Polymer swelling: 11. A molecular interpretation of association in polystyrene–liquid systems

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The number (α_s) of adsorbed molecules per phenyl group of polystyrene in solution (determined in this laboratory) was compared with the corresponding number ($\bar{\alpha}$) remaining after all of the excess non-adsorbed molecules were eliminated from the corresponding polystyrene–liquid (P–L) system (reported by Guenet). These correlations showed that, for P–L systems with the same polymer tacticity and the same class of liquids (based on similarity of molecular structure), $\bar{\alpha}$ varies linearly with α_s. The fraction of solvated polymer that formed microdomains of associated polymer (owing to the change from α_s to $\bar{\alpha}$) and the average number of monomer units in the solvated segments between these microdomains, which serve as quasi-crosslinkages, were estimated on the basis of the corresponding ratio of $\bar{\alpha}$ to α_s. It was inferred from the results obtained that such microdomains of 'rigidized' polymer segments can evolve either via expulsion of already adsorbed solvent molecules or via incorporation of more solvent molecules to those already immobilized by adsorption.

(Keywords: swelling; association; polystyrene; liquid)

INTRODUCTION

We reported[1–5] that it is possible to establish the number, α_s, of adsorbed molecules per phenyl group of polystyrene in solution by measuring the specific volumes (S) sorbed at liquid saturation by a set of microporous composite samples, comprised of poly(styrene-*co*-divinylbenzene) [hereafter referred to as either poly(Sty-*co*-DVB) or $(\text{Sty})_{1-x}(\text{DVB})_x$] particles enmeshed in polytetrafluoroethylene (PTFE) microfibres. The slope (C) of the linear relationship [equation (1)], obtained when S is plotted as a function of the cube root of the corresponding number (λ) of backbone carbon atoms between crosslinked junctions (equal approximately to $1/x$ when x is <0.1), is defined as the relative swelling power (C in ml g^{-1}) of the sorbed liquid.

$$S=C(\lambda^{1/3}-\lambda_0^{1/3}) \tag{1}$$

The crosslink density, above which S is virtually zero, is given by the reciprocal of λ_0. The number α_s of adsorbed solvent molecules per accessible phenyl group of $(\text{Sty})_{1-x}(\text{DVB})_x$ at liquid–saturation, or in solution when x is zero, is calculated by means of equation (2) and the observed value of C^1.

$$\alpha_s=104Cd/M \tag{2}$$

Here 104 and M are the formula weights of styrene and the test liquid, respectively, and d is the density of that liquid.

In the course of our ongoing study of polymer swelling in homologous series of liquids ZR, where Z is a functional group or substituent with relatively strong affinity for the functional group in the polymer and R is the rest of the molecule that is varied systematically, we showed[1–5] that α_s reflects sensitively the molecular structure of the sorbed liquid ZR, as expected on the basis of principles of physical–organic chemistry (i.e. α_s increases with the affinity of the functional group Z of the adsorbed molecule for the phenyl group in the polymer, and decreases with greater bulkiness of the alkyl group R attached to Z). The values of α_s determined thus far range from 0 to ~ 3.5, and they are determinable reproducibly within ± 0.01.

It was also shown[6] that the Flory–Huggins interaction parameter (χ_v) for polystrene–liquid (P–L) systems[7] varies with C (equation (1)] in accordance with equation (3):

$$\chi_v=0.49+1.01v-0.061vC \tag{3}$$

Here v is the volume fraction of polymer in the P–L system. Thus, at $v=1$, where χ_v is most sensitive to the molecular structure of the sorbed liquid (as indicated by C), equation (3) reduces to equation (4).

$$\chi_1=1.50-0.61C \tag{4}$$

Since C is proportional to the product of α_s and the molar volume (M/d) of the sorbed liquid [equation (2)], χ varies with α_s as indicated by equation (5).

$$\chi_1=1.50-0.00587(M/d)\alpha_s \tag{5}$$

These observations [equations (3)–(5)] support the conclusion that C and α_s are parameters of fundamental scientific significance. It follows, therefore, that they are potentially useful in understanding other phenomena in which molecular association plays an important role. The results reported by others[8–23], regarding gelation of P–L

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solutions by thermally induced phase separation (TIPS), appeared to offer suitable means for testing the above suggestion.

The purpose of this paper, therefore, is to report results that show how α_s correlates meaningfully with the reported gelation data, and how the relationships derived therefrom enable one to estimate, on the basis of α_s, not only the fraction of solvated polymer that undergoes some form of association to produce a quasi-crosslinked network that supports the gel, but also to estimate the average number of solvated monomer units in the polymer segments between the microdomains of associated polymer segments.

EXPERIMENTAL

Determination of C, α *and* χ *by polymer swelling*

The preparation of microporous composite films [consisting of $(\mathrm{Sty})_{1-x}(\mathrm{DVB})_x$ particles ($<20\,\mu$m, >80 wt%) enmeshed in PTFE microfibres], and the use of these films to establish the relative swelling power (C in ml g^{-1}) of the test liquid, are described elsewhere[1–6]. Briefly, this involves allowing swatches, cut from each of six composite films that contain polymer particles having a known DVB mole fraction x, to swell to saturation in excess test liquid. The weight of liquid sorbed by the enmeshed particles in each sample is used to calculate the corresponding specific volume S (in ml g^{-1}) of sorbed liquid. The six S values obtained are plotted as a function of the corresponding $\lambda^{1/3}$ to establish the characteristic linear relationship [equation (1)] for the given test liquid. The square of the correlation coefficient (r^2) for the straight line of best fit through the set of data points for a given test liquid was in all cases >0.99, and the intercept, $\lambda_0^{1/3}$ [equation (1)], with the abscissa was in all cases within the range of experimental reproducibility reported in earlier studies[1–6], i.e. 1.78 ± 0.02 at 23°C. The coefficient C of the relationship [equation (1)] established for a given test liquid was used to calculate the corresponding α_s [equation (2)] and χ_1 [equation (4)]. Most of the α_s values needed for correlation with the gelation data reported by Guenet *et al.*[14–18] had already been published[1–6]; the α_s values for some additional liquids were needed to allow a fuller appreciation of such correlations. These additional liquids are listed in *Table 1*, along with the corresponding adsorption data.

Table 1 Adsorption data for various poly(Sty-*co*-DVB)–liquid systems

Liquid	d (g cm^{-3})	$\lambda_0^{1/3\,a}$	C	$\alpha_s{}^b$	$\chi_1{}^c$
Carbon disulphide	1.266	1.80	1.95	3.37	0.31
Cyclopentene	0.774	1.76	1.39	1.65	0.49
Cyclohexene	0.811	1.76	1.47	1.51	0.60
Cycloheptene	0.824	1.76	1.45	1.30	0.62
Cyclopentanone	0.949	1.80	1.95	2.29	0.31
Hexene-1	0.673	1.70	0.38	0.31	1.31
Trimethylene oxide	0.893	1.76	2.07	3.31	0.24
Tetrahydrofuran	0.889	1.77	2.00	2.57	0.28
Tetrahydropyran	0.881	1.80	2.08	2.21	0.23
Oxepane	0.890	1.76	1.94	1.79	0.32
1,3-Dichloropropane	1.190	1.75	1.86	2.04	0.37
1,4-Dichlorobutane	1.160	1.76	1.82	1.73	0.39

[a] $\lambda_0^{1/3}$ is the intercept of the relationship [equation (1)] with the abscissa

[b] α_s is the number of adsorbed molecules per accessible phenyl group in $(\mathrm{Sty})_{1-x}(\mathrm{DVB})_x$ at liquid saturation or in true solution when x is zero as defined in equation (2)

[c] χ_1 is the calculated Flory–Huggins interaction parameter for P–L systems having polymer fraction $v=1$ [equation (4)]; χ_v at any other volume fraction v is given by: $\chi_v = 0.49 + v(\chi_1 - 0.49)$

Time studies of evaporation from P–L systems

The details for the protocol used to monitor evaporation of the volatile component from a P–L system are described elsewhere[24–29]. Briefly, it involves recording frequently (initially every 20 s) the weight of residual sorbed liquid in a composite film sample comprised of poly(Sty-*co*-DVB) particles enmeshed in PTFE microfibres that had been saturated with a test liquid, and restrained from shrinking by a rigid frame as the liquid-swollen sample was allowed to evaporate to dryness. Sequential 'breakpoints' in the kinetics of evaporation signal the compositions that mark: α'_s, i.e. complete elimination of sorbed but not adsorbed molecules and incipient elimination of adsorbed molecules, α'_g, i.e. incipient transition of the P–L system from the rubbery state to the glassy state, and α_g, i.e. the completion of this transition. Typical examples of such time studies are shown in Figures 2, 3 and 4 of reference 27.

RESULTS AND DISCUSSION

Correlation of $\bar{\alpha}$ *and* $\bar{\alpha}^*$ *with* α_s

It is well known[8–22] that when certain polymer solutions are chilled to below room temperature, they undergo gelation owing to some form of polymer association. The microdomains of associated polymer segments formed thereby serve as quasi-crosslinkages, which afford a three-dimensional network that extends throughout the bulk of the P–L system. This phenomenon is thermoreversible, i.e. a clear solution is regenerated when the system is reheated to the gel melting temperature (T_m), which is well above the gel formation temperature (T_f). The T_m characteristic of the P–L system is in fact the temperature at which all of the monomer units in the microdomains of associated polymer segments become re-solvated. The gel form of the P–L system is restored when it is chilled again to T_f.

Although the nature of the TIPS is not well understood even in the case of isotactic P–L systems, the gel appears to consist of two phases, i.e. a polymer-poor phase (essentially solvent) supported by a polymer-rich phase distributed in spinodal[23] form throughout the bulk of the mixture. The polymer-rich phase, in the case of isotactic polymer, is said to have a 'liquid-crystalline-like' nematic structure[14–19], the 'microcrystalline' domains of which consist of aggregated monomer units in a 3_1-helical configuration.

Guenet *et al.*[15,16] reported that the spacings within the helix vary characteristically with the molecular structure of the solvent. They also noted[14–19] that the number ($\bar{\alpha}$ for atactic P–L systems and $\bar{\alpha}^*$ for isotactic P–L systems) of residual adsorbed molecules per monomer unit of polymer after gelation and elimination of all of the mobile non-adsorbed molecules in the P–L gel system, also appears to be characteristic of the liquid. This number was determined by monitoring the heat of fusion (ΔH) of the P–L system as a function of the ratio of liquid to polymer in the system. Since only the non-adsorbed molecules contribute to ΔH, extrapolation of ΔH to zero identifies $\bar{\alpha}$ reproducibly, i.e. within a calculated possible error (presumably 3+ standard deviations) that is $\leqslant 20\%$[19]. It was assumed tacitly that

$\bar{\alpha}^*$ at the equilibrium gel state is not affected significantly during the post-elimination of the non-adsorbed molecules, most of which were in the polymer-poor phase. Guenet *et al.* also showed that the same value of $\bar{\alpha}^*$ (or $\bar{\alpha}$) is arrived at (within experimental reproducibility) from the opposite direction by measuring ΔH for a series of dry polymer samples that had been allowed to equilibrate with increasing amounts of test liquid.

Since the system remaining after thickening and/or gelation (and elimination of the non-adsorbed molecules) consists of polymer in two states, i.e. the fraction (y) in the microdomains of associated polymer segments, and the remainder $(1-y)$ that are not in these domains, Guenet's $\bar{\alpha}$ is the average of these two fractions, as given by:

$$\bar{\alpha}=(1-y)\alpha_s+y\alpha_a \tag{6}$$

where α_s is the number of adsorbed (solvent) molecules per monomer unit of solvated polymer between the microdomains of associated polymer segments, and α_a is the corresponding number for the monomer units of polymer contained in the microdomains.

If one accepts that y at the composition where $\Delta H=0$ does not differ significantly from that at the equilibrium state established when isotactic P–L solutions undergo phase separation and gelation (i.e. there is no significant increase in y owing to the elimination of non-adsorbed molecules that comprise the polymer-poor phase of a P–L system) then it should be possible to estimate y by comparing the average number of adsorbed molecules per monomer unit of polymer before (α_s) and after ($\bar{\alpha}$) such P–L systems undergo gel formation.

The adsorption values determined by Guenet (13 $\bar{\alpha}$ values using atactic polystyrene and four $\bar{\alpha}^*$ values using isotactic polystyrene) are recorded in *Table 2*, along with the corresponding 17 α_s values determined in this laboratory using atactic poly(Sty-*co*-DVB). The correlation of these $\bar{\alpha}$ and $\bar{\alpha}^*$ values with α_s (*Figure 1*) show that the data points for liquids with similar molecular structures tend to fall along straight lines characteristics of the liquid classification and polymer tacticity.

That the P–L systems must belong to the same classification in order to exhibit such linear relationships is consistent with expectation based on relationships observed in our ongoing studies of sorption of $Z(CH_2)_nH$ liquids, described briefly in the Introduction, which show that $\alpha_{z,n}$ (i.e. α_s for liquids in such homologous series) varies with Z and n ($n=<8$) of that series as expressed by:

$$\log\alpha_{z,n}=\log\alpha_{z,0}-A_z n \tag{7}$$

where $\alpha_{z,0}$ and A_z are constants characteristic of the functional group Z (see Figure 2 of reference 5). Similar correlations[1–4,24] of the logarithms of α_s with the corresponding Hildebrand solubility parameter (δ_{ZR}) show that $\log\alpha_{ZR}$ varies linearly with the square of the difference $(\delta_{pol}-\delta_{ZR})$ as expressed by:

$$\log\alpha_{ZR}=\log\alpha_{max}-A'_z(\delta_{pol}-\delta_{ZR})^2 \tag{8}$$

Here α_{max} is the maximal α_{ZR} value noted for the ZR liquids, and δ_{pol} is the solubility parameter for the polymer, i.e. δ_{ZR} for the liquid that produced α_{max}. Again the constants δ_{max}, A'_z, and δ_{pol} are characteristic of Z of the ZR liquids (see Figure 2 of reference 7, Figure 7 of reference 2, Figure 5 of reference 3 and Figure 5 of reference 4).

Thus, in our correlations of data collected by Guenet with data collected independently in this laboratory, the straight lines (*Figure 1*) drawn through each set of data points $(\bar{\alpha},\alpha_s)$, obtained for systems comprised of structurally related liquids and atactic polystyrene, pass through the origin. The general equation that expresses these relationships, therefore, is given by:

$$\bar{\alpha}=Y\alpha_s \tag{9}$$

The straight lines drawn through the data points $(\bar{\alpha}^*,\alpha_s)$ for systems comprised of structurally related liquids and isotactic polystyrene do not intersect the abscissa at $\alpha_s=0$ but rather at $\alpha_s=-0.5$. Hence, the general equation for these relationships is expressed by:

$$\bar{\alpha}^*=Y(\alpha_s+0.5)=Y\alpha_s^* \tag{10}$$

The displacement of the common point of intersection on the abscissa from $\alpha_s=0$ to -0.5 reflects the better packing efficiency of adsorbed molecules on a pendant phenyl group of polystyrene when the polymer is isotactic as compared to atactic; the apparent result is that phenyl groups are more accessible to solvent molecules in the isotactic case.

The values of Y for five of the P–L systems investigated by Guenet (*Table 2*) are $Y=0.75\pm0.01$. Two of these (1-chlorodecane and 1-chlorododecane) were determined using isotactic polystyrene, and three (CCl_4, CH_2Cl_2, and CS_2) were determined using atactic polystyrene. The liquids, however, are in the same category based on molecular structure, i.e. the non-hydrogen substituents are on the α carbon atom of the molecule. In four out of the five cases (*Table 2*), these are chloro substituents. If one accepts that $Y=3/4$ is characteristic for such α-substituted alkanes then it becomes possible to calculate the corresponding $\bar{\alpha}$ (complementary to $\bar{\alpha}^*$) for 1-chlorodecane and 1-chlorododecane using equation (9), and $\bar{\alpha}^*$ (complementary to $\bar{\alpha}$) for CH_2Cl_2 and CCl_4 (and perhaps CS_2) using equation (10).

Since $CHCl_3$ and the homologous series of $Cl(CH_2)_nH$ liquids are in this classification with Y equal to 3/4, and with the α_s of these liquids having already been reported[9], it should be possible to predict $\bar{\alpha}$ and $\bar{\alpha}^*$ for these P–L systems using equations (9) and (10). These calculated values are collected in *Table 3*.

It is curious to note in *Table 2* that the two liquids, which have more than one non-hydrogen substituent located on different carbon atoms of the molecule [i.e. $ClCH_2Cl$ and $O(CH_2CH_2)_2O$], exhibit values of Y that are about half the values exhibited by similar liquids in which the non-hydrogen substituents are on the same carbon atom. It is suspected that this decrease in Y may reflect a qualitative change in the mode of adsorption. When the P–L system consists of a large excess of sorbed but not adsorbed molecules in equilibrium with adsorbed molecules, only one of the two functional groups of the adsorbed molecule occupies an adsorption site. The other is associated with the mobile molecules above the adsorption site, i.e. the immobilized molecule is restrained only by monodentate adsorption. On the other hand when the P–L system is concentrated to the composition $\bar{\alpha}$ (or $\bar{\alpha}^*$), where the system contains only adsorbed molecules, the possibility for bidentate adsorption is markedly increased, and the number of adsorbed molecules per monomer unit of polymer is decreased accordingly.

If one accepts, tentatively, that $Y=0.42$ is characteristic of $Cl(CH_2)_nCl$ liquids with $n>1$, then $\bar{\alpha}$ and $\bar{\alpha}^*$ for such liquids can be estimated by means of equations (9)

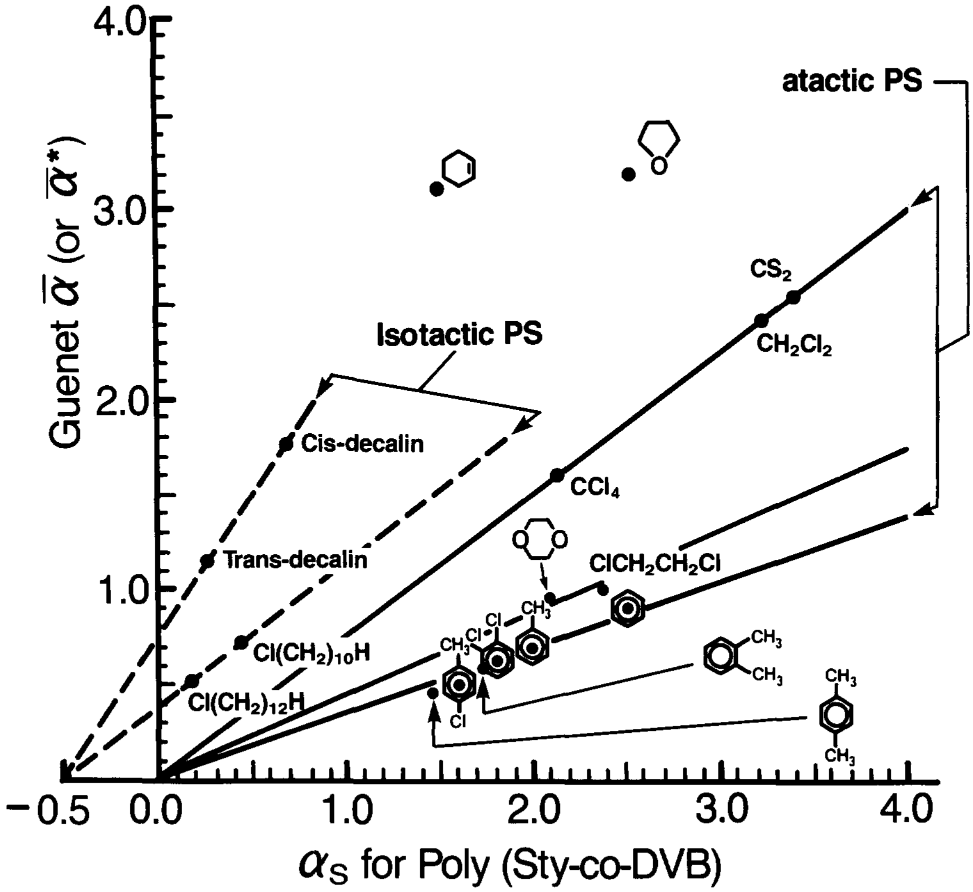

Figure 1 Correlation of Guenet's $\bar{\alpha}$ with the corresponding α_s. For atactic polystyrene: $\bar{\alpha} = Y\alpha_s$. For isotactic polystyrene: $\bar{\alpha}^* = Y(\alpha_s + 0.5)$

Table 2 Comparison of the Guenet adsorption parameters for atactic ($\bar{\alpha}$) and isotactic ($\bar{\alpha}^*$) polystyrenes with the corresponding α_s values determined for atactic poly(Sty-*co*-DVB)

Liquid	$\bar{\alpha}^{*a}$	$\bar{\alpha}^{b}$	α_s	Y^c	y^d	$\bar{\lambda}^e$
THF	(3.83)	3.22	2.57^f	1.25	0.25	90*
Cyclohexene	(4.14)	3.10	1.51^f	2.07	1.00	168*
Carbon disulphide	(2.90)	2.55	3.37^f	0.76	0.24	44
Methylene chloride	(2.81)	2.40	3.24^g	0.74	0.26	42
Carbon tetrachloride	(1.96)	1.60	2.12^g	0.75	0.25	37
1,2-Dichloroethane	(1.21)	1.00	2.39^g	0.42	0.58	19
p-Dioxane	(1.14)	0.97	2.10^g	0.46	0.54	20
BenZene	(1.02)	0.92	2.50^g	0.37	0.63	16
Toluene	(0.84)	0.70	1.98^g	0.35	0.65	15
o-Dichlorobenzene	(0.78)	0.64	1.80^g	0.36	0.64	15
o-Xylene	(0.76)	0.59	1.74^g	0.34	0.66	14
p-Chlorotoluene	(0.71)	0.50	1.59^g	0.31	0.69	14
p-Xylene	(0.67)	0.46	1.46^g	0.32	0.68	13
cis-Decalin	1.75	(1.01)	0.68^g	1.48	0.48	47*
trans-Decalin	1.15	(0.41)	0.28^g	1.47	0.47	21*
1-Chlorodecane	0.70	(0.33)	0.44^h	0.74	0.25	15
1-Chlorododecane	0.50	(0.14)	0.18^h	0.74	0.26	10

[a] Data in parentheses were calculated using $\bar{\alpha}^* = Y(\alpha_s + 0.05)$
[b] Data in parentheses were calculated using $\bar{\alpha} = Y\alpha_s$
[c] Y is the ratio $\bar{\alpha}/\alpha_s = \bar{\alpha}^*/(\alpha_s + 0.5)$ (*Figure 1*)
[d] y is the fraction of monomer units in microdomains of self-associated polymer segments that serve as quasi-crosslinkages. When Y is <1, $y = 1 - Y$, but when Y is >1, $y = Y - 1$
[e] $\bar{\lambda}$ is the average number of backbone carbon atoms in the solvated polymer segments between microdomains of self-associated polymer segments. Mathematically $\bar{\lambda}$ is given by equation (18); $\bar{\lambda}$ data for cyclic liquids are marked with an asterisk to indicate that these data are not directly comparable to those of acyclic liquids for reasons stated in the text
[f] Recorded in *Table 1*
[g] Data taken from reference 1
[h] Data taken from reference 3

Table 3 Estimated $\bar{\alpha}$, $\bar{\alpha}^*$ and $\bar{\lambda}$ for polystyrene–chloroalkane systems

Chloroalkane	α_s^{a}	$\bar{\alpha}^{b}$	$\bar{\alpha}^{*b}$	$\bar{\lambda}^b$
Methyl chloride	3.21	2.40	2.78	43
Ethyl chloride	2.23	1.67	2.05	37
1-Chloropropane	1.94	1.46	1.83	35
1-Chlorobutane	1.55	1.16	1.46	31
1-Chloropentane	1.29	0.97	1.31	28
1-Chlorohexane	1.04	0.78	1.16	25
1-Chloroheptane	0.96	0.72	1.10	24
1-Chlorooctane	0.78	0.59	0.96	21
1-Chlorononane	0.57	0.43	0.80	18
1-Chlorodecane	0.44	0.33	0.71	15
1-Chloroundecane	0.29	0.22	0.59	12
1-Chlorododecane	0.18	0.14	0.51	10
1,3-Dichloropropane	2.04	0.86	1.06	18
1,4-Dichlorobutane	1.73	0.73	0.92	17
Chloroform	2.99	2.24	2.62	42

[a] Data for 1-chloroalkanes are taken from reference 3, whereas those for α, ω-dichloroalkanes and chloroform are taken from *Table 1*
[b] $\bar{\alpha}$, $\bar{\alpha}^*$ and $\bar{\lambda}$ were calculated using equations (10), (17) and (18), respectively, where Y is 3/4 for 1-chloroalkanes and for chloroform, but Y is 0.42 for the α, ω-dichloroalkanes as indicated in *Table 2*

and (10). Thus, $\bar{\alpha}$ and $\bar{\alpha}^*$ for 1,3-dichloropropane and 1,4-dichlorobutane were calculated on the basis of their respective α_s (*Table 1*) values, and these data are also recorded in *Table 3*.

The values of Y for the six aromatic liquids (*Table 2*) studied by Guenet using atactic polystyrene are 0.34 ± 0.03. If one accepts that $Y = 1/3$ is characteristic for aromatic liquids, then $\bar{\alpha}$ and $\bar{\alpha}^*$ for such liquids can be calculated in a similar fashion based on the corresponding observed α_s values. The calculated $\bar{\alpha}^*$ values for the six

Table 4 Estimated $\bar{\alpha}^*$, $\bar{\alpha}$ and $\bar{\lambda}$ for polystyrene–aromatic liquid systems

Aromatic liquid	$\alpha_s{}^a$	$\bar{\alpha}^b$	$\bar{\alpha}^{*c}$	$\bar{\lambda}^d$
Chlorobenzene	2.23	0.76	0.93	15.1
Fluorobenzene	2.19	0.74	0.89	15.0
Bromobenzene	2.04	0.69	0.86	14.7
Iodobenzene	1.75	0.60	0.77	14.1
Trichloromethylbenzene	1.66	0.56	0.73	13.9
Trifluoromethylbenzene	0.59	0.20	0.37	10.0
Anisole	1.92	0.65	0.48	14.5
Dimethylaniline	1.84	0.62	0.72	14.3
Aniline	1.70	0.58	0.75	14.0
Nitrobenzene	1.14	0.39	0.55	12.4
Tetrahydronaphthalene	1.69	0.57	0.74	14.0
m-Xylene	1.53	0.52	0.69	13.6
o-Chlorotoluene	1.77	0.60	0.77	14.2
m-Chlorotoluene	1.68	0.57	0.74	13.9
m-Dichlorobenzene	1.87	0.64	0.81	14.4
Ethylbenzene	1.55	0.53	0.70	13.6
n-Propylbenzene	1.33	0.45	0.62	13.0
n-Butylbenzene	1.13	0.38	0.55	12.8
1-Phenylpentane	0.93	0.32	0.49	11.6
1-Phenylhexane	0.80	0.27	0.44	11.0
1-Phenylheptane	0.66	0.22	0.39	10.3
1-Phenyloctane	0.50	0.17	0.34	9.4
1-Phenylnonane	0.40	0.14	0.31	8.3
1-Phenyldecane	0.30	0.10	0.27	8.1

[a] Data were taken from reference 1

[b] $\bar{\alpha}=0.34\alpha_s$

[c] $\bar{\alpha}^*=0.34(\alpha_s+0.5)$

[d] $\bar{\lambda}=[1.78+\alpha_s(\alpha_s+1)]^3$, i.e. equation (18) with $Y=1/3$ for aromatic liquids (*Table 2*)

aromatic liquids, the $\bar{\alpha}$ values of which were determined by Guenet using atactic polystrene, are recorded in *Table 2* (data in parentheses), and the predicted values for both $\bar{\alpha}$ and $\bar{\alpha}^*$ for other aromatic liquids not yet considered by Guenet are listed in *Table 4*.

The $\bar{\alpha}$ values for *cis*- and *trans*-decalin, the $\bar{\alpha}^*$ values of which were determined by Guenet using isotactic polystyrene, were calculated as described above. These data, like the $\bar{\alpha}^*$ data for the aromatic liquids (*Table 2*), are placed in parentheses to emphasize that they are predicted values, whereas the other values were determined experimentally.

Having shown that the linear relationships established for atactic P–L systems pass through the origin [equation (9), *Figure 1*], it is reasonable to assume that the Y values for cyclic ethers and for cyclic olefins can be established by the respective straight lines that can be drawn from the origin to the data points (*Figure 1*) for tetrahydrofuran (THF, $\bar{\alpha}=3.22$, $\alpha_s=2.53$) and for cyclohexene ($\bar{\alpha}=3.10$, $\alpha_s=1.50$). The $\bar{\alpha}$ and $\bar{\alpha}^*$ for all other members of these two homologous series, therefore, can then be predicted using the appropriate Y value deduced thereby and the corresponding α_s values determined experimentally. Examples of calculated $\bar{\alpha}$ and $\bar{\alpha}^*$ values for such cyclic liquids (*Table 1*) are collected in *Table 5*.

Modes of association that afford gels

Since α_s is the average number of adsorbed molecules per phenyl group of polystyrene in solution, and $\bar{\alpha}$ is the corresponding number after gel formation and/or elimination of the non-adsorbed molecules from the P–L system, the ratio Y (equal to $\bar{\alpha}/\alpha_s$ in the case of atactic P–L systems or to $\bar{\alpha}^*/\alpha_s^*$ in the case of isotactic P–L systems) can be used to infer the mode of association by which the thermoreversible gel was established. When Y is <1, polymer association must have occurred via displacement of solvent molecules that previously had been immobilized by adsorption in solution, i.e. by self-association to form microdomains that serve as quasi-crosslinkages; but when Y is >1, association must have occurred via addition of more solvent molecules to those already adsorbed in solution. The Y ratios determined for the 17 P–L systems studied by Guenet *et al.* (*Table 2*) show that these values range from $Y=0.31$ for *p*-chlorotoluene to $Y=2.07$ for cyclohexene. Most of these (13 of 17) show Y values <0.8, but the remaining four show Y values >1.2, which permits unambiguous differentiation of the two possible modes of polymer association.

It is easy to rationalize qualitatively how this occurs when Y is <1. Fortuitous local alignment of the mobile solvated polymer segments in proper orientation, when the thermodynamic conditions of temperature and polymer concentration favour displacement of already adsorbed solvent molecules, leads to nucleation of microdomains of self-associated polymer, which are created randomly throughout the P–L system. These nuclei grow by 'infection' (i.e. induced self-association) of adjacent monomer units, until the driving force for self-association is balanced by the opposing force due to polymer swelling, i.e. when the rate of 'unravelling' of polymer from the microdomains of associated polymer segments by solvation of monomer units at the extremities of these microdomains is equal to that for the reverse process. Apparently this is statistically reproducible, since the ratio Y is reproducible and constant for a given class of liquids ZR, which implies that Y depends primarily on the affinity of substituent Z for the phenyl group of the polymer. At this thermodynamically stable end point, the polymer of the P–L system is at two levels of solvation as expressed by equation (6), i.e. a fraction y that contains a markedly reduced complement of adsorbed solvent molecules (α_a) and the remainder $(1-y)$ that still has its original full complement (α_s). Both y and the average number ($\bar{\lambda}$) of backbone carbon atoms in the polymer segments between microdomains of self-associated polymer should vary with the affinity of Z for the phenyl groups of the polymer.

It is assumed that when Y is <1, α_a [equation (6)] is $<0.1\alpha_s$ for two reasons: (1) $\bar{\alpha}$ varies linearly with the corresponding α_s (*Figure 1*), which would be impossible unless α_a is much smaller than α_s; and (2) it was observed[14–17] that the T_m of the gel formed by chilling isotactic polymer–liquid systems is often almost equal to T_g for the polymer neat. Since T_m varies inversely with α_a, the observation that T_m is close to T_g implies

Table 5 Estimated $\bar{\alpha}$, $\bar{\alpha}^*$ and $\bar{\lambda}$ for polystyrene–cyclic liquid systems

Cyclic liquid	$\alpha_s{}^a$	$\bar{\alpha}^b$	$\bar{\alpha}^{*b}$	$\bar{\lambda}^b$
Cyclopentene	1.65	3.38	4.41	180
Cycloheptene	1.30	2.67	3.70	148
Trimethylene oxide	3.31	4.13	4.76	101
Tetrahydropyrane	2.21	2.76	3.38	83
Oxepane	1.79	2.23	2.86	73

[a] Data taken from *Table 1*

[b] $\bar{\alpha}$, $\bar{\alpha}^*$ and $\bar{\lambda}$ were calculated using equations (10), (12) and (18), respectively. The value of Y in these calculations was 1.25 for the cyclic ethers and 2.07 for the cyclic olefins. The $\bar{\lambda}$ values for cyclic liquids are not directly comparable to those listed for acyclic liquids (*Tables 2–4*) for reasons given in the text

that α_a must be close to zero. If the above assumption is valid then it follows that equation (6) reduces to:

$$\bar{\alpha}^* = (1-y)\alpha_s^* \qquad (11)$$

and therefore y, under such conditions, is given approximately by:

$$y = 1 - Y \qquad (12)$$

where $Y = (1-y)$ is $\bar{\alpha}/\alpha_s$, equal to $\bar{\alpha}^*/\alpha_s^*$. The y values thus calculated for the 13 P–L systems, for which Y is <1, are reported in *Table 2*.

How gelation occurs when Y is >1 is more difficult to rationalize. In such cases the gel is not supported by rigid microdomains of self-associated polymer, but rather by microdomains of solvated polymer that contain additional solvent molecules, which presumably serve as 'bridges' between monomer units as suggested by guenet and Klein[16,19]. Consequently one cannot calculate the fraction [y as defined in equation (6)] of available solvated monomer units that undergo this form of association, unless α_a can be established independently by some physical method. Unfortunately this is not yet possible.

Nevertheless, it may be possible to determine a relative order of such associations on the basis of the observation that $\bar{\alpha}^*$ for the isotactic P–L systems for the decalins appears to vary linearly with the corresponding α_s of the system (*Figure 1*). This implies that for systems with $Y > 1$ the product $y\alpha_a$ may be constant, i.e. α_a as well as y may be constant for this system. Assuming that this were also true for the other P–L systems with $Y > 1$, and that the value of $Y = 2.07$ determined for cyclohexene (*Table 2*) represents the extreme case in which y is equal to one, then it follows from equation (6) that α_a for this system is equal to $2\alpha_s$.

If one accepts tentatively that the value $\alpha_a = 2\alpha_s$ may be valid for P–L systems with $Y > 1$, then direct substitution of this value in equation (6) gives equation (13):

$$y = (\bar{\alpha}/\alpha_s - 1) = (\bar{\alpha}^*/\alpha_s^* - 1) = (Y - 1) \qquad (13)$$

Thus, the value of y for P–L systems may be $\sim 1/4$ when the liquids are cyclic ethers ($Y = 1.25$, *Table 2*), and $\sim 1/2$ when the liquids are bicyclic hydrocarbons such as the two decalins ($Y = 1.48$, *Table 2*).

It is curious to note in *Table 2* that the P–L systems with $Y > 1$ are systems in which the liquid is a cyclic aliphatic liquid, the ring structure of which contains no more than one atom that is not carbon, whereas not one of the solvents in the P–L systems with $Y < 1$ is in this category. Because the number of experimentally determined $\bar{\alpha}$ and $\bar{\alpha}^*$ are relatively few (owing to the time-consuming procedure and high technical skill required to obtain these data via the protocol described by Guenet) it is not yet possible to adjudicate with certainty whether or not this cyclic *versus* acyclic differentiation is a real phenomenon.

The above observations, however, are consistent with those made in ongoing studies of sorption by poly(Sty-*co*-DVB) at liquid saturation. These latter studies show that α_s for a cyclic $ZCR(CH_2)_n$ liquid, where Z is a phenyl or halogen substituent, is much greater than expected on the basis of anticipated decrease in steric hindrance owing to cyclization of the corresponding linear molecule $ZCHR(CH_2)_nH$. The observation that α_s for monosubstituted cyclic alkanes is much greater than that for a corresponding acyclic alkane, which contains the same number of carbon atoms, is not unique to this class of liquids. Instead it appears to be general for all classes of liquids[1–5] as indicated by the data collected in *Table 6*. That such anomalous results occur in both types of swelling phenomena suggests that the observation regarding the qualitative difference in mode of gel formation, on the basis of molecular structure of the solvent, may be real rather than fortuitous, and that both results may stem from the same cause. It is expected, therefore, that when one learns the reason why α_s for cyclic aliphatic molecules is much greater than that of analogous acyclic aliphatic molecules, one will also understand why the Y value for the cyclic P–L systems are >1 and those for acyclic P–L systems are <1. Until then, however, the rationale proposed to explain the results observed in such P–L systems with $Y > 1$, can only be accepted tentatively as a working hypothesis.

Table 6 Comparison of α_c for cyclic molecules with α_L for the corresponding linear molecules

Cyclic	α_c	Linear	α_L	$\alpha_c - \alpha_L$
Cyclohexanol	0.47^a	$H(CH_2)_6OH$	$<0.01^a$	0.46
Cyclohexane	0.56^a	$H(CH_2)_6H$	$<0.10^a$	0.55
Cyclohexene	1.51^b	$H(CH_2)_4CH{=}CH_2$	0.31^b	1.20
cis-Decalin	0.68^a	$H(CH_2)_{10}H$	$<0.01^a$	0.67
Cyclopentanone	2.29^b	$(CH_3CH_2)_2CO$	1.50^a	0.79
THF	2.36^b	$(CH_3CH_2)_2O$	0.64^a	1.22
Phenylcyclohexane	1.11^a	$Ph(CH_2)_6H$	0.80^a	0.31
Tetrahydronaphthalene	1.69^a	$Ph(CH_2)_4H$	1.13^a	0.56
Iodocyclohexane	1.43^c	$I(CH_2)_6H$	1.22^d	0.21
Bromocyclohexane	1.62^c	$Br(CH_2)_6H$	1.22^e	0.40
Chlorocyclohexane	1.66^c	$Cl(CH_2)_6H$	1.04^f	0.62

[a] Data from reference 1
[b] Data from *Table 1*
[c] Data from reference 5
[d] Data from reference 2
[e] Data from reference 4
[f] Data from reference 3

Relevance of polymer swelling, drying and TIPS

The mechanism for swelling crosslinked and non-crosslinked polystyrene in excess liquid at 23°C is the same. In both cases it begins by adsorption of solvent molecules to exposed monomer units at the polymer–liquid interface. The change in chemical potential of the adsorbed species causes more solvent molecules to be sorbed resulting in localized swelling, which in turn renders the adjacent monomer units accessible to further adsorption. Thus, swelling proceeds by 'infection', i.e. diffusion-controlled permeation away from the surface in contact with the liquid. The kinetics of sorption is not Fickian, however, but rather Case II[30,31], i.e. the swelling front trails close behind the diffusion front so that the entire system becomes saturated with sorbed liquid soon after the permeation front reaches the furthest possible distance from the original liquid–solid interface. Saturation occurs when the driving force for sorption of liquid (which varies with the product of the difference in chemical potential between an adsorbed molecule and non-adsorbed molecule and the number, α_s, of adsorbed molecules per accessible monomer unit of polymer) is equal to the forces in opposition to swelling. In the case of crosslinked polymer, the restraining force is imparted by the (solvated) polymer segments between covalently bonded crosslinked junctions, whereas in the case of non-crosslinked polymer, this restraining force is provided by those (solvated) polymer segments between microdomains of strongly associated polymer, which are in effect quasi-crosslinkages.

A difference occurs when the temperature is raised above the solution or melting temperature T_m of the microdomains of well-associated polymer. These microdomains then dissociate and become solvated, and consequently these systems form solutions at temperatures above T_m. In contrast, the liquid-saturated gels supported by covalently bonded crosslinkages undergo only a quantitative change in S [equation (1)], which varies with the effect of temperature on the product of α_s and the molar volume of the liquid [equation (2)], but does not cause a qualitative change from a liquid-saturated gel to a solution.

When P–L solutions are chilled or concentrated by evaporation at room temperature, a fraction of the monomer units in the solvated polystyrene undergo some form of association to produce relatively rigid microdomains that serve as quasi-crosslinkages as described earlier. The fraction of the available monomer units that are present in such microdomains of associated polymer, and the distribution of these microdomains along the solvated polymer chain, depends on the molecular structure of the solvent ZR and the polymer concentration in the P–L system.

In contrast, when liquid-saturated poly(Sty-*co*-DVB) is allowed to remain at room temperature, no such association occurs because movement of the solvated polystyrene segments between covalently bonded crosslink junctions is restricted severely such that attainment of the proper correlated molecular orientation, which is a necessary prerequisite for nucleation of microdomains of associated polymer segments, is highly improbable. Such microdomains, which serve to increase the number of effective crosslinkages and increase accordingly the restraint on polymer swelling, are not created in poly(Sty-*co*-DVB)–liquid systems until the amount of residual sorbed liquid is so low that the P–L system begins to undergo transition from the rubbery state to the glassy state[26–28].

Our studies of evaporation from liquid-saturated poly(Sty-*co*-DVB) systems[25–32] verified that the molecules of the sorbed liquid in such systems are of two types: those that are immobilized by adsorption to the polymer that supports the gel, and those that are not. These time studies of evaporation were monitored both gravimetrically[25–29] and spectrometrically[32–34]. The kinetics of such studies show that the non-adsorbed molecules are eliminated first, the adsorbed molecules being eliminated more slowly thereafter. The depletion of the former and onset of elimination of the latter is signalled by a qualitative change in kinetics from zero order to first order, which is accompanied by a sharp change in spectrometric signals owing to elimination of the non-adsorbed molecules from the system. The composition, α'_s, at this breakpoint varies with α_s [equation (2)]; and for molecular species that are immobilized by monodentate adsorption, its value is given by:

$$\alpha'_s = 0.33(\lambda^{1/3} - \lambda_0^{1/3})(\alpha_s + 1) \tag{14}$$

Similar breakpoints, indicated both kinetically and spectrometrically, occur at compositions that signal incipience and completion of polymer transition from the rubbery state to the glassy state. The compositions at the start (α'_g) and completion (α_g) of this transition also vary with α_s as expressed by equations (15) and (16).

$$\alpha'_g = 0.10(\lambda^{1/3} - \lambda_0^{1/3})(\alpha_s + 1) \tag{15}$$

$$\alpha_g = 0.055(\alpha_s + 1) \tag{16}$$

The difference $(\lambda^{1/3} - \lambda_0^{1/3})$, noted in equations (1), (14) and (15), reflect the relative 'looseness' of the polymer macrostructure, which affects the compositions at liquid saturation [α_G, equations (1) and (2)], at incipient elimination of adsorbed molecules [α'_s, equation (14)] and incipient transition from the rubbery state to the glassy state [α'_g, equation (15)], but not the composition at the end of this transition [α_g, equation (16)].

The compositon α'_s, observed for a given crosslinked P–L system in 3M Laboratories, corresponds formally to the compositions $\bar{\alpha}$ and $\bar{\alpha}^*$ (*Table 2*), observed by Guenet for the respective atactic and isotactic quasi-crosslinked P–L systems; i.e. both α'_s and $\bar{\alpha}$ (or $\bar{\alpha}^*$) reflect the compositions of the respective P–L system when only adsorbed molecules are present and yet all of the available adsorption sites are still occupied. Equation (14), therefore, can be used to calculate the effective number, $\bar{\lambda}$, of backbone carbon atoms in the polystyrene segments between the microdomains of associated polymer segments, which are involved in TIPS and/or evaporation to attain the composition $\bar{\alpha}$ (or $\bar{\alpha}^*$) of such P–L systems. Direct substitution of $\bar{\alpha}$ for α'_s and $\bar{\lambda}$ for λ, and rearrangement of terms gives:

$$\bar{\lambda} = [\lambda_0^{1/3} + 3\bar{\alpha}/(\alpha_s + 1)]^3 \tag{17}$$

and direct substitution of $Y\alpha_s$ for $\bar{\alpha}$ [equation (9)] into equation (17) gives:

$$\bar{\lambda} = [\lambda_0^{1/3} + 3Y\alpha_s/(\alpha_s + 1)]^3 \tag{18}$$

Since $\lambda_0^{1/3}$ for poly(Sty-*co*-DVB)–liquid systems is equal to 1.78 ± 0.02, and Y is a constant, characteristic of Z for a given homologous series of liquids ZR, $\bar{\lambda}$ for a P–L system in a given homologous series of P–L systems that have a $Y < 1$ can be calculated using equation (18) (*Tables 2–4*).

Earlier it was noted that $Y = \bar{\alpha}/\alpha_s$ had a value of 0.42 for $ClCH_2CH_2Cl$, which is about half the value ($Y = 0.74$) established for $Cl(CH_2)_nH$ liquids (*Table 2*), and it was suggested that this difference might be attributable to a change in the mode of adsorption for $ClCH_2CH_2Cl$ away from a monodentate mode in solution (in which case the adsorbed molecules are in equilibrium with a sea of mobile non-adsorbed molecules) to a bidentate mode when these non-adsorbed molecules have been eliminated. To evaluate the validity of this suggestion, the weight of residual sorbed molecules per gram of $(Sty)_{98}(DVB)_2$ particles that had been saturated with $ClCH_2CH_2Cl$ were monitored gravimetrically as the P–L system evaporated from α_g to $<\alpha_g$ as described in the Experimental section. The breakpoints in the kinetics of desorption that mark the compositions α'_s, α'_g and α_g were, respectively, 1.03, 0.37 and 0.09 molecules per phenyl group of polymer. Each of these values is about half that (2.16, 0.65, and 0.19) calculated on the basis of monodentate adsorption using equations (14)–(16). These results are consistent with the point of view that the mode of adsorption for $ClCH_2CH_2Cl$ changes from monodentate at liquid saturation (i.e. at α_g) to bidentate as the mobile non-adsorbed molecules are eliminated from the P–L system.

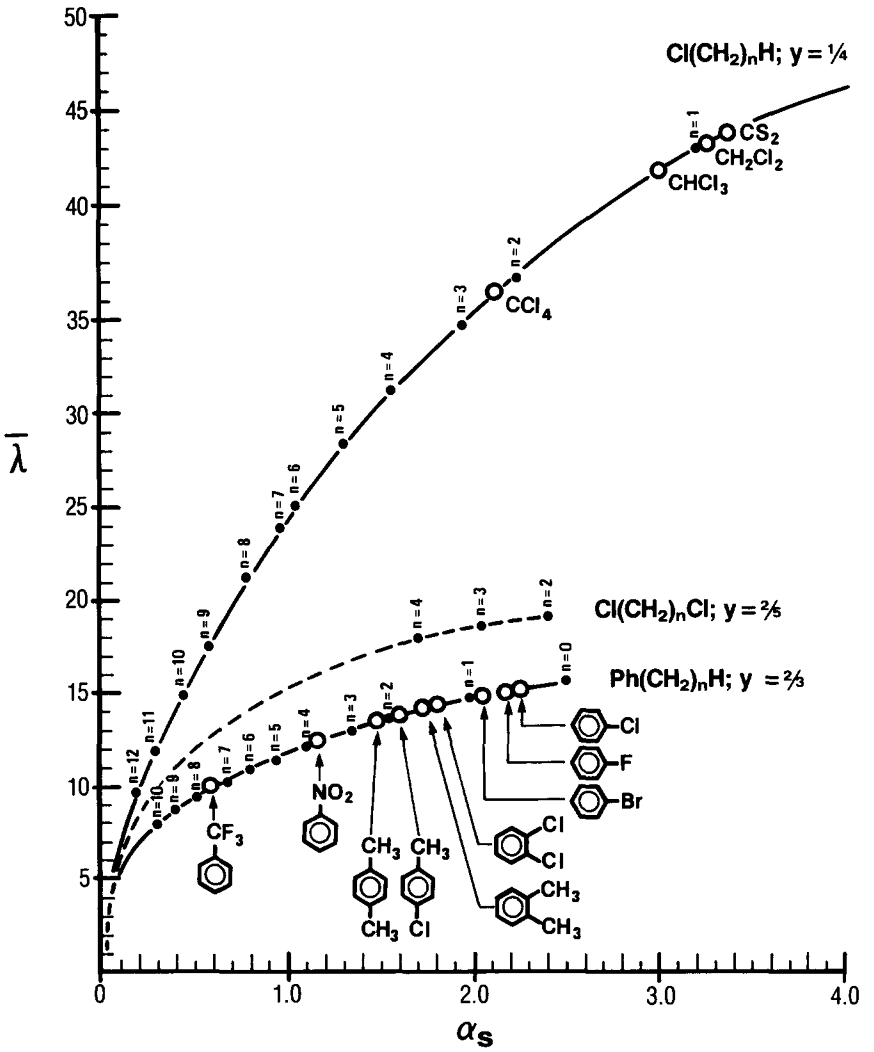

Figure 2 Correlation of the calculated [equation (18)] average number ($\bar{\lambda}$) of backbone carbon atoms in the polystyrene segments between microdomains of self-associated polymer in P–L systems, which were produced by TIPS, with the corresponding α_s of the liquid

The physical significance of $\bar{\lambda}$, calculated for a P–L system with $Y > 1$, is more difficult to interpret than that for P–L systems with $Y < 1$, because the microdomains of associated polymer segments in those with $Y > 1$ consist of associated polymer segments that carry more adsorbed solvent molecules than they do in true solution. The cohesive forces that hold such microdomains together by the postulated molecular 'bridging' must be considerably weaker than those existing in microdomains of self-associated polymer segments. It follows therefore that the macrostructure of such domains must be in a continuous 'state of flux' of forming the unravelling solvated polymer segments, thus making for a very indistinct definition of the boundaries between associated and non-associated segments. The numerical values of $\bar{\lambda}$ for P–L systems with $Y > 1$ (from 21 to 180, *Tables 2* and *5*) usually are considerably greater than those for P–L systems with $Y < 1$ (from 8 to 44, *Tables 2–4*). This of course is consistent with the intuitive feeling that P–L systems with $Y > 1$ are much looser than those with $Y < 1$, but prevents one from making a meaningful quantitative comparison of the two types of associated systems.

That one can get a relative feel for $\bar{\lambda}$ on the basis of the molecular structures of the components that comprise a P–L system may have particular relevance for making microporous membranes by TIPS processes, since the microporosity of such membranes should increase with $\bar{\lambda}$. The plots (*Figure 2*) of $\bar{\lambda}$ *versus* α_s for three types of homologous series of liquids ZR in P–L systems show that $\bar{\lambda}$ increases with α_s to an apparent asymptotic limit that reflects the affinity of the functional group Z for the functional group in the polymer. This suggests that it should be possible to affect systematically the morphology of such microporous membranes by varying the molecular structure of the liquid chosen for the polymer solution from which the microporous membrane is to be produced.

CONCLUSIONS

The Guenet adsorption values for atactic ($\bar{\alpha}$) and isotactic ($\bar{\alpha}^*$) P–L systems were correlated with the α_s values determined in our laboratories for the corresponding P–L systems. Despite that these parameters were determined independently and represent adsorption values at markedly different levels of solvation, these correlations (*Figure 1*) show linear relationships within a given liquid classification (based on similarity of molecular structure) and polymer tacticity. The ratio $\bar{\alpha}/\alpha_s$ [or $\bar{\alpha}^*/(\alpha_s + 0.5)$ in the case of isotactic polymer] is a constant equal to Y, which is characteristic of the functional group Z in the homologous series of liquids ZR. This implies that $\bar{\alpha}$ and $\bar{\alpha}^*$ reflect the molecular structure of the sorbed liquid as does α_s at their respective levels of polymer solvation. It follows, therefore, that once Y is determined on the basis of one or more paired measurements, it then becomes possible to predict $\bar{\alpha}$ and $\bar{\alpha}^*$ for all other such P–L systems in that classification of solvents, provided that α_s for those liquids of that system be known or determinable, as noted in *Tables 2–5*.

Since α_s is the average number of adsorbed molecules per monomer unit of polymer in solution (i.e. no association between solvated polymer molecules) and $\bar{\alpha}$ (or $\bar{\alpha}^*$) is the corresponding number after the P–L system has attained an equilibrium state of associated polymer segments (induced either thermally or by elimination of all non-adsorbed molecules by evaporation) the ratio $Y=\bar{\alpha}/\alpha_s=\bar{\alpha}^*/(\alpha_s+0.5)$ enables one to infer the mode of association. It also enables one to estimate the fraction (y) of available monomer units of polymer that comprise the microdomains of associated polymer segments [equations (12) and (13)], and to estimate the number ($\bar{\lambda}$) of backbone carbon atoms in the polymer segments between the microdomains of associated polymer segments.

A value of $Y=<1$ (as is the case in 13 of the 17 P–L systems studied by Guenet, *Table 2*) indicates that gel formation has occurred by self-association of polymer, which involves expulsion of adsorbed molecules. On the other hand a value of $Y=>1$ (as noted in 4 of the 17 P–L systems studied by Guenet, *Table 2*) indicates that polymer association has occurred by incorporation of more solvent molecules to those already immobilized by adsorption in solution. The former presumably serve as bridges between solvated monomer units, creating the microdomains of associated (solvated) polymer segments as suggested by Guenet *et al.*[15,16].

The values of y and $\bar{\alpha}$ for each P–L system that comprise representative homologous series of liquids with characteristic Y are collected in *Tables 2–5*. These data show that on the basis of only 13$\bar{\alpha}$ values for atactic P–L systems and 4$\bar{\alpha}^*$ values for isotactic P–L systems reported by Guenet, it is possible to estimate $\bar{\alpha}$ and $\bar{\alpha}^*$ for a considerably larger number of P–L systems based on the observed linear correlation with the corresponding α_s values.

It is hoped that more experimentally determined Guenet $\bar{\alpha}$ and $\bar{\alpha}^*$ values for other P–L systems will be forthcoming. Such determinations would enable the accuracy and validity of the values predicted here to be tested on the basis of the initial correlations of α_s with the 17 values listed in *Table 2*. If the experimental values agree with the predicted values (*Tables 2–5*), this would show unambiguously that the Guenet $\bar{\alpha}$ and $\bar{\alpha}^*$ values reflect how well the molecular structure of the adsorbed molecules are accommodated by the molecular structure of the monomer unit of the polymer at the level that marks saturation of all available sorption sites in the absence of non-adsorbed molecules. If the expected agreement is in fact demonstrated, then it would be worth the effort to determine $\bar{\alpha}$ or $\bar{\alpha}^*$ values for esters, ethers, ketones, etc., to see whether or not these data also correlate meaningfully with the corresponding α_s values of such liquids from this laboratory. Hopefully such studies will lead to mathematical relationships that indicate quantitatively the affinity of the functional group Z of the sorbed liquid ZR for the phenyl groups in the polymer, and how this electronic attractive force is mitigated by steric hindrance resulting from the 'bulkiness' of its molecular structure.

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