% as checked by GC analysis) at the equilibrium by using a sufficient large amount of the starting mixture (about 200 mL for 3–4 g polymer).

The swelling contribution of each liquid was then determined after desorption in a glass apparatus composed of a desorption tube and a condensation trap that can be separated from each other by a stopcock. The apparatus used was also designed to avoid any contamination of the condensed liquid by atmosphere moisture. The desorbed liquid was recovered under reduced pressure by cold condensation (liquid air) of the vapors released from the swollen polymer slowly heated from 20°C to 80°C for 8 h. For highly volatile compounds (i.e., BuOMe, MTBE), the heating was restricted to the last 3 h to avoid a too sudden release of solvents. The condensed mixture was then allowed to warm to room temperature under atmospheric pressure after it was isolated from the dry polymer to prevent any reabsorption of organic vapors.

The experiment was checked by a mass balance and the weight composition (weight fractions C_{alcohol} and C_{ether}) was determined by GC analysis and the partial swellings calculated as follow:

partial weight swelling G_{w_i}

$$= C_i G_w \text{ in g liquid/g dry polymer}$$

partial molar swelling G_{m_i}

$$= \frac{G_{w_i} \times 1000}{M_i} \text{ in mmol of liquid/g dry polymer}$$

M_i = molecular weight of liquid "i."

Solvent Polarity Parameters Determination

Most of the values needed were already reported in the literature.¹³ However, some missing values (ETBE, BuOMe) were determined as usual with the more lipophilic Reichardt dye¹⁸ at 25°C (reference temperature) as well as some values that had to be reconsidered (MTBE, n-BuOAc).

A few crystals of the probe were dissolved in the liquid introduced in a 0.5 cm thermostated quartz cell. Only a very small amount of the dye was required so that values of the observed absorbance at the maximum of the longest Vis wavelength ($\lambda > 500$ nm) were between 1 and 2. Spectra were recorded on a spectrophotometer Shimadzu UV-2101 PC and the data were computed with a software allowing the determination of the wavelength of peak maxima. Each measurement was repeated not less than five times and in the worst cases, i.e., for the less polar ethers, the measurement precision was in the range of ± 0.7 nm. An E'_T value was then defined from the measured λ^{max} (nm) by the equation: $E'_T = 28, 590/\lambda^{\text{max}}$ and converted into the related $E_T(30)$ polarity value according to the linear following relationship, valid for all solvents except alcohols:¹⁸

$$E'_T = 0.9424 E_T(30) + 1.808 \quad (r = 0.9990 ; s = 0.17).$$

The following values were, thus, determined, $E_T(30)$ in kcal/mol: ETBE: 33.7; BuOMe: 34.3; MTBE: 34.5; n-Bu-OAc: 37.0.

RESULTS AND DISCUSSION

Sorption of Pure Solvents in PUI

The study of PUI sorptions were carried out at 30°C with two series of aliphatic liquids, ethers, and alcohols, of different solvation power. The acyclic ethers used, which are moderately polar aprotic solvents, exhibit increasing polarity in the E_T scale in the following order: BuOBu < ETBE < BuOMe < MTBE < 1,2-dimethoxymethane < DME (1,2-dimethoxyethane or monoglyme), whereas for alcohols, known as very polar solvents, the order is: t-BuOH < 2-BuOH < i-PrOH < n-PrOH < EtOH < 2-methoxyethanol < MeOH < TFE (1,1,1-trifluoroethanol) < HFIP (hexafluoroisopropanol).

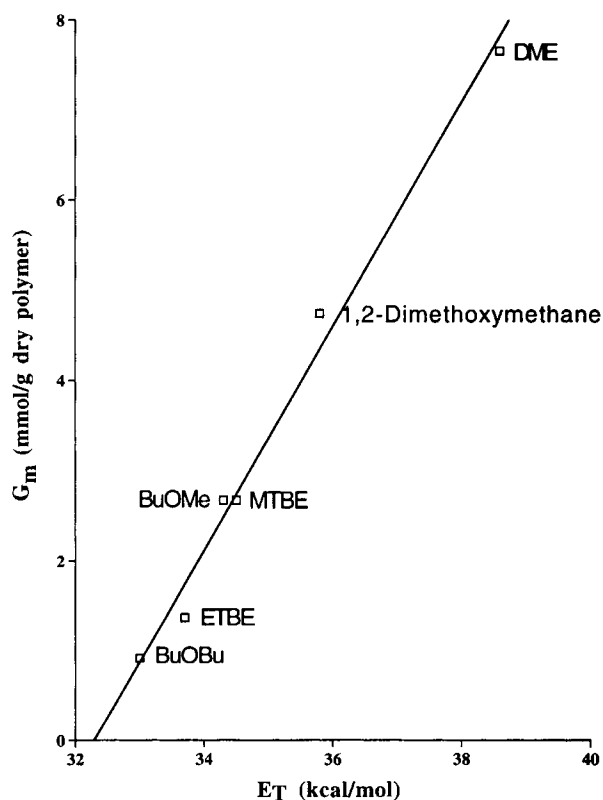
Ethers (Table I)

This first case brings to light the major effect that must be taken into account when one wants to relate

Table I Weight and Molar Swellings of PUI in Pure Ethers at 30°C

| Solvent | E_T (kcal/mol) | M (g/mol) | G (g/g) | G_m (mmol/g) |
|----------------------|------------------|-------------|-----------|----------------|
| BuOBu | 33.0 | 130 | 0.120 | 0.92 |
| ETBE | 33.7 | 102 | 0.141 | 1.38 |
| BuOMe | 34.3 | 88 | 0.235 | 2.67 |
| MTBE | 34.5 | 88 | 0.235 | 2.67 |
| 1,2-Dimethoxymethane | 35.8 | 76 | 0.360 | 4.74 |
| 1,2-Dimethoxyethane | 38.6 | 90 | 0.689 | 7.65 |

the swelling power of a given liquid to its molecular structure: indeed, the compounds considered have the same type of chemical function (ether function), which is one of the simplest, and they can only be distinguished, in addition to the polarity, by their molecular weight or their size. However, these two last parameters have not the expected effect if one refers to two examples: for an equal molecular weight, DME swells the polymer roughly three times more than BuOMe; on the other hand MTBE, a bulky ether, swells the PUI in the same extent as its straight chain isomer BuOMe.

**Figure 1** Molar swellings of ethers in PUI at 30°C vs. $E_T(30)$ values.

On the opposite, the variation of the molar swelling seems to be very well related to the increase of the polarity (E_T parameter) and appears to be the determining factor governing the observed sorption: the experimental G_m values quasi linearly follow the increase of the E_T parameter (Fig. 1) and the relationship (1), hereafter, can be drawn by least squares method:

$$G_m = -40.0 + 1.24E_T(30) \quad (r = 0.994) \quad (1)$$

The swelling variations range from 12 to 69 wt % and reflect the strong polar interactions, mainly due to permanent and induced dipoles between the soft oligoether segment of the polymer and a compound having a similar chemical structure.

Aliphatics Alcohols (Table II)

In these liquids, a part of the occurring interactions are polar ones, but the strongest and preponderant ones result from hydrogen bonds that have been already reported in the case of ethanol and water in related polymers such as polyurethanes^{19,20} or polyimides.²¹ These strong interactions between protic solvent and polymers generally induce the highest swelling, which is at least greater than the swelling due to the least polar ethers (BuOBu, ETBE, BuOMe, MTBE). The molar swelling G_m increases regularly with the protic character of the alcohol: tertiary < secondary < primary < fluorinated alcohols.

The swelling of wholly aliphatic alcohols, which represent the majority of the investigated cases, can be also linearly correlated with the E_T polarity parameter (Fig. 2), which takes into account the protic interactions. G_m variation can be described by the relationship (2), whose weaker slope shows that the reference polymer is less sensitive to the increase of alcohol polarity than to the ether one:

$$G_m = -15.86 + 0.398E_T(30) \quad (r = 0.982) \quad (2)$$

Table II Weight and Molar Swellings of PUI in Pure Alcohols at 30°C

| Solvent | E_T (kcal/mol) | M (g/mol) | G (g/g) | G_m (mmol/g) |
|------------------------|------------------|-------------|-----------|----------------|
| 2-BuOH | 47.1 | 74 | 0.232 | 3.14 |
| i-PrOH | 48.4 | 60 | 0.197 | 3.28 |
| n-PrOH | 50.7 | 60 | 0.260 | 4.33 |
| EtOH | 51.9 | 46 | 0.205 | 4.46 |
| 2-methoxyethanol | 52.3 | 76 | 0.431 | 5.67 |
| MeOH | 55.4 | 32 | 0.205 | 6.41 |
| 1,1,1-trifluoroethanol | 59.8 | 100 | 3.76 | 37.6 |
| HFIP | 65.3 | 168 | Soluble | — |

The sensitivity of the method herein described is pointed out by the fact that the relation (2) can be accurately applied only to the wholly aliphatic alcohols. Indeed, if one considers the swelling (43 wt %) due to 2-methoxyethanol, a value of 5 wt % higher to that predicted by the relation (2) is reached: although weak, this deviation takes into account the effect of the polar ether function in addition to that of the alcohol one.

Fluorinated alcohols, i.e., extremely polar alcohols, well represent the case of liquids used close to polymer solubilization: PUI is, indeed, quickly soluble in HFIP at 30°C and leads to an extremely high swelling (> 300 wt %) in TFE in which it is soluble on heating. Obviously, this type of phenomena cannot be quantitatively predicted by the previous relation that no more applies, but they can be described in the same way as an increase of swelling with solvent polarity in the $E_T(30)$ scale.

Extension to Various Binary Systems

As it was exposed above, the study of the binary systems PUI-alcohols and PUI-ethers shows the possibility to correlate in a very satisfactory way the molar swelling due to a given liquid and its E_T polarity parameter. Therefore, we have examined whether or not this type of relationship could be generalized to other systems published in the literature, whatever the polarity of the polymer or of the swelling liquids. Indeed, lots of swelling studies are already available but, unfortunately, their real interest is often limited by the low number of liquids tested in a given family, and we have selected some of the most exhaustive sets of data.

The molar swellings used hereafter were either calculated from the corresponding weight or volume swellings whenever possible, or obtained from the extended sorption kinetic curves when no data were available; even if such values are less accurate than

straight G measurements, they lead to unequivocal results.

Polar Polymer/Polar Solvent Systems

This first case is quite related to the one previously studied, as it describes swelling phenomena between polar polymer and moderate to strongly polar solvents, as defined on the $E_T(30)$ polarity scale, such as esters, ketones, and alcohols.

Only a few sorption values of organic solvents in polyurethanes are available because most of the

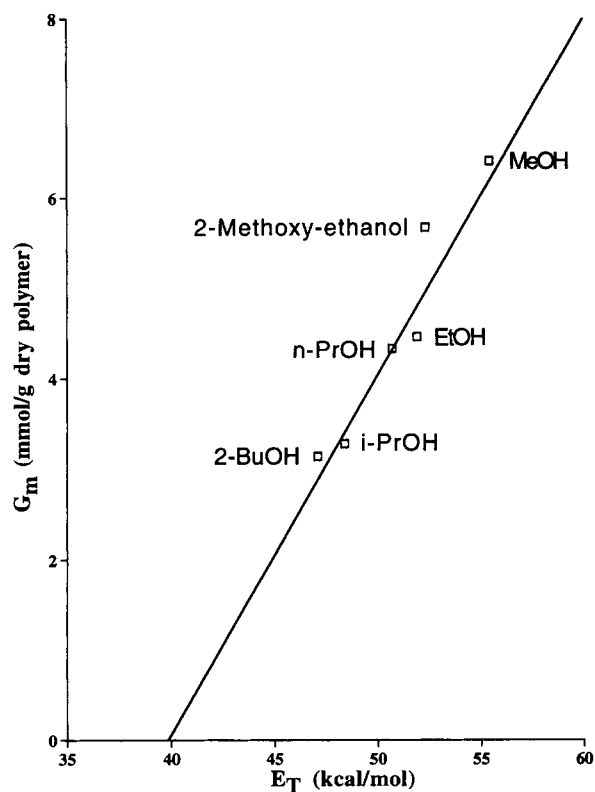


Figure 2 Molar swellings of alcohols in PUI at 30°C vs. $E_T(30)$ values.

studies published until now have been concerned with water sorption in these polymers.¹⁹⁻²¹

G. W. C. Hung and J. Autian have, however, studied the sorption at 30°C of eight aliphatic alcohols in a crosslinked polyurethane.²² Like in the previous case of the PUI studied in our laboratory, it is obvious from Figure 3 that the data correlate very nicely with the $E_T(30)$ parameter of the alcohols except for 1-Octanol, and the following linear relation can be drawn:

$$G_m = -21.59 + 0.526E_T(30) \quad (r = 0.990) \quad (3)$$

T. M. Aminabhavi and colleagues²³ have reported the sorption of some aliphatic acetic esters (R = Me, Et, n-Pr, n-Bu) in a commercial polyurethane at 25°C. The same type of correlation applies (Fig. 4) and can be written as:

$$G_m = -36.27 + 1.104E_T(30) \quad (r = 0.988) \quad (4)$$

This set of esters has also been used by J. M. Charlesworth and colleagues²⁴ who studied the sorption due to a bisphenol A-based epoxide resin

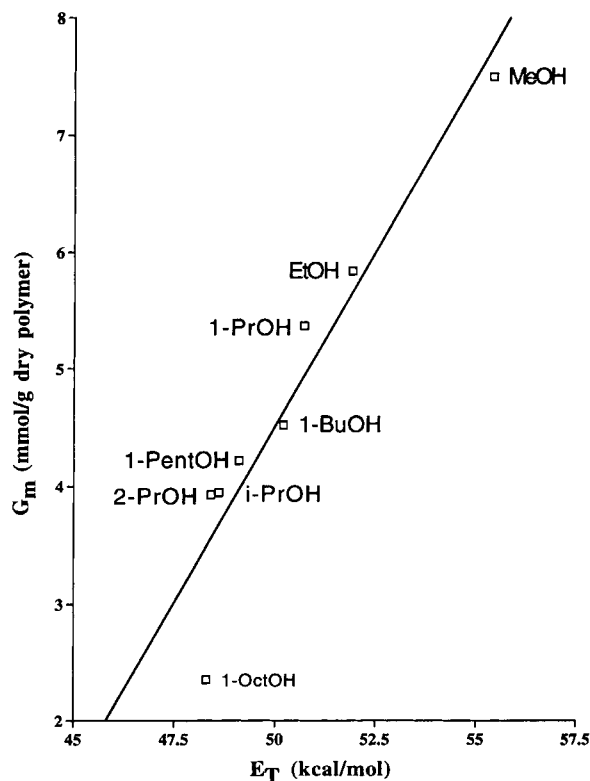


Figure 3 Molar swellings of alcohols in a polyurethane at 30°C (calculated from ref. 22) vs. $E_T(30)$ values.

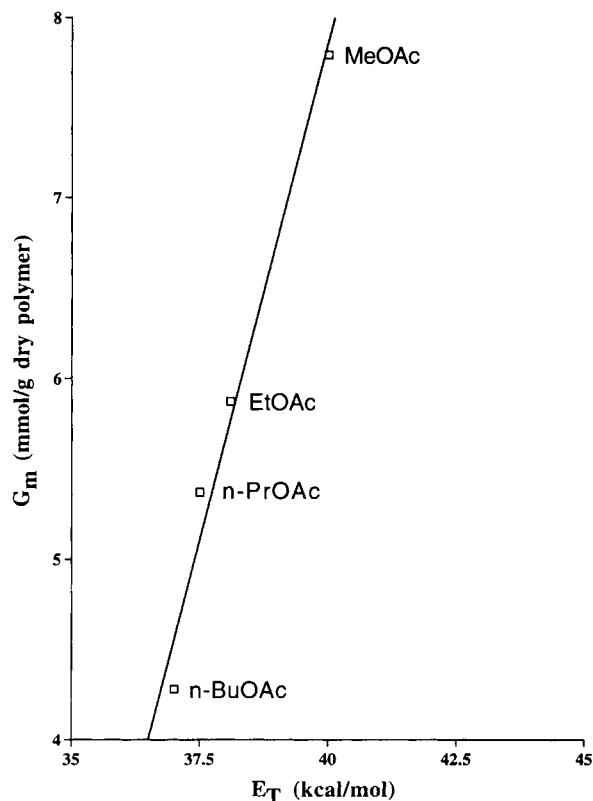


Figure 4 Molar swellings of esters in a polyurethane at 25°C (calculated from ref. 23) vs. $E_T(30)$ values.

(crosslinking density $X_C = 2.571$ mol/kg) cured by di-amino diphenylmethane (DDM). Although the swelling values are low ($G_m < 3$ mmol/g), a linear relationship (Fig. 5) could also be observed between the molar swelling and the E_T parameter:

$$G_m = -16.93 + 0.489E_T(30) \quad (r = 0.989) \quad (5)$$

The weaker slope noted in this case underlines the lower sensitivity of the epoxy resin to the ester polarity, which might be due, in part, to the crosslinking density limiting the swelling extent.

An other interesting related case reported by S. Takahashi²⁵ describes the sorption of a series of aliphatic ketones (acetone, 2-butanone, 2-pentanone, 4-methyl-2-pentanone) in unsaturated polyesters of various crosslinking density (I_x) at 25°C. Even if the values of the molar swellings calculated for a slightly crosslinked polymer (I1) appear to be fairly scattered, they correlate quite well with the corresponding $E_T(30)$ parameters (Fig. 6):

$$G_m = -161.7 + 4.26E_T(30) \quad (r = 0.962) \quad (6)$$

The authors also investigated the sorption of aliphatic alcohols (MeOH, EtOH, n-PrOH, i-PrOH, n-BuOH, i-BuOH) in these polyesters. When the G_m vs. E_T correlation is applied to the corresponding data, a very good relationship is obtained (Fig. 7), except for i-PrOH, in the case of the slightly cross-linked polymer I2:

$$G_m = -47.2 + 1.01 E_T(30) \quad (r = 0.998) \quad (7)$$

However, the same data have shown that the increase of the crosslinking density (I3, I4, . . .) results for the least polar alcohols in drastically reduced swelling, which remains almost constant with respect to polarity. An E_T polarity threshold is then found, above which swelling suddenly increases and a quasi linear relation is observed, as it can be seen from Figure 8 (polymer I3). An other characteristic feature appeared when the influence of the crosslinking density was examined: the value of the previous defined threshold increases with the degree of crosslinking.

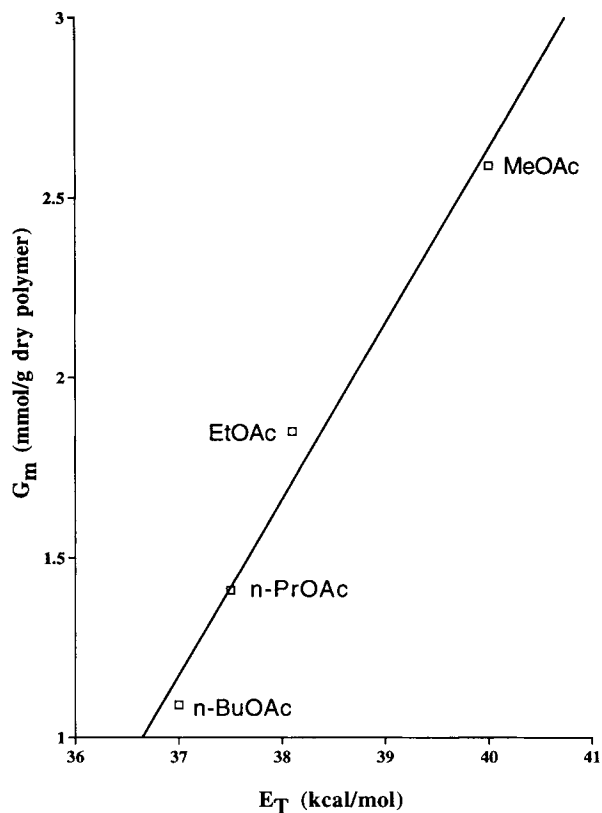


Figure 5 Molar swellings of esters in an epoxide resin at 30°C (calculated from ref. 24) vs. $E_T(30)$ values.

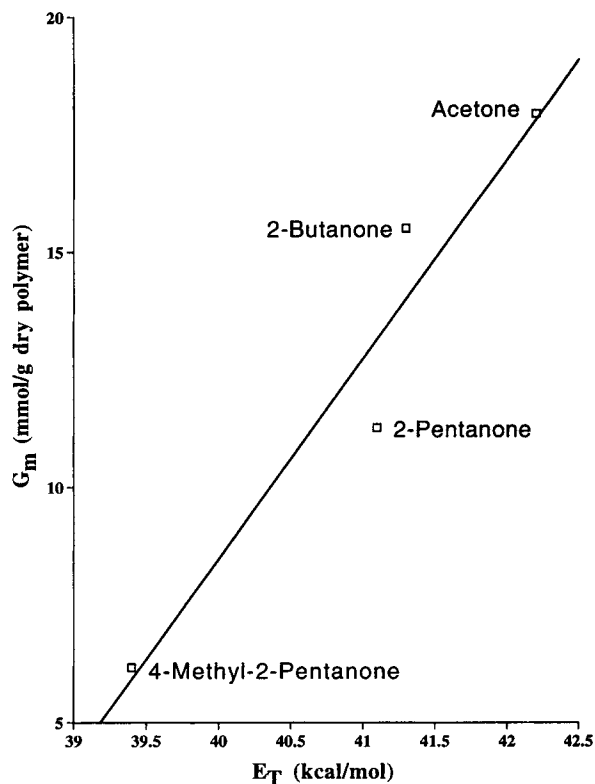


Figure 6 Molar swellings of ketones in insaturated polyester (I1) at 25°C (calculated from ref. 25) vs. $E_T(30)$ values.

Polar Polymer/Apolar Liquid Systems

To our knowledge, few studies of this type have already been reported in the literature dealing with series of related liquids. We report (Fig. 9) the values calculated from the sorption kinetics curves obtained by U. S. Aithal and colleagues²⁶ for a set of aromatic solvents (benzene, toluene, xylene, mesitylene) in the previously mentioned crosslinked polyurethane (Vibrathane B 600). In that case, the molar swelling due to an apolar solvent in the considered polar polyurethane still obeys to the same type of relationship:

$$G_m = -114.3 + 3.58 E_T(30) \quad (r = 0.980) \quad (8)$$

Apolar Polymer/Polar Liquid Systems

Sorption measurements on different systems of this type have been reported in the literature, in particular, by T. M. Aminabhavi and colleagues.²⁷ However, we have limited our investigations to a single

system describing the sorption at 25°C of the previously mentioned esters in a simple polymer structure, natural rubber,²³ well known for its apolar feature. From the linear variation of the G_m values with the E_T parameter (Fig. 10), it is clear that in this third case, too, the data lead to a good correlation expressed by:

$$G_m = 61.91 - 1.494E_T(30) \quad (r = 0.992) \quad (9)$$

However, in that case, a new phenomenon appears that is characteristic of the apolar nature of the polymer: the slope coefficient, b , is negative, on the contrary to those corresponding to the systems composed of polar polymers and polar or apolar solvents. That negative slope value reflects the higher affinity of the apolar polymer towards the least polar solvents, as one could expect. Other calculations made on analogous systems (synthetic rubbers)²⁷ confirm that the sorption can be described by the same type of relationship where b is always a negative value.

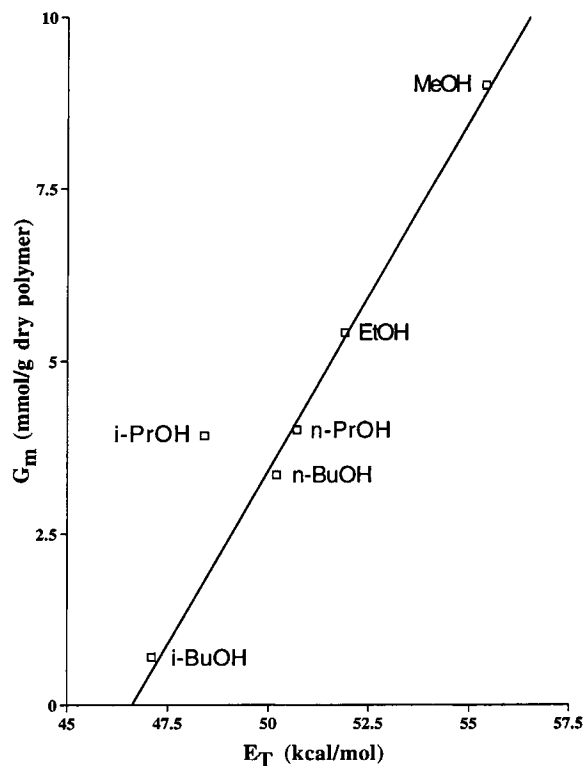


Figure 7 Molar swellings of aliphatic alcohols in an unsaturated polyester (I2—lightly crosslinked) at 25°C (calculated from ref. 25) vs. $E_T(30)$ values.

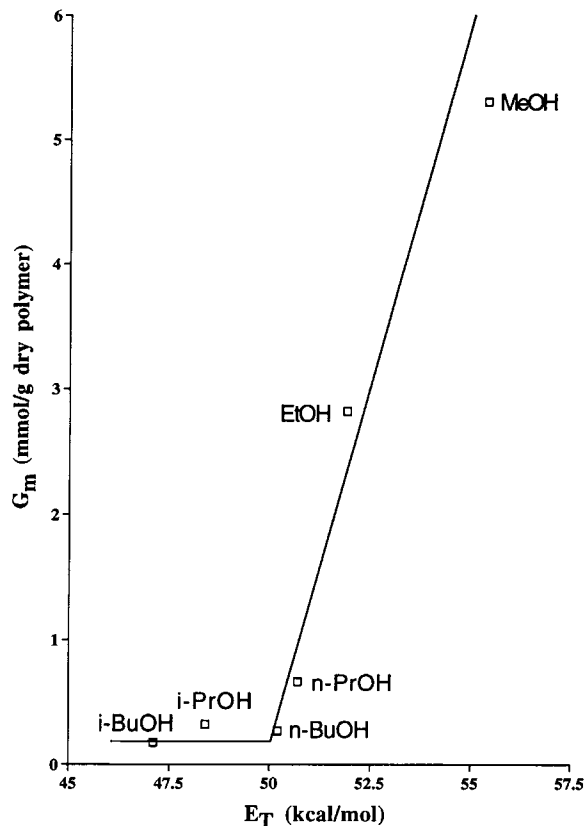


Figure 8 Molar swellings of aliphatic alcohols in an unsaturated polyester (I3—highly crosslinked) at 25°C (calculated from ref. 25) vs. $E_T(30)$ values.

Apolar Polymer/Apolar Liquid Systems

In these systems, polymer-liquid interactions mainly due to dispersive forces are among the weakest. Most of the published data on series of comparable liquids come from the work of T. M. Aminabhavi and colleagues;²⁷ by way of example, the sorption data at 25°C of the system SBR/aromatic hydrocarbons (benzene, toluene, *p*-xylene, mesitylene) have been used in a similar correlation attempt, and it can be seen from the Figure 11 that, in this last type of polymer liquid interactions, a fairly good linear relationship is also obtained:

$$G_m = -164.22 + 5.46E_T(30) \quad (r = 0.973) \quad (10)$$

Applied to other related systems concerning natural rubber, this method showed that the sorption of apolar aromatics can always be described by a similar relation, with coefficients depending on the polymer kind.

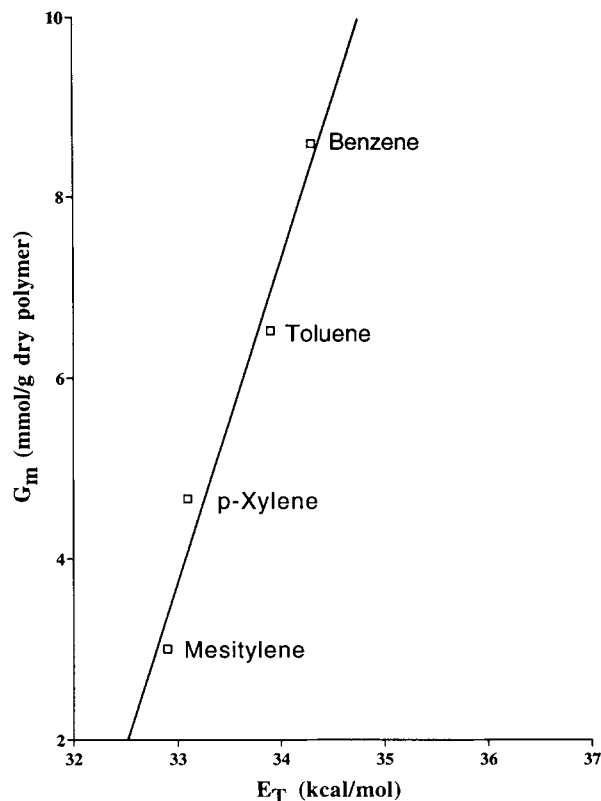


Figure 9 Molar swellings of aromatic hydrocarbons in a polyurethane at 25°C (calculated from ref. 26) vs. $E_T(30)$ values.

Swelling- $E_T(30)$ Parameter Correlation in the Case of Ternary Systems

The study of various binary systems has shown the general feature of this type of correlation, and it was, thus, particularly interesting to examine the case of ternary systems in which the polymer swells in a mixture of two solvents. In this situation, synergic effects can occur, and it becomes very difficult to predict the sorption of a polymer in a given mixture from the sorption properties in the pure solvents.^{29,30} Correlation attempts have, thus, to be made with the partial molar swellings of each solvent of the mixture.

Attempts were carried out with the PUI reference polymer (cf., Part I), which had been studied in two series of pure liquids: aliphatic alcohols and linear aliphatic ethers, and, presently, it was examined in mixtures of these two types of liquid. Mixtures were divided in two series: a reference alcohol (EtOH) with various ethers (BuOBu, ETBE, BuOMe, MTBE) and a reference ether (ETBE) with various alcohols (i-PrOH, n-PrOH, EtOH, MeOH). These

solvents have been chosen because they can alone induce only moderate swellings that remain limited in the mixtures. That leads to eliminate the solvents of too high polarity, like monoglyme or dimethoxymethane, to avoid problems of poor mechanical resistance of the swollen polymer.

The sorption of a compound in a given polymer depends on its activity and, rigorously, only the influence of mixtures that have the same alcohol or ether activity should be examined. However, thermodynamical data necessary to calculate the alcohol and ether activities in the selected mixtures are not available in the literature. Thus, mixtures of the same molar composition (i.e., with an alcohol molar fraction equal to 0.357) have been used as a first approximation.

EtOH/Ether Mixtures

Results of partial ether swellings (Table III) in binary mixtures containing ethanol and different ethers with the same molar composition yield the same conclusions as for the pure ethers at the same temperature (30°C). Despite the slight spread of

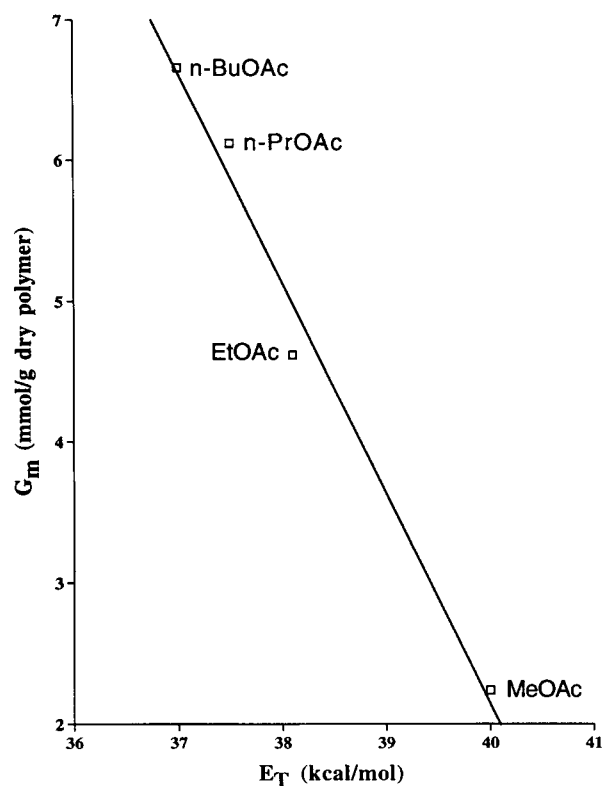


Figure 10 Molar swellings of esters in natural rubber at 25°C (calculated from ref. 23) vs. $E_T(30)$ values.

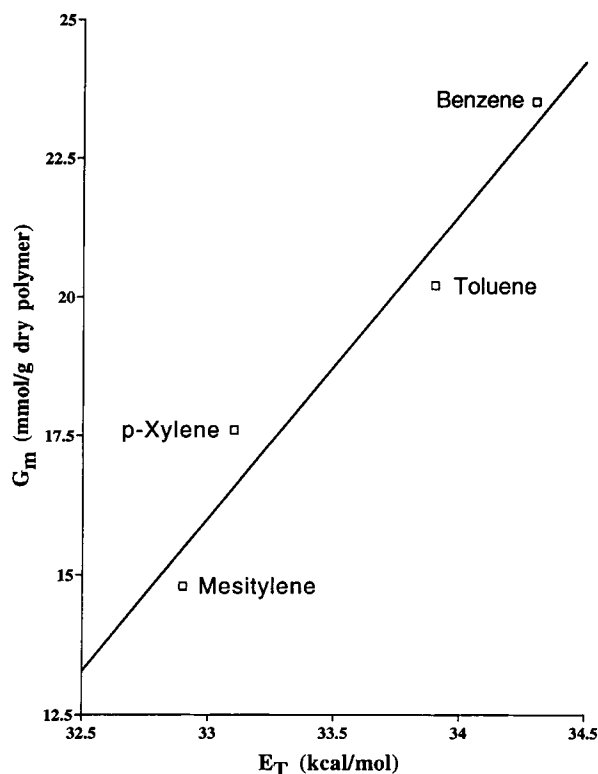


Figure 11 Molar swellings of aromatic hydrocarbons in styrene-butadiene-rubber at 25°C (calculated from ref. 27) vs. $E_T(30)$ values.

the experimental values that might be due to the exposed approximations, the partial molar swellings vary linearly with respect to the ether polarity parameter (Fig. 12) as:

$$G_{m_{\text{ether}}} = -31.71 + 0.987 E_T(30) \quad (r = 0.941) \quad (11)$$

ETBE/Alcohol Mixtures

In the same way, the partial alcohol molar swellings (Table IV) increases with the value of the alcohol polarity parameter $E_T(30)$ (Fig. 13) following the relationship:

$$G_{m_{\text{alcohol}}} = -4.276 + 0.119 E_T(30) \quad (r = 0.987) \quad (12)$$

In these ternary systems, it is noteworthy that the molar swelling due to each type of solvent can still be linearly correlated with its own polarity; the related slope express the swelling sensitivity towards the liquids as in the case of pure liquids: high sensitivity for the aprotic polar solvents, low sensitivity for the protic liquids. However, in the two cases, it

Table III Sorption of PUI in Different EtOH/Ether Mixtures of the Same Molar Compositions (Alcohol Molar Fraction = 0.357) at 30°C

| Ether | E_T (kcal/mol) | G (g/g) | C_{ether} (g/g) | $G_{m_{\text{ether}}}$ (mmol/g) |
|-------|---------------------|--------------|-----------------------------|------------------------------------|
| BuOBu | 33.0 | 0.231 | 0.552 | 0.98 |
| ETBE | 33.7 | 0.215 | 0.582 | 1.23 |
| BuOMe | 34.3 | 0.304 | 0.685 | 2.37 |
| MTBE | 34.5 | 0.288 | 0.692 | 2.26 |

can be observed a decrease of the straight line slope compared to that concerning the corresponding pure liquids. Polymer has, thus, a lower sensitivity to the polarity of the two mixed solvents, which may be related to the decrease of their activity.

CONCLUSION

From our own sorption experiments carried out with a polyurethaneimide (PUI) as well as from the

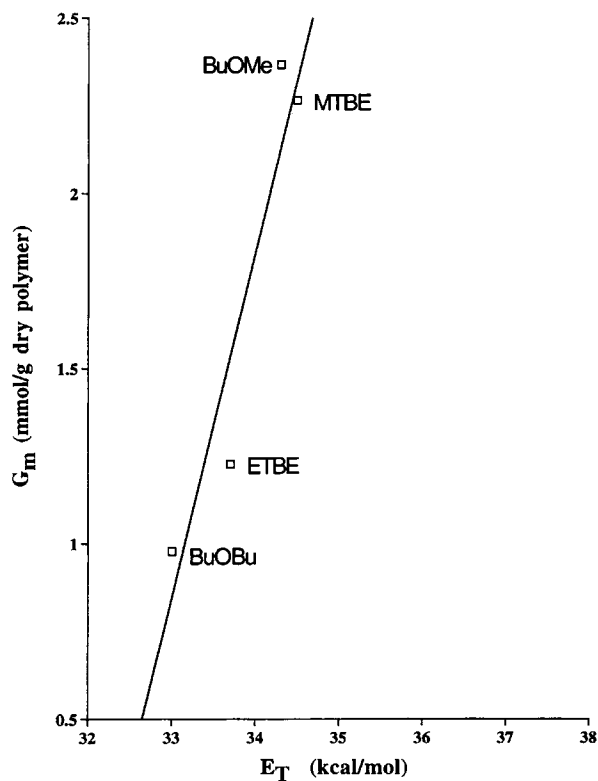


Figure 12 Partial molar swellings of EtOH/ether mixtures (with the same alcohol molar fraction = 0.357) in PUI at 30°C vs. $E_T(30)$ values.

analysis of sorption data of nine types of systems reported in literature, it is clear that, in binary systems, the molar polymer swelling G_m due to a given solvent is linearly related to its polarity parameter $E_T(30)$: $G_m = a + b E_T(30)$, a and b being constant for solvents of the same chemical family (like aliphatic alcohols). Polymer sensitivity to polar effect, as defined by the slope parameter b , highly depends on the solvent type and would be worth analyzing more precisely; b as well as a also depends on the chemical nature of the polymer and of the degree of crosslinking. A different correlation G_m vs. E_T must be used for each type of polymer-solvent systems. The knowledge of the deep meaning of parameters a and b could possibly allow to provide relationships of more wide generality.

However, such a new approach affords many interests; the most direct is the quantitative prediction of the swelling of a given polymer in a pure solvent, particularly in the case of apolar binary systems whose sorption is generally well described by the Flory-Huggins theory.¹ In that case, indeed, the swelling in the pure solvent (activity = 1) allows the calculation of the interaction parameter χ , nearly constant in these systems, and, thus, the prediction of the polymer swelling for every solvent activity.

When applied to the case of the ternary systems PUI-alcohols-ethers, this type of relationship fits quite well the data of the partial molar swellings of each mixture family according to a tendency close to that observed with the pure liquids.

Even if the two studied cases of ternary systems give very promising results, more examples are needed before any general trend could be established, like for the binary systems. Furthermore, it is reasonable to think that these cases will be more complex and their interpretation closely linked to the ideality or nonideality of the liquid mixture.

In case of such correlation could be proposed, the meaning of the slope will have to be examined with respect to the two related binary systems, and the

Table IV Sorption of PUI in Different Alcohol/ETBE Mixtures of the Same Molar Composition (Alcohol Molar Fraction = 0.357) at 30°C.

| Alcohol | E_T (kcal/mol) | G (g/g) | C_{alcohol} (g/g) | $G_{m\text{alcohol}}$ (mmol/g) |
|---------|---------------------|--------------|-------------------------------|-----------------------------------|
| i-PrOH | 48.4 | 0.220 | 0.402 | 1.47 |
| n-PrOH | 50.7 | 0.239 | 0.420 | 1.67 |
| EtOH | 51.9 | 0.215 | 0.418 | 1.95 |
| MeOH | 55.4 | 0.236 | 0.309 | 2.28 |

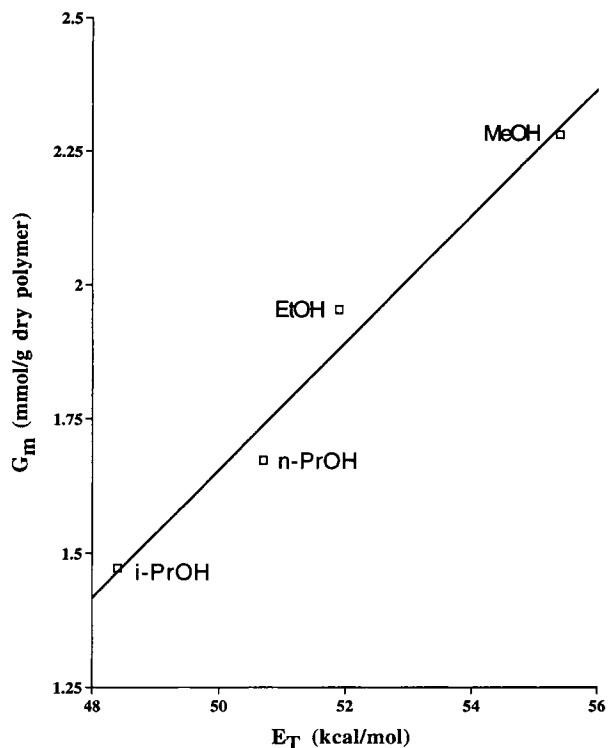


Figure 13 Partial molar swellings of alcohol/ETBE mixtures (with the same alcohol molar fraction = 0.357) in PUI at 30°C vs. $E_T(30)$ values.

knowledge of the activities of the liquids in the mixture will be required to understand more deeply its physicochemical meaning in polymer-liquids interactions.

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