Polymer Swelling. XXIII. Molecular Structure–Affinity Correlation Studies Involving Poly(styrene-*co*divinylbenzene) Exposed to Acyclic Olefinic Liquids

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ABSTRACT: The adsorption parameters (α) of 45 olefinic liquids with respect to poly-(styrene-co-divinylbenzene) were established gravimetrically in the usual way. Those for the structures that comprise $R_a R_b C = CR_c R_d$, where each R is H or an alkyl group, can be fitted to log $\alpha_f = \log \alpha_i - D_s (N_f - N_i)$ relationships, where N_i and N_f are the initial and final number of mass units in the subseries of the above general molecular structure (GMS). The constant α_i reflects the number of methyl groups in lieu of H atoms and their positional relationship to each other on the double bond, whereas the constant D_s reflects the unit change in log α_i caused by incrementation of a (CH₂)_nR substituent from n = 1 to its allowable limit while the rest of the molecular structure is kept constant. The results observed thereby confirm that these adsorption phenomena involve a liaison between the pendent phenyl groups of the sorbent polymer and the double bond of the sorbate liquid. The adsorption data accumulated in these studies show that in the cases of olefinic liquids carrying other kinds of functional groups, such as aromatic or ether groups, the adsorption preference usually favors the other functionality, leaving the olefinic group in the "nonadsorbed" portion of the adsorbed molecule where it can exert a positive influence on adsorptivity due to dynamic associative interactions with the mobile sorbed molecules of its own kind. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1583-1609, 1999

Key words: polymer swelling; adsorption parameter (α) ; polystyrene; ethylenes

INTRODUCTION

Earlier publications¹ in this series, devoted to studies of liquid sorption by poly(styrene-*co*-divinylbenzene) [hereinafter referred to either as poly(Sty-*co*-DVB) or (Sty)_{1-x}(DVB)_x], reported the concept of an adsorption parameter for the sorbed liquid with respect to the sorbent polymer. This parameter is defined as the number (α) of adsorbed molecules per accessible phenyl group in the polymer at liquid saturation. It can be estable

lished gravimetrically by means of a set of six $(Sty)_{1-r}(DVB)_r$ samples having known values of x as described in considerable detail elsewhere¹⁻¹⁶ and recounted briefly here in the Experimental Section. The α values reported thus far (>500) range from 0 to 4, and they are reproducible to within ± 0.01 . These values reflect very sensitively the molecular structure of the adsorbed species and how it is accommodated by that of the repeat unit in the polymer. Consequently, they are particularly useful in adsorption studies involving homologous series (based on the atom or functional group having the relatively stronger affinity for the polymer) in which one variable in a homologous series having a given general molecular structure (GMS) is incremented systemat-

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ically from 1 to its allowable limit while the others are held constant. It was observed in such studies²⁻¹⁶ that the logarithms of the α values determined for a given homologous subseries exhibit a linear relationship with the total number (N) of methylene mass units (or the equivalent) as expressed by eq. (1).

$$\log \alpha_f = \log \alpha_i - D_s (N_f - N_i) \tag{1}$$

Here N_i and N_f are the initial and final N values, respectively, of the homologous series being considered; α_i and α_f are the corresponding α values; and D_s is the characteristic decrementation constant (i.e., the decrease in log α per unit increase in N) for that series. Thus, after only a relatively few α values for some of the key smaller molecules were established experimentally, it was possible to calculate with reasonable confidence those for the many other molecular permutations that comprise the GMS classification.

The above studies also demonstrated that the mode of adsorption to the adsorption site (in this case the pendent phenyl group of the polymer at liquid saturation) is a most important uncontrolled variable that must remain constant if the network of log α versus N linear relationships (i.e., vectors in multidimensional space) is to reproduce the experimental data. A change in the mode of adsorption within a given homologous series is signalled by a sharp progressive deviation from linearity, as illustrated by several examples reported in the literature.^{11–15}

Our preceding publication¹⁶ reports that even saturated hydrocarbons, which bear neither a hetero atom nor a functional group, have a small but measurable affinity for poly(styrene). The log α versus N relationship for the linear series $H(CH_2)_nH$, however, is abnormal in that the decrementation constant $[D_s; eq. (1)]$ is 0 (or slightly less than 0) for n < 6, such that α_f may have a maximal value of 0.08 ± 0.04 at about n = 6. It was inferred from this observation that the mode of adsorption of these molecules may involve a liaison not only with the pendent phenyl group of the polymer but also with the backbone, because the magnitude of the attractive forces involved are so small that they approach those reported for self-association between $H(CH_2)_n H$ molecules when $n > 6.^{17-19}$

The log α versus *N* linear relationship for the cyclic $(CH_2)_n$ series, however, is quite normal $(\alpha_i = 0.863 \text{ at } n = 4; D_s = 0.0875 \text{ from } n = 4-10)$; and

it is almost parallel to but below that ($\alpha_i=3.25~{\rm at}$ $n = 3; D_s = 0.0888$ from n = 3-8) for the corresponding cyclic ether series $(CH_2)_n O$ (see fig. 2 of Errede and Tiers¹⁶). The displacement between the two linear relationships reflects the affinity of the ether oxygen atom relative to that of the methylene unit, despite the statistical factor that favors the latter. It was inferred from this observation that the mode of adsorption for $(CH_2)_n$ [see fig. 1(b) of Errede and Tiers¹⁶] is essentially the same as that suggested for $(CH_2)_n O$ [see fig. 3(d) of Errede and Tiers¹⁴; i.e., the association is predominantly with the pendent phenyl groups of the polymer] and that the attitudinal angle (ϕ) at which the "nonadsorbed" portions of the cyclic structures that comprise these two series project away from the adsorption sites are about the same.

Having established the above reference data base, we were in a position to elucidate how systematic changes in the molecular architecture for the corresponding acyclic olefinic liquids affect not only the attitude in the mode of adsorption but also the polarizability–polarizability interactions of these molecules with the pendent phenyl groups on the polymer, the net effect of which determines the respective α values. The purpose of this publication is to report the results observed in these sorption studies and the conclusions derived therefrom.

EXPERIMENTAL

The set of six composite film samples, which were employed as the polymeric sorbent in all our previous studies of $(Sty)_{1-x}(DVB)_x$ swelling to saturation in hundreds of test liquids, were used again in this study of sorption of acyclic olefinic liquids. A large portion of this study was carried out before each of the original set of composite film samples had been subdivided into five unequal smaller portions (as described in our publication regarding sorption of sulfur-containing liquids¹⁵), which was done to permit us to use a "scaled down" version of the original protocol in the evaluation of liquid samples that were only available to us in small amounts (<10 mL). The procedure for making these composite film samples, comprising $(Sty)_{1-x}(DVB)_x$ particles (>80%) by weight) enmeshed in polytetrafluoroethylene microfibers, and the distribution of these particles in the microporous composite films produced thereby (see figs. 1, 6, 7, and 20 of Errede¹) are

No.	R	bp (°C)	N	d	$\lambda_o^{1/3}$	С	α	χ_1
1	(CH ₂) ₃ H	30	5	0.640	1.71	0.26	0.25	1.34
2	$-(CH_2)_4^{H}$	64	6	0.673	1.72	0.38	0.31	1.27
3	$-(CH_2)_5H$	94	7	0.697	1.71	0.36	0.27	1.28
4	$-(CH_2)_6H$	122	8	0.715	1.71	0.34	0.23	1.29
5	$-(CH_2)_7H$	146	9	0.730	1.71	0.34	0.20	1.29
6	$-(CH_2)_8H$	168	10	0.741	1.80	0.31	0.17	1.31
7	$-(CH_2)_9H$	192	11	0.750	1.81	0.24	0.12	1.35
8	$-(CH_2)_{10}H$	213	12	0.758	1.65	0.18	0.08	1.39
9	$-CH(CH_3)_2$	20	5	0.627	1.40	0.18	0.17	1.39
10	$-C(CH_3)_3$	41	6	0.653	1.71	0.079	0.064	1.45
11^{a}	-CH(CH ₃)CH ₂ CH ₃	54	6	0.670	1.70	0.16	0.14	1.40
12^{a}	$-CH_2CH(CH_3)_2$	53	6	0.665	1.80	0.22	0.18	1.37
13	$-Si(\bar{C}H_3)_3$	55	7	0.649		< 0.01	< 0.01	> 1.5
14	$-\!\!\!\operatorname{CH}_2\mathrm{Si}(\mathrm{CH}_3)_3$	84	8	0.719	—	< 0.01	< 0.01	> 1.5

Table I Monosubstituted Olefins CH₂=CHR

N, total number of methylene mass units or equivalent; d, density of the liquid; $\lambda_o^{1/3}$, value of $\lambda^{1/3}$ extrapolated to S = 0; C, relative swelling power, as defined in eq. (2) [those for samples having bp < 60°C were determined at least 4 times as described

in the text]; α , adsorption parameter, as defined in eq. (3); χ_1 , Flory-Huggins interaction parameter, calculated using eq. (4). ^a Determinations made using the scaled down version of the original analytical procedure as described in the Experimental Section.

described in considerable detail elsewhere.^{1–12} Reagent grade samples of test liquids were obtained from commercial sources, and they were used as such without further purification.

A set of composite film samples, each having a known value of x (i.e., x = 0.01, 0.02, 0.03, 0.04,0.08, or 0.11), was allowed to swell to saturation in excess test liquid at $23 \pm 1^{\circ}$ C. Thereafter, the volumes (S) of sorbed liquid per gram of enmeshed particles in these samples were determined gravimetrically in the usual way.^{1–12} The slope of the straight line, obtained when the Svalues are plotted as a function of the corresponding cube root of the average number λ [i.e., the ratio (1 + x)/x calculated for the sample having the average composition $(Sty)_{1-r}(DVB)_r$ of backbone carbon atoms between covalent crosslinked junctions in the respective samples, identifies the relative swelling power (C, in milliliters of adsorbed liquid per gram of particles) of the sorbed test liquid in accordance with eq. (2).

$$S = C(\lambda^{1/3} - \lambda_o^{1/3})$$
(2)

Here λ_0 is the value of λ extrapolated to S = 0. The corresponding adsorption parameter (α) was calculated from the observed *C* values by means of eq. (3).

$$\alpha = 104Cd/M \tag{3}$$

The letters d and M refer to the density and formula weight, respectively, of the test liquid.

The Flory–Huggins interaction parameter (χ_{ν}) is also calculated from *C* by means of eq. (4) as described elsewhere.²⁰

$$\chi_{\nu} = 0.49 + 1.01\nu - 0.61\nu C \tag{4}$$

Here v is the volume fraction of the polymer in the polystyrene–liquid system. Because it was noted that χ_v is most sensitive to the molecular struc-

No.	n	bp (°C)	Ν	d	$\lambda_o^{1/3}$	С	α	χ1
15	2	60	6	0.692	1.40	0.49	0.43	1.20
16	4	114	8	0.746	1.10	0.46	0.32	1.22
17	6	169	10	0.750	1.50	0.40	0.23	1.26

Table II α, ω -Divinyl-Substituted Polymethylenes $CH_2 = CH(CH_2)_n CH = CH_2$

		Value of n in \mathbb{R}_n = $(\mathrm{CH}_2)_n \mathrm{H}$									
No.	R_a	R_b	\mathbf{R}_d	\mathbf{R}_d	bp (°C)	Ν	d	$\lambda_o^{1/3}$	С	α	χ1
Disubstitute	d										
18 ^a gem	0	0	1	2	31	5	0.650	1.85	0.34	0.33	1.29
19 ^a	0	0	1	3	62	6	0.682	1.62	0.36	0.30	1.28
20^{a}	0	0	2	2	64	6	0.680	1.75	0.38	0.32	1.27
21 ^a trans	0	1	2	0	37	5	0.650	1.95	0.36	0.34	1.28
$21a^{\rm a}$ 98%	0	1	2	0	37	5	0.647	1.80	0.33	0.32	1.30
22^{a}	0	2	2	0	67	6	0.677	1.60	0.34	0.29	1.29
23^{a}	0	1	4	0	98	7	0.701	1.64	0.30	0.22	1.32
$24^{\rm a}$	0	3	3	0	122	8	0.715	1.80	0.31	0.21	1.31
25ª cis	0	1	0	2	37	5	0.650	2.10	0.44	0.43	1.23
26^{a}	0	1	0	4	98	7	0.708	1.72	0.50	0.37	1.20
27^{a}	0	1	0	iso-pr	57	6	0.671	1.60	0.19	0.16	1.38
Trisubstitut	ed			-							
28^{a}	0	1	1	1	35	5	0.662	1.77	0.38	0.37	1.27
29^{a}	0	1	2	1	69	6	0.698	1.45	0.43	0.37	1.24
30^{a}	0	2	1	1	67	6	0.690	1.40	0.26	0.26	1.34
Tetrasubstit	uted										
31^{a}	1	1	1	1	73	6	0.708	1.70	0.57	0.49	1.15

Table III Polysubstituted Ethylenes $R_1(R_2)C = CR_3(R_4)$ Where $R_i = (CH_2)_n H$ and n = 0-8

 $^{\rm a}$ Determinations made using the scaled down version of the original analytical procedure as described in the Experimental Section.

ture of the sorbed species at v = 1 (see fig. 4 of Errede and Tiers¹⁶), only the χ_1 values are reported in Table I. The χ_v values at any other value of v can be calculated using eq. (5).

$$\chi_{v} = 0.49 + v(\chi_{1} - 0.49) \tag{5}$$

The α values for analytes having low swelling power (C < 0.4) and low boiling points (bp $\leq 60^{\circ}$ C)

	e			-			
No.	Molecular Structure	N	d	$\lambda_o^{1/3}$	С	α	χ_1
32^{a}	CH ₃ SCH ₂ CH=CH ₂	6	0.878	1.87	1.88	1.94	0.35
33^{a}	$C_6H_5CH = CH_2$	8	0.909	1.85	2.09	1.91	0.23
34	$C_6H_5CH_2CH = CH_2$	9	0.892	1.87	1.92	1.51	0.33
35	$C_6H_5OCH_2CH=CH_2$	10	0.978	1.88	1.99	1.51	0.29
36	trans CH ₃ O ₂ CCH=CHCH ₃	7	0.944	1.70	1.49	1.46	0.59
37	trans H(CH ₂) ₂ O ₂ CCH=CHCH ₃	8	0.918	1.81	1.51	1.26	0.58
38	H(CH ₂) ₃ CO ₂ CH ₂ CH=CH ₂	9	0.902	1.70	1.24	0.90	0.74
39	$CH_3CO_2CH_2CH=CH_2$	7	0.928	1.70	0.90	0.86	0.95
40	$O(CH_2CH=CH_2)_2$	7	0.803	1.72	1.37	1.17	0.66
41	H(CH ₂) ₂ OCH ₂ CH=CH ₂	6	0.760	1.75	1.10	1.01	0.83
42	H(CH ₂) ₃ OCH ₂ CH=CH ₂	7	0.767	1.65	0.99	0.79	0.90
43	H(CH ₂) ₄ OCH ₂ CH=CH ₂	8	0.783	1.65	0.88	0.62	0.96
44	(cyclo C ₆ H ₁₁)CH=CH ₂	8	0.805	1.70	1.04	0.79	0.86
45	CH2=CHCH2C6F5	10	1.358	2.60	0.57	0.38	1.15

 Table IV
 Miscellaneous Olefins Having a Second Functional Group

 $^{\rm a}$ Determinations made using the scaled down version of the original analytical procedure as described in the Experimental Section.

GMS and Subseries	Series No.	$lpha_i:N_i$	D_s	$\alpha_f:N_f$	r^2
cyclic (CH ₂) _n	Reference line in Figure 1	0.863:4	0.0875	[0.172]:12	←0.993
$CH_2 = CHCH_{2-q}(CH_3)_q(CH_2)_{n-1}H$	0				
q = 0, n = 2-8	1	[0.418]:4	0.06406	[0.129]:12	←0.9992
q = 1, n = 2-9	1a	0.164:5		0.0504:13	
q = 1, n = 2-9	1b	0.064 :6		0.0197:14	
		$\uparrow \mathrm{Srs}\; 2$		$\uparrow \mathrm{Srs}\ 2\mathrm{h}$	
q = 0-2, n = 2	2	[0.418]:4	0.4075	0.064 :6	←0.9994
q = 0-2, n = 3	2a	[0.361]:5		0.0557:7	
q = 0-2, n = 4	2b	0.31 :6		0.0475:8	
q = 0-2, n = 5	2c	0.27 :7		0.0413:9	
q = 0-2, n = 6	2d	0.23 :8		0.0352:10	
q = 0-2, n = 7	2e	0.20 :9		0.0306:11	
q = 0-2, n = 8	2 f	[0.173]:10		0.0265:12	
q = 0-2, n = 9	$2 \mathrm{g}$	[0.149]:11		0.0228:13	
q = 0-2, n = 10	2h	[0.129]:12		0.0197:14	
		$\uparrow \mathrm{Srs} \ 1$		$\uparrow \mathrm{Srs} \ \mathrm{1b}$	
$CH_2 = CHCH_2 CH_{3-q} (CH_3)_q$					
q = 0 - 3	3	[0.361]:5	0.3018	0.090:7	
$CH_2 = CH(CH_2)_n CH = CH_2$					
n = 1 - 7	4	0.506:5	0.06794	0.0198:11	←0.9990
$CH_2 = C(CH_3)(CH_2)_d H$					
d = 1 - 8	5	0.363:4	0.04139	0.186:11	
$CH_2 = C[(CH_2)_n H]_2$					
n = 1 - 8	6	0.363:4	0.02738	0.150:18	
$\mathrm{CH}_{2} = \mathrm{C}[(\mathrm{CH}_{2})_{c}\mathrm{H}][(\mathrm{CH}_{2})_{8}\mathrm{H}]$	_				
c = 1-8	7	0.186:11	0.01335	0.150:18	
$\mathbf{CH}_{2} = \mathbf{C}[(\mathbf{CH}_{2})_{c+n}\mathbf{H}][(\mathbf{CH}_{2})_{d+n}\mathbf{H}]$	0				
c = 1, d = 2, n = 0 - 8 - d	6a	0.33 :5	0.02738	0.155:17	
c = 1, d = 3, n = 0 - 8 - d	6b	0.30:6		0.160:16	
c = 1, d = 4, n = 0 - 8 - d	6c	0.272:7		0.165:15	
c = 1, d = 5, n = 0 - 8 - d	6d	0.248:8		0.170:14	
c = 1, d = 6, n = 0 - 8 - d	6e	0.225:9		0.175:13	
c = 1, d = 7, n = 0-8 - d	61	0.205:10		0.180:12	
		\uparrow Srs 5		\uparrow Srs 7	
trans $CH_3CH = CH(CH_2)_cH$	0	0.400.4	0.07510	0.100.11	
c = 1 - 8	8	0.403:4	0.07512	0.120:11	€0.9996
trans $H(CH_2)_n CH = CH(CH_2)_n H$	0	0.400.4	0.07077	0.0410.10	
$n = 1-\delta$	9	0.403:4	0.07077	0.0412:18	€0.9999
trans $\Pi(\Box \Pi_2)_b \Box \Pi = \Box \Pi(\Box \Pi_2)_8 \Pi$	10	0 190.11	0.0500	0.0419.19	
0 = 1-8	10	0.120:11	0.0980	0.0412:18	
d = 1.8	11	0 464.4	0 0226	0.979.11	
u = 1-0	11	0.404.4	0.0320	0.275.11	
a = 0, d = 2, 8	11	0 42.5	0 0296	0.972.11	
q = 0, a = 2-8 a = 1, d = 2, 9	11	0.45.5	0.0020	0.275.11	
q = 1, a = 2-5 a = 2, d = 2-9	11a 11b	0.10.0		0.0340.13	
q = 2, a = 2 - 3	110	10.0000.1 ↑ Srg 12		↑ Srs 12σ	
a = 0 - 2 $d = 2$	19	0 43.5	0 4294	0 595.7	
q = 0 - 2, d = 3	12	0.40.0	0.1201	0.0552.8	
a = 0-2, d = 4	12a 19h	0.370.7		0.0512.0	
q = 0-2, d = 5	190	0.343.8		0.0475.10	
a = 0-2, d = 6	12d	0.318.9		0.0440.11	
a = 0-2, d = 7	12e	$0.295 \cdot 10$		0.0409.12	
a = 0-2, d = 8	120 12f	0.274.11		0.0379.13	
· · · · · · ·		\uparrow Srs 11		↑ Srs 11b	
		1.510 11		1	

Table V $\log \alpha_f = \log \alpha_i - D_S(V_f - N_i)$ Relationships for various Olemnic Serie
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 α_i , α_f , initial and final α values, respectively, in the series being considered; N_i , N_f , corresponding number of methylene mass units or equivalent; the bold numerals indicate experimentally determined values.



Figure 1 The log α versus N relationships for monosubstituted olefins and saturated cyclic hydrocarbons. (- - -) The log α versus N linear relationship for series 2a–2h will be parallel to that for series 2 and the log α versus N linear relationship for series 1a and 1b should be parallel to that for the linear portion of series 1. (•) Experimental data; (•) data obtained by extrapolation or interpolation; (•) phantom data (i.e., data points that would have been exhibited by the homologous series being considered if it did not undergo a change in the mode of adsorption characteristic of the series), as described in the text.

are particularly troublesome with respect to attaining good reproducibility (i.e., ± 0.01). This is not only because of the relatively small difference in weights of each sample before and after swelling to saturation, but also even more so because of the rapid rate of evaporation from these samples, which makes it difficult to establish correction factors that accurately reflect the weights of residual sorbed-but-not-absorbed liquid remaining in the interstices between the enmeshed particles in the respective composite film samples. In order to minimize the error from these uncertainties, the weight of sorbed liquid after attaining saturation was remeasured at least 3 more times. After each weighing, the liquid-swollen samples were reimmersed in the test liquid and allowed to remain overnight therein at 23.0 \pm 0.1°C before the volume of sorbed liquid was redetermined gravimetrically. The averages of the *S* values observed for each of the composite film samples were correlated with $\lambda^{1/3}$ and the best straight line was established by linear regression to obtain the corresponding values for *C* and $\lambda^{1/3}_{0}$, as described above.

RESULTS AND DISCUSSION

Accumulation of Sorption Data

The *acyclic olefinic liquids* studied thus far for which log α versus N relationships are established are noted in Table I and (in part) in Figure 1. The data are subdivided into five categories:

- 1. the monosubstituted ethylenes CH₂=CHR (nos. 1–14 in Table I);
- 2. the α,ω -divinyl-substituted polymethylenes CH₂=CH(CH₂)_nCH=CH₂ (nos. 15–17 in Table II);
- 3. the disubstituted ethylenes having a gem CH_2 — $CR_c(R_d)$, a trans $(R_b)CH$ — $C(H)R_c$, or a cis $(R_b)CH$ — $CH(R_d)$ configuration (nos. 18–20, 21–24; and 25–27, respectively, in Table III);
- 4. the trisubstituted ethylenes $(R_b)CH=CR_c(R_d)$ (nos. 28–30 in Table III); and
- 5. the tetrasubstituted ethylenes $R_a(R_b)C = CR_c(R_d)$ (no. 31 in Table III).

The adsorption data for a set of miscellaneous functional olefins are collected in Table IV (olefins 32-42).

The double bonded carbon atom bearing an H and an R substituent (or another H) in these ethylenes is recorded arbitrarily on the lower left side of the double bond to identify the end actually making a liaison with the adsorption site; the rest of the molecule extends away from this site because of dynamic associative interactions with the mobile sorbed but not sorbed molecules in the system at liquid saturation as shown in Figure 2.

The test liquids that were evaluated using the scaled-down version of the original protocol are identified in Tables I–IV. The relative swelling power [*C*; eq. (2)] of a volatile liquid sample (bp $< 60^{\circ}$ C) was determined at least 4 times in order to ensure good reproducibility of *C* because of the



Figure 2 Suggested modes of adsorption for mono-, di-, and trisubstituted olefins.

observed small degree of swelling and rapid rate of evaporation as described in the Experimental Section. The adsorption parameter (α) and the Flory–Huggins interaction parameter (χ) for the test liquids were calculated from the corresponding observed *C* value by means of eqs. (3) and (4), respectively.

Interpretations of Sorption Data

Monosubstituted Ethylenes, CH2=CHR

The data points (Table I) for the olefins $CH_2 = CH(CH_2)_n H$ are recorded in Figure 1, which shows that the log α versus N relationship for series 1 (Table V) is linear only for the members having n = 4-7 ($D_1 = 0.06406$; $r^2 = 0.9992$). The observed deviation from linearity for the higher members (n < 9) was expected on the basis of an analogy with the results reported earlier for similar series having the GMS $Z(CH_2)_n H$ (e.g., see figs. 32–36 in Errede¹). This form of deviation is attributable to self-association on the part of the sorbed molecules due to correlated molecular orientation of methylene units in the segment $(CH_2)_n H$, which becomes significant when n ex-

ceeds a critical value n' > 6 and usually about 8, as discussed previously.^{1,17–19} The exact n' depends on the nature of substituent Z that makes a liaison with the adsorption site (see table 8 of Errede¹).

The marked deviation from projected linearity exhibited by the member having n = 3 was unexpected, however. Although it was not possible to establish the α values for the lower members (i.e., 1-butene, propylene, and ethylene, which are gases at 23°C), it was assumed that α would continue to decrease as n is decreased. Our studies involving sorption of carbonyl liquids,* such as $CH_3CO(CH_2)_nH$ and $H(CH_2)_nCO_2CH_3$, exhibited patterns similar to that recorded in Figure 1: a monotonic increase in α from n = 0 to about 3, followed by a linear decrease in log α thereafter to the onset of deviation at n' = -8. The cause of the observed maxima exhibited in these series, however, was not elucidated until our investigations involving sorption of ethers^{10–14} and thioethers¹⁵ showed that such progressive deviations from linearity exhibited by the members having n < 9 are caused by a progressive change in the mode of adsorption.

In the present case, which deals with sorption of CH_2 — $CH(CH_2)_nH$ liquids, it is suggested that the cause of the observed increase in α from 0.25 at n = 3 to 0.31 at n = 4 may be attributed to a progressive change from the "flat" mode of adsorption believed to be operative for ethylene [Fig. 2(a)] to the more "vertical" mode of adsorption characteristic for the higher members [Fig. 2(c)] in which the nonadsorbed segment $(CH_2)_nH$ extends away from the adsorption site.

It is also possible that the CH_2 — CH_2 , being free of alkyl substituents, might be able to associate simultaneously with two phenyl groups to produce effective physical crosslinks between polymer chains as suggested in Figure 2(b). Such a "bridge" would serve to decrease the magnitude of swelling accordingly. This phenomenon is analogous to that observed by Guenet et al., who studied reversible thermo-induced gel formation in polystyrene solutions.^{21–26} They showed that such formations involved small solvent molecules that serve as bridges between adjacent phenyl groups in the coiled forms of isotactic polystyrene solutions, which afford rigid gels on cooling to well below room temperature. The original solution of coiled polymer is reproduced when the system is reheated to well above room temperature. If such "bridging" also occurs in liquified ethylene, then it is logical to expect that the tendency to do so will be less for propylene, because of a less favorable accommodation in molecular architectures, and that this tendency should diminish progressively with each additional methylene unit in CH_2 — $CH(CH_2)_nH$, such that it is virtually eliminated for the members having n> 3. Further evidence supporting the reality of the bridging concept will be presented in subsequent publications.

It was observed^{7,11} that when the mode of adsorption remains constant in a given $Z(CH_2)_nH$ series, the log α versus N linear relationships for the corresponding methyl-substituted series $ZCH_{2-q}(CH_3)_q(CH_2)_{n-1}H$, in which q is 1 or 2 and n is incremented from 2 to 9, are parallel to that for the q = 0 series (n = 2-8). Consequently, the corresponding crossover relationships in which nis constant at 3-8 while *q* is incremented from 0 to 2 are parallel to that having n = 2. It was also noted¹⁵ that even in those cases in which the mode of adsorption does not remain constant when q = 0, as indicated by the deviation from linearity similar to that shown in Figure 1, the log α versus N relationships for the corresponding q = 1 and 2 series are linear when n = 2-9 and in fact they are parallel to the linear portion of the parent q = 0 series, such that the straight line drawn through the data points for the second and third members of a given crossover series (i.e., those for which q is incremented from 0 to 2 at a given n) extend to within ± 0.01 of the α value that would have been exhibited by the first member of the crossover series if the lower members [n]< 3; and the higher members (n > 8)] of the q = 0series had not undergone a progressive change in the mode of adsorption from that characteristic of the middle members (3 < n < 8). The log α values that would have related linearly in the usual way to those for the corresponding second and third members in the nonlinear portions of the q = 0series were named "phantom values".¹⁵ In the present case (Fig. 1, and in subsequent figures as needed) these values are indicated by square symbols lying on the dashed line extensions from the linear portion of the log α versus N linear relationship for series 1. It is necessary to establish the phantom values in the q = 0 series because they enable one to establish the α values for the

^{*}The studies involving sorptions of ketones and esters were completed before 1989, but meaningful interpretations of the results obtained thereby were not possible until after completion of the studies involving sorption of ethers, which is described in the literature.¹⁰⁻¹³ The results of the ketone and ester studies and the conclusions derived therefrom are now being prepared in forms suitable for publication.

corresponding members in the q = 1 and 2 series as described in the following paragraph.

It is reasonable to assume that the above relationships should also exist when Z in such a series is CH₂=CH-. This is supported by the observation that the "phantom data point" (0.418 at N= 4) deduced for CH₂=CHCH₂CH₃ of series 1 and the observed data points for $CH_2 = CHCH(CH_3)_2$ and CH₂=CC(CH₃)₃ (i.e., olefins 9 and 10, respectively, in Table I) define the log α versus N linear relationship for series 2 (i.e., q incremented from 0 to 2 at $n = 2, D_2 = 0.4075, r^2 = 0.9994$ in Table V). Reasoning by analogy with the earlier studies, the log α versus N linear relationship for series 2a-2h (i.e., those in which q is incremented from 0 to 2 at n = 3-9, using the phantom values where appropriate) will be parallel to that for series 2 as indicated in Table V and Figure 1. It follows, therefore, that the log α versus N linear relationship for series 1a (q = 1, n incremented from 2 to 9) and series 1b (q = 2, n incremented from 2 to 9) should be parallel to that for the linear portion of series 1 (q = 0, n incremented from 4 to 7) as recorded in Table V and Figure 1.

Having established this array, we were in a position to test the predicted values for the members that comprise the GMS CH_2 — $CHCH_{2-q}(CH_3)_q$ - $(CH_2)_{n-1}H$ using small liquid samples thereof. The first of these was a 10-mL sample of the second member of series 1a, namely, CH_2 — $CHCH(CH_3)$ - $(CH_2)_2H$. The α value for this analyte (no. 11 in Table I) was observed to be 0.14, which compares very favorably with the value of 0.142 calculated by means of the log α versus N linear relationship for series 1a (Table V).

Additional samples of liquids that comprise the above classification would enable us to test the accuracy of the above predicted values more rigorously and, if necessary, to modify accordingly the constants α_i and D_s for the appropriate log α versus N linear relationships.

It is inferred from the above results that the most probable mode of adsorption for monosubstituted ethylenes CH_2 —CHR involves polarizability-polarizability interactions of a π orbital on the unsubstituted carbon atom of the double bond with a π orbital most probably (on the basis of steric considerations) at the para position of the pendent phenyl group of the polymer (at liquid saturation). The forces of dynamic associative interaction between the R group and the mobile sorbed-but-not-adsorbed molecules in the gel system at liquid saturation causes the R group to extend away from the adsorption site and also

causes the double bond to rotate to a more vertical orientation with respect to that site, such that the hydrogen atom trans to the R group is forced up against the adsorption site [Fig. 2(c)]. This serves to fix the attitudinal angle (ϕ) such that the R group projects away from the adsorption site, which determines the decrementation constant (D_1) for the log α versus N linear relationship unique to series 1.

It is interesting to consider the log α versus N linear relationship deduced for series 3 [Table V; i.e., CH₂=CHCH₂CH_{3-q}(CH₃)_q] using the phantom value (0.361) for the member having q = 1 and the observed value ($\alpha_2 = 0.18$) for the member having q = 2 (no. 12 in Table I). These data enable one to calculate by means of eq. (1) that the decrementation constant for series 3 is $D_3 = 0.3018$ (i.e., log 0.361 – log 0.18) and then to calculate that the α_3 value for the q = 3 member is 0.090.

It is noted that D_3 is significantly less than the decrementation constant ($D_2 = 0.4075$) established for $CH_2 = CHCH_{3-q}(CH_3)_q$ (series 2 in Table V). This result is consistent with results reported earlier in studies that involved sorption of the branched ethers $RO(CH_2)_n CH(CH_3)_2$ and $RO(CH_2)_n C(CH_3)_3$. The decrementation constants for these series, in which *n* is incremented from 1 to 10 at constant q, decrease with q (i.e., the slope becomes less negative, see fig. 8 in Errede¹¹ and fig. 5 in Errede and Tiers¹⁴). This moderating effect is attributable not only to a decrease in the negative influence from steric hindrance, which is caused by the presence of a methylene "spacer" between the olefinic group and branched group, but also to improved dynamic associative interactions of a branched group at the ω position (relative to the corresponding linear molecular architecture) with the mobile sorbed-but-not-adsorbed molecules in the gel system at liquid-saturation.

In this regard we considered it of interest to test the effect on α caused by replacing the $C(CH_3)_3$ group of olefin 10 in Table I by $Si(CH_3)_3$ (olefin 13 in Table I). This replacement, however, caused a sharp decrease from 0.064 for the former to <0.01 for the latter. In order to establish whether this decrease was the result of electronic or steric contributions, CH_2 =CHCH₂Si(CH₃)₃ was also tested. The results (no. 14 in Table I) were the same, suggesting that the pronounced negative effect on the α value was due primarily to the bulkier size of Si(CH₃)₃ relative to C(CH₃)₃.

In retrospect the complex log α versus N pattern for CH_2 — $CH(CH_2)_nH$, as indicated by the

members having n = 3-10 (filled circles on the lowest of the three continuous lines shown in Fig. 1), provides justification for the reluctance, which was expressed in our preceding publication,¹⁶ to extrapolate the log α versus N linear relationships for both the $(CH_2)_n$ series (highest bold reference line in Fig. 1) and the corresponding series of monosubstituted polymethylene derivatives {i.e., $cyclo[(CH_2)_{m-1}CH](CH_2)_nH$ } to the corresponding lower members (i.e., m = 2 or 3; see fig. 2 of Errede and Tiers¹⁶). The reasons given at the time were that the mode of adsorption might change from a rather vertical to a flatter orientation and/or that the electronic nature of the ring architecture at n = 2 would be that of a double bond; either or both would dramatically change the mode of adsorption.

The pattern recorded in Figure 1 for $CH_2 = CH(CH_2)_n H$ shows that both of these concerns were justified. The negative deviation exhibited by the lower members (n < 4) from the linearity exhibited by the higher members shows that a change in the mode of adsorption from a vertical to a flatter orientation does indeed occur in both the cyclic $(CH_2)_m$ series and the corresponding monosubstituted $cyclo[(CH_2)_{m-1}CH]$ $(CH_2)_n H$ series when m = 2 or 3 but not in the latter series when n > 3. It is noted that the decrementation constant $D_s = 0.0875$ for $cyclo[(CH_2)_{m-1}CH](CH_2)_nH (m > 3 \text{ in fig. } 2 \text{ of}$ Errede and Tiers¹⁶) is greater than that $(D_1$ = 0.0641) for CH_2 =CH(CH₂)_nH (series 1 in Fig. 1 and Table V). This marked difference is caused primarily by the negation of the entropic factors that favor efficient self-assembly on the adsorption site characteristic of cyclic molecules, when that cyclic structure carries an alkyl substituent covalently bonded thereto.

It is suspected that D_s for $cyclo[(CH_2)_2CH]$ -(CH₂)_nH will have a value between the two D_s values cited above for the set of m > 3 series and that for the m = 2 series. The indicated monotonic decrease in D_s reflects the corresponding change in the electronic character of the cyclic portion of $(CH_2)_{m-1}$ CHR, as m decreases from 4 to 2 (i.e., as it approaches being a proper double bond at m = 2).

α, ω -Divinyl-Substituted Polymethylenes, CH₂=CH(CH₂)_nCH=CH₂

The log α versus *N* linear relationships for these α, ω -disubstituted polymethylenes (series 4 in Table V) is given by the best straight line (es-

tablished by linear regression; $r^2 = 0.9990$) through the data points for the n = 2, 4, and 6 members (nos. 15, 16, and 17 in Table II; filled circles on the middle continuous line in Fig. 1). The values of the constants for this relationship are $\alpha_i = 0.506$ at N = 5 and $D_4 = 0.06794$. The log α versus N linear relationship deduced thereby was then used to establish by interpolation and/or extrapolation the α values for the n = 1, 3, 5, and 7 members (i.e., 0.506, 0.370, 0.271, and 0.198, respectively; dot-in-an-emptycircle symbols on the middle continuous line in Fig. 1).

However, extrapolation of this relationship down to n = 1 may not be justified. It was observed in earlier studies^{8,12} involving α, ω -disubstituted polymethylenes $X(CH_2)_n X (X = Cl, Br, or$ alkoxy; n = 1-12) that X_2CH_2 is indeed the first member of series $X_2CH(CH_2)_nH$, but it is not the first member of series $X(CH_2)_{n+2}X$, the log α versus N linear relationships for which lie uniformly above those of the former. In order to establish unequivocally the adsorption series for which divinyl methylene (i.e., 1,4-pentadiene) is the first member, the α value for $(CH_2 = CH)_2 CH_2$ will have to be determined experimentally. Unfortunately, samples of the liquids that comprise the latter series are not yet available to us, which precludes unambiguous assignment of the adsorption series for which $(CH_2=CH)_2CH_2$ is the first member.

Figure 1 shows that the loci of the data points for the members of series 4 (which tentatively includes n = 1 lies between the log α versus N linear relationship for the reference series $(CH_2)_n$ (topmost bold straight line in Fig. 1) and the complex relationship observed for series 1, $CH_2 = CH(CH_2)_n H$ (lowest bold continuous line in Fig. 1). This comparison shows that the negative slope of the log α versus N linear relationship for $CH_2 = CH(CH_2)_n CH = CH_2 \text{ (series 4; } D_4 = 0.0679\text{)},$ is slightly greater than that $(D_1 = 0.0641)$ for the linear portion of $CH_2 = CH(CH_2)_n H$ when n= 4-7, but considerably less than that (D_{ref}) = 0.0875) for $(CH_2)_n$, such that the reference relationship intersects the log α versus N linear relationship for series 4 at about N = 12 and that for the phantom projected portion of series 1 at about N = 17.

The α values for the diolefins, however, are uniformly greater than those of the monoolefins at the same value of *N*. This is additional confirmation that the mode of adsorption for polyfunctional molecules is monodentate. It also supports the point of view that the nonadsorbed functional groups can have a positive influence on the manner in which the rest of that molecule projects away from the adsorption site, because of improved dynamic interactions (attributable to the terminal olefinic group) with the mobile sorbed-but-not-adsorbed molecules in the polymer-liquid system at saturation as discussed in earlier publications.^{8,12,13} That the log α versus N linear relationship for the diolefins is uniformly above (and almost parallel to) that for the corresponding monoolefins might be ascribed in part to the twofold greater statistical opportunity for a terminal olefin group to make a liaison with the adsorption site in the former case relative to the latter.

It is inferred from this observation that the attitudinal projection of the polymethylene segment away from the adsorption site in the case of the diolefins must be essentially the same as that in the case of the monoolefins [Fig. 2(c)]. The fact that the decrementation constant ($D_4 = 0.0679$) for CH_2 — $CH(CH_2)_nCH$ — CH_2 is actually slightly greater than that ($D_1 = 0.0641$) for CH_2 — $CH-(CH_2)_nH$ might reflect the difference in magnitude of contributions to steric hindrance offered by a terminal CH— CH_2 group relative to that by a terminal CH_2CH_3 group.

Polysubstituted Ethylenes $R_a(R_b)C = CR_c(R_d)$ [R = (CH₂)_nH and n = 0-8]

The adsorption data for the analytes tested thus far in this category (nos. 18–31) are recorded in Table III, which also notes the number of methylene units (**n**) in each of the respective R substituents (a, b, c, or d) attached to the carbon atoms of the double bond. Substituents R_a and R_c are on one side of the double bond, and R_b and R_d are on the other (i.e., R_a and R_c are cis to one another whereas R_a and R_d are trans). The disubstituted *trans*-olefinic liquids listed in Table III are in fact cis–trans mixtures but are more than 80% in the trans configuration, unless otherwise specified (e.g., olefin 21a is 98% *trans*-2pentene). The purities of the disubstituted *cis* olefins listed therein (nos. 25–27) are > 98%.

The α values $(\alpha_{a,b,c,d})$ for these molecules reflect the net result of the electronic, steric, and associative contributions from the four R substituents attached to the double bond. Consequently, progressive replacement of the hydrogen atoms by methyl groups should exhibit a nonlinear log α versus N relationship in the manner discussed earlier^{8,12} for $CH_{4-q}R_q$ where q is an integer from 0 to 4 and R is a hetero atom, such as chloro or bromo (see fig. 2 in Errede⁸), or an alkoxy group (see figs. 6–9 in Errede and Tiers¹²). These earlier considerations represent relatively simple examples that exhibit maxima at about q= 3, but the present consideration is much more complex because it involves progressive substitution on a double bond rather than on a single carbon atom. Hence, the pattern for α versus the degree of substitution should vary accordingly in a more complicated manner yet to be determined. Nevertheless, the patterns of rigidly interconnected log α versus N linear relationships for each of these classifications can be established by the approach (described in the Introduction) used to solve the molecular adsorptivity-structure relationships for the complex ethers and thioethers.^{11–15}

In the case of the olefins $R_a(R_b)C = CR_c(R_d)$, where R is either CH₃ or H, there are six possible permutations, each of which represent the first member of a homologous series that can be incremented systematically from CH₃ to (CH₂)₈H while the others are held constant, such that each series will exhibit a unique log α versus N linear relationship that reflects the net result of the other contributing factors that are held constant. The α value for the first member of a given series will primarily reflect the net electronic contributions of the four substituents (H or CH₃), whereas the decrementation constant $[D_s; eq. (1)]$ will primarily reflect the mode of adsorption and attitudinal angle at which the $(CH_2)_n$ H substituent being incremented projects away from the adsorption site, as illustrated by the examples that follow.

The first case, involving sorption of CH₂=CHR and the complications thereof, was already discussed (series 1-4 in Table V). The abnormal deviation exhibited by the lower members of $CH_2 = CH(CH_2)_n H$ from the log α versus N linear relationship exhibited by the higher members (n> 3) does not occur in the cases of the olefin series that bear more than one alkyl substituent because of the additional opportunities for dynamic associative interactions that are even greater than those noted for CH_2 =CHR in which R is a branched alkyl group. In the cases of di-, tri-, and tetrasubstituted olefins, each combination of two or more alkyl substituents will afford a log α versus N linear relationship that is unique to the combination.

In the second case, which involves sorption of disubstituted olefins, there are three subclassifications: those in which the two substituents have a gem, trans, or cis configuration [Fig. 2(d-f), respectively]. The $\alpha_{0,0,c,d}$ values for only three members of the gem classification have been determined thus far: 2-methyl-1-butene, 2-methyl-1-pentene, and 2-ethyl-1-butene (olefins 18-20, respectively, in Table III). The selectivity, however, is such that even this small set of sorption results is enough to permit one to estimate with reasonable confidence the $\alpha_{0,0,c,d}$ values for the remaining 33 members that comprise the classification $CH_2 = C[(CH_2)_c H][(CH_2)_d H]$ in which c is held constant at 1-8 while *d* is incremented from c to 8.

Thus, the difference $(\log \alpha_{0,0,1,2} - \log \alpha_{0,0,1,3})$ for the second and third members of CH_2 =CCH₃(CH₂)_dH (olefins 18 and 19 in Table III) indicated that the D_s for series 5 (Table V) is $D_5 = 0.04139$. Having established D_5 , it was then possible to calculate the $\alpha_{0,0,1,d}$ values for the other members of series 5 (i.e., those having d = 1 and 4-8, as indicated in Table V).

Because the $\alpha_{0,0,1,1}$ value (0.363) deduced for $CH_2 = C(CH_3)_2$ in series 5 is also that for the first member of $CH_2 = C[(CH_2)_n H]_2$ [i.e., series 6 in which the number of methylene groups (n) in both polymethylene chains are incremented simultaneously from 1 to 8], the D_s value for series 6 is given by the difference (log $\alpha_{0,0,1,1} - \log \alpha_{0,0,2,2})$, namely $D_6 = 0.02738$. Having established D_6 , it was then possible to calculate the $\alpha_{0,0,n,n}$ values for the remaining members of series 6 (i.e., those having n = 3-8, as indicated in Table V).

The difference $(\log \alpha_{0,0,1,8} - \log \alpha_{0,0,8,8})$ for the first (c = 1) and eighth (c = 8) members of CH₂—C[(CH₂)_cH][(CH₂)₈H] gives the D_s value for series 7 (i.e., $D_7 = 0.01335$), which enables one to calculate the $\alpha_{0,0,c,8}$ values for the other members of series 7 by interpolation using eq. (1), as indicated in Table V.

That the decrementation constant for series 5 $(D_5 = 0.04139)$ is significantly greater than that for series 7 $(D_7 = 0.01335)$ shows that incrementation of the longer chain causes a greater negative affect on log α than does subsequent incrementation of the shorter chain. Thus, the log α versus N linear relationships for series 5, 6, and 7 are rigidly interconnected in a triangular array (Fig. 3), such that $2D_6 = D_5 + D_7$. Similar triangular arrays were deduced for dialkyl ethers having two or more structural variables (for examples see fig. 3 in Errede,¹⁰ figs. 9–14 in Errede,¹¹ and fig. 4 in Errede and Tiers¹⁴) and for the dialkyl thioethers (see figs. 2, 4, 5, and 6 in Errede and Tiers¹⁵), such that the intersections of the three sets of mutually parallel log α versus N linear relationships identified the α values for all 36 permutations of the classification being considered, as shown, for example, here in Figure 3 for CH₂=C[(CH₂)_cH][(CH₂)_dH].

The exact $\alpha_{0,0,c,d}$ values for these members can be calculated by means of eq. (1) using $D_6 = 0.02738$ and the appropriate $\alpha_i = \alpha_{0,0,1,d}$ (i.e., the α values for the members that comprise series 5, in which d = 1-8) to establish the set of log α versus N linear relationships that are parallel to that for series 6: series 6a–6f (Table V). Thus, the $\alpha_{0,0,c,8}$ values for the members that comprise CH₂ ==C[(CH₂)_cH][(CH₂)₈H] (i.e., series 7) are given by the α values for the set of final members in series 6 and 6a–6f, which are shown in Table V and Figure 3.

Next we considered the three subseries of dialkyl olefins $R_bCH = CHR_c$ having a trans configuration [Fig. 2(e)]: series 8 in which R_b is CH_3 and R_c is $(CH_2)_cH$ where *c* is incremented from 1 to 8; series 9 in which R_b and R_c both have the same number (n) of methylene units that are incremented simultaneously when n = 1-8; and series 10 in which b in R_b is incremented from 1 to 8 while R_c is held constant at $(CH_2)_8H$. The log α versus N linear relationships for series 8, 9, and 10 were deduced as follows: the α values for the second ($\alpha_{0,1,2,0} = 0.34$) and fourth ($\alpha_{0,1,4,0} = 0.24$) members of series 8 (olefins 21 and 23, respectively, in Table 1; filled circles in Fig. 4) were used to determine the difference (log $\alpha_{0,1,2,0}$ – log $\alpha_{0,1,4,0}$), which indicated the approximate decrementation constant [eq. (1); $D_8 = 0.0756$] for series 8. This was then used to calculate the α value for the first member of series 8 (i.e., $\alpha_{0.1,1,0}$ = 0.405). In like fashion, the α values observed for the second ($\alpha_{0,2,2,0} = 0.29$) and third ($\alpha_{0,3,3,0}$) = 0.21) members of series 9 (olefins 22 and 24 in Table I, filled circles in Fig. 4) were used to determine the difference (log $\alpha_{0,2,2,0} - \log \alpha_{0,3,3,0}$), which indicated the approximate decrementation constant $(D_9 = 0.0701)$ for series 9. This was then used to calculate, by means of eq. (1), the α value for the first member of series 9 (i.e., $\alpha_{0,1,1,0}$ = 0.401). This second calculation of the α value for trans CH₃CH=CHCH₃ was remarkably close to that established via extrapolation using the log α versus N linear relationship established above for series 8. It was concluded therefrom that the



Figure 3 The log α versus N linear relationships for disubstituted gem- and cisolefins. (•) Experimental data; (\bigcirc) extrapolation data used to calculate D_s for eq. 1; (•) data obtained by extrapolation as described in the text.

mode of adsorption is essentially the same in series 7 and 8.

Accordingly, the average $(\alpha_{0,1,1,0} = 0.403 \pm 0.002)$ of these two determinations was accepted as the best value for *trans* CH₃CH ==CHCH₃ (empty circle in Fig. 4). The decrementation constant $(D_8 = 0.0751; r^2 = 0.9999)$ calculated by linear regression using the α values for the first, second, and fourth members of series 8 and the decrementation constant $(D_9 = 0.0708; r^2 = 0.9999)$ calculated using the α values for the first, second, and third members of series 9 were used to calculate the rest of the respective members of these two series and are recorded in Table V.

The perimeter of the triangular areas of rigidly interconnected log α versus *N* linear relationships for all the subseries of the trans-disubstituted olefins having the GMS H(CH₂)_bCH=CH(CH₂)_cH, where the variables b and c can be incremented independently or simultaneously, is given by the log α versus N linear relationships for series 8, 9, and 10. These three relationships are recorded in Figure 4, which shows that they define a long narrow triangle, such that almost all the data points for the entire set of 36 structural permutations of the above GMS can be identified almost within experimental reproducibility by a single line. Apparently, the moderating effect on the attitudinal angle of projection, caused in this case by systematic incrementation of $H(CH_2)_b$, is virtually nullified by the concomitant electronic and steric changes produced thereby. Hence, it is meaningless to deduce the set of six relationships that parallel the one for series 9 to identify more precisely the α values for these permutations,



Figure 4 The log α versus N linear relationships for disubstituted *trans*-olefins. (\bigcirc) Experimental data; (\bigcirc) data-point obtained via extrapolation of both subseries *trans*-ethylenes; (\bullet) data obtained via extrapolation of one subseries.

because of the uncertainty for measuring those for the lower members (filled circles in Fig. 4), which were used initially to establish this triangular relationship.

The reader is reminded that the disubstituted olefinic liquids used to establish the diagram shown in Figure 4 were in fact cis-trans mixtures, only about 80% of which had the trans configuration, which was estimated by their respective indices of refraction. It is certain that an analogous study using pure trans-disubstituted olefins will exhibit log α versus N linear relationships that are displaced uniformly below the linear relationships exhibited by the corresponding 4/1 mixtures, which is indicated by the comparison of the α values observed for the 80% ($\alpha_{0,1,2,0} = 0.34$) and 98% ($\alpha_{0,1,2,0} = 0.32$) pure samples of trans-2-pentene (olefins 21 and 21a, respectively, in Table III).

In the case of the cis-disubstituted olefins [Fig. 2(f)], again only three samples (all of which are

> 98% pure) were determined thus far (olefins 25–27 in Table III), but in this case the selectivity does not allow one to establish the full triangular array of rigidly interconnected log α versus N linear relationships as described above for gemand trans-disubstituted olefins. This set, however, does allow one to establish the log α versus N linear relationship for cis $CH_3CH = CH(CH_2)_dH$ (i.e., series 11 in which d is incremented from 1 to 8; Table V). The difference (log $\alpha_{0,1,0,2}$ – log $\alpha_{0,1,0,4}$) for the second (d = 2) and fourth (d = 4)members (olefins 25 and 26 in Table III) gives the D_s value for series 11 (i.e., $D_{11} = 0.0326$), which enables one to calculate the $\alpha_{0,1,0,d}$ values for the remaining members of series 11 as recorded in Table V. As expected, the plot of these data (Fig. 3) shows that their loci lie uniformly above that for those comprising series 5, which supports the point of view that cis-disubstituted olefins should offer less steric hidrance to adsorption than the gem-disubstituted olefins.

If and when one or more members of *cis* $H(CH_2)_n CH = CH(CH_2)_n H$ (n = 2-8) become available to us, it will be possible to deduce the triangular network of rigidly interconnected log α versus N linear relationships for the subseries of $H(CH_2)_b CH = CH(CH_2)_d H$ and thereby identify the α values for all 36 permutations having this GMS. It is believed that the triangular network of log α versus N linear relationships for the subseries in the cis classification will be similar to that for those in the gem classification (Fig. 3) and that it will lie uniformly above the latter.

Having established the log α versus N linear relationship for series 11, it then became possible to use the $\alpha_{0,1,0,i\text{-pr}}$ value (olefin 27 in Table III) in conjunction with the above relationship to establish the rectangular array of rigidly interconnected log α versus N linear relationships for a subseries of cis CH₃CH=CHCH_{2-q}(CH₃)_q(CH₂)_{d-1}H. Thus, the difference (log $\alpha_{0,1,0,2}$ – log $\alpha_{0,1,0,i\text{-pr}}$) for the first (q = 0) and second (q = 1) members of cis CH₃CH=CHCH_{2-q}(CH₃)_q(CH₂)_{d-1}H (series 12 in which d = 2 and q is incremented from 0 to 2) gives the D_s value for series 12 (i.e., $D_{12} = 0.4294$). This enables one to calculate the α value for the third member ($\alpha_{0,1,0,t\text{-bu}} = 0.0595$) of series 12 as indicated in Table V.

Because the linear relationships for cis $CH_3CH = CHCH(CH_3)(CH_2)_{d-1}H$ and cis CH_3CH =CHC(CH₃)₂(CH₂)_{d-1}H (series 11a and 11b in which q is kept constant at 1 and 2, respectively, while d is incremented from 2 to 9) are expected to be parallel to that for series 11 in which q = 0while d is incremented from 2 to 8, the remaining members of series 11a and 11b can be calculated by means of eq. (1) using for the constants D_{11a} and D_{11b} the value determined for series 1 (i.e., $D_{11} = 0.0326$) and for the constants α_i the value of $\alpha_{0,1,0,i\text{-pr}}$ at N = 6 for series 11a and the value of $\alpha_{0,1,0,t-bu}$ at N = 7 for series 11b (or alternatively by the set of log α versus N linear relationships, series 12a-12f, that are parallel to that for series 12 and pass through the data points of series 11 at d = 2-8), which is shown by the rhomboidal array of data points in Figure 5. Thus, the intersections of these two sets of parallel log α versus N linear relationships for the subseries of cis $\label{eq:CH3} \textbf{CH}_3\textbf{CH} \hspace{-1mm}= \hspace{-1mm} \textbf{CHCH}_{2-q}(\textbf{CH}_3)_q(\textbf{CH}_2)_{d-1}\textbf{H} \text{ identify the}$ α values for all 26 possible permutations of this GMS.

When this rhomboidal array of data points (Fig. 5) representing the log α versus N linear relationships for the subseries of *cis* CH₃CH ==CHCH_{2-q}(CH)_q(CH)_{n-1}H (series 11, 11a, and

11b in Table V) is compared with that (dashed straight lines in Fig. 1) representing series 1, 1a, and 1b in Table V [i.e., $CH_2 = CHCH_{2-q}(CH)_q$ - $(CH)_{n-1}H$, one notes some interesting similarities. The α values for the members having the same q and mass N are unusually close, especially those for the members at N = 4 ($\alpha_{0,1,0,1} = 0.43$ for *cis* CH₃CH=CHCH₃ and $\alpha_{0,0,0,2} = 0.42$ for $CH_2 = CHCH_2CH_3$). The decrementation constant $(D_{12} = 0.429)$ for *cis* CH₃CH=CHCH_{2-q}(CH₃)_q (q = 0-2; series 12 in Table V) is also very close to that $(D_2 = 0.408)$ for $CH_2 = CHCH_{2-q}(CH_3)_q$ (q= 0-2; series 2 in Table V), but the decrementation constant $(D_{11} = 0.031)$ for *cis* CH₃CH $= CHCH_{2-q}(CH_3)_q(CH_2)_{n-1}H (n = 2-8 \text{ at } q = 0,$ 1, and 2; series 11, 11a, and 11b, respectively, in Table V) is only about half that $(D_1 = 0.064)$ for those having the GMS $CH_2 = CHCH_{2-q}(CH_3)_q$ - $(CH_2)_{n-1}H$ (n = 2-8 at q = 0, 1, and 2; series 1, 1a, and 1b, respectively, in Table V), which is primarily responsible for the observed differences in α values at the same mass N and a given q. These data clearly show that the presence of a cis-methyl substituent serves to lessen the negative effect on α caused by incrementation of n from 2 to 8 at constant q, but it does not significantly alter that caused by incrementation of qfrom 0 to 2 at constant n.

In view of the above observation, we decided to broaden such studies to include comparisons of the log α versus N linear relationships for *trans* $CH_3CH = CH(CH_2)_nH$ and $CH_2 = CHCH_3(CH_2)_nH$ (n incremented from 2 to 8; series 8 and 5, respectively, in Table V) with the corresponding rela- $CH_2 = CH(CH_2)_n H$ tionships for and cis $CH_3CH = CH(CH_2)_nH$ (series 1 and 11, respectively, in Table V). To this end, the latter two relationships are used as reference lines in Figure 6 to permit easy side by side comparison with those for series 5 and 8, thereby allowing one to visually appreciate the relative affect on such relationships caused by a methyl group placed in a cis, trans, or gem orientation with respect to the $(CH_2)_n$ H substituent.

This comparison (Fig. 6) shows that the beneficial effect attributed to a methyl group having a cis orientation with respect to the $(CH_2)_n$ H substituent is not produced when this orientation is trans rather than cis. In fact, just the opposite is true. Thus, the α_i value at N = 4 for trans $CH_3CH=CHCH_3$ ($\alpha_{0,1,1,0} = 0.40$) is slightly less than that for $CH_2=CHCH_2CH_3$ ($\alpha_{0,0,0,2} = 0.42$), but considerably less than that for *cis* $CH_3CH=CHCH_3$ ($\alpha_{0,1,0,1} = 0.46$). Moreover, the



Figure 5 The log α versus N linear relationships forcis-olefins having the GMS CH₃CH=CHCH_{2-q}(CH₃)_q(CH₂)_dH, where d is 2-8 and q is 0-2. (•) Experimental data; (•) data obtained by extrapolation or interpolation; (•) phantom data.

decrementation constants for their respective homologous series (nos. 8, 1, and 11) are in the order $D_8 = 0.075 > D_1 = 0.064 > D_{11} = 0.033$.

This comparison (Fig. 6) also shows that the α_i value at N = 4 for $CH_2 = CH(CH_3)_2$ ($\alpha_{0,0,1,1} = 0.36$) is considerably less than those for $CH_2 = CHCH_2CH_3$ or *cis* $CH_3CH = CHCH_3$, which reflects the decrease in electronic contribution from the methyl group to the carbon atom making liaison with the adsorption site, when that methyl group is moved to the carbon atom adjacent thereto. The decrementation constant for the gem-disubstituted series ($D_5 = 0.041$), however, is less than that for the monosubstituted series ($D_1 = 0.064$) but greater than that for the cisdisubstituted series ($D_{11} = 0.033$). It can be inferred from these results that the magnitude of steric hindrance to adsorption, based on the observed D_s values for these four series, is in the relative order $D_8 = 0.075 > D_1 = 0.064 > D_5$ = 0.041 > $D_{11} = 0.033$.

The results observed for the three types of disubstituted olefins clearly show that the number, position, and mass of the substituents on the dou-



Figure 6 Comparisons of the log α versus N linear relationships for disubstituted olefins with that for the corresponding monosubstituted olefins. (\bigcirc) Experimental data; (\bigcirc) extrapolation or interpolation data; (\bigcirc) phantom data obtained by extrapolation.

ble bond in a homologous series of olefinic hydrocarbons affect the constants α_i and D_s that characterize the log α versus N linear relationship for the series being considered. It is believed on the basis of an analogy with earlier studies^{8,12} involving sorption of $CH_{4-x}X_x$ liquids (X = Cl, Br, or alkoxy; x = 1-4) that these results reflect the modes of adsorption of their respective homologous series to the adsorption site.

Accordingly, the above results are interpreted to mean that each series represents a quantitative alteration in molecular orientation at the adsorption site from that characteristic of the monosubstituted olefins (series 1) to that characteristic of the series modified by replacement of an H atom by an alkyl substituent. In the reference case, dynamic associative interactions between the $(CH_2)_n$ H chain and the mobile sorbed-but-not-

adsorbed molecules in the system at liquid-saturation not only causes the nonadsorbed portion to project away from the adsorption site, but it also imparts a torque that twists the adsorbed molecule onto its side. This causes the hydrogen atom trans to the $(CH_2)_n$ H substituent to be forced up against the pendent phenyl group of the polymer, while the rest of the molecule projects away from that site at a fixed orientation as shown in Figure 2(b). In the gem-disubstituted olefins there are two substituents on the nonadsorbed positions of the double bond that participate in dynamic associative interactions with the mobile molecules. In such cases, the second substituent provides a counterrotatory torque about the double bond. This enables the adsorbed molecule to "swivel" about the pivotal point of association that involves interaction of a polarizable methylene π orbital from the olefin with a polarizable π orbital from a phenyl group. Consequently, the nonadsorbed portion of the adsorbed molecule is allowed to self-adjust to a less sterically hindering trajectory [Fig. 2(d)], thereby lessening the negative effect on log α caused by incrementation in (CH₂)_nH.

When the second hydrogen is replaced by a methyl substituent to produce the trans configuration (series 8) instead of the gem configuration (series 5), the lift from the combined effect of dynamic associative interaction imparted by the two trans substituents is much less than that produced by two gem substituents. Moreover, the magnitude of moderating torque about the double bond is also much less in the case of the trans configuration than in the gem structure. Consequently, the magnitude of steric hindrance caused by the projection of the trans- $(CH_2)_n H$ substitutent toward the adsorption site is exacerbated rather than alleviated, as indicated in Figure 2(e), such that the D_s for series 8 ($D_8 = 0.0751$) is even greater than that for series 1 ($D_1 = 0.0641$).

When the second hydrogen replaced by a methyl substituent produces the cis configuration (series 11), the torques upon the double bond imparted by the two substituents are in the same direction. This causes the two *cis*-hydrogen atoms on the other side of the double bond to be forced up against the adsorption site. In so doing the attitudinal orientation angle of the adsorbed molecule is fixed such that both alkyl substituents project away from the adsorption site, as shown in Figure 2(f). This serves to minimize steric hindrance from the accumulated mass of these two polymethylene substituents. Consequently, the D_s for series 11 ($D_{11} = 0.0326$) is less than that for series 1 ($D_1 = 0.0641$).

These suggested models for adsorption [Figs 2(a-f)] imply that the mode of adsorption for the disubstituted olefins is qualitatively similar to that for the monoolefins. There are important quantitative differences, however, due to the molecular attitudes in the adsorbed state, which reflect the number and relative positioning of the hydrocarbon substituents covalently bonded thereto. The adsorption attitudes suggested in Figure 2 were deduced by intuitive reasoning processes to be consistent with the observed results. That the rationalization is self-consistent, however, is sufficient reason to accept the suggestions only tentatively as working hypotheses that may represent reality with reference to their respective molecular attitudes in the adsorbed state.

Supportive evidence obtained by some physical means, spectroscopic or otherwise, is needed to enable one to characterize the adsorbed molecular architecture while in the presence of a much larger amount of mobile sorbed-but-not-adsorbed molecules of its own kind, which are present when the polymer system is at liquid-saturation. Because such a physical means is not yet known, we will continue to use such models as working hypotheses, so long as they remain consistent with experimental results and serve reliably for comparative and predictive purposes.

In this respect it is intended that the results observed in this study involving sorption of cisdisubstituted ethylenes be compared with those obtained in our studies involving the corresponding cyclic olefins, which will be reported in our next publication, allowing one to evaluate the effect on α caused by the physical constraints of the ring.

The behaviors of the tri- and tetrasubstituted olefins are even more complicated than those outlined above for the disubstituted olefins, and unfortunately the number of α values established thus far for the multisubstituted olefins (nos. 28–31 in Table III) are relatively few. Before undertaking these considerations, therefore, it is good to compare the α values deduced for ethylene and its methyl substituted derivatives to note the effect on α caused by progressive replacement of hydrogen atoms by methyl substituents. In such considerations it is assumed that the mode of adsorption is essentially the same: it involves liaison of the less hindered end (or side) of the double bond with the adsorption site, while the other end (or side) bearing the larger alkyl substituents extends away from this site as suggested in Figure 2(c-e).

This correlation is recorded in Figure 7. The phantom values for ethylene and propylene, which were deduced by extrapolation to n = 0 and 1, respectively, using the log α versus N linear relationship for $CH_2 = CH(CH_2)_n H$ (i.e., series 1 in Table V) are also identified in the figure. The "real" α values for the liquid forms of these two molecules, if measured, are expected to be much less than those for the phantom values recorded here because of a change in the mode of adsorption from the vertical orientation characteristic of the higher members [Fig. 2(c)] to the flat [Fig. 2(a); perhaps even a bridging orientation unique to ethylene (Fig. 2(b)], which was explained in the discussion of monosubstituted olefins. The figure also identifies the α values for the three dimethyl-



Figure 7 Effect on α for the ethylenes caused by progressive replacement of the hydrogen atoms by methyl substituents. (•) Experimental data; (•) data obtained by extrapolation or interpolation; (•) phantom data.

substituted olefins (i.e., gem, trans, and cis) that were deduced by extrapolation to the first member of their respective series, as explained in the above discussions. The α values observed for 3-methyl-2-butene and 2,3-dimethyl-2-butene (olefins 28 and 31, respectively, in Table III) are also shown. The anticipated linear decrease in α with *x*, the number of hydrogen atoms replaced by methyl groups, is given by the dashed straight line that passes through the data points for ethylene, propylene, and trans-2-butene. That the data point for the trimethyl-substituted ethylene is somewhat above the dashed reference line can be rationalized on the basis of small quantitative changes in orientation and/or projection of the nonadsorbed portion away from the adsorption site, as explained in the discussion of the disubstituted ethylenes. However, it cannot be rationalized on the basis that the data point for the tetramethyl-substituted ethylene is well above the reference line, and in fact has an α value that is even greater than the phantom value for propylene. The anomaly noted in Figure 7 is a "red flag," suggesting that a qualitative change in the mode of adsorption may have started at x = 3 and became fully realized at x = 4.

Up to this point, the mode of adsorption was consistent with the point of view that one or more hydrogen atoms on the olefin molecule was projected into the plane of π orbitals on the phenyl ring. In the cases involving tetrasubstituted ethylenes this mode of adsorption is not possible. That adsorption does indeed occur, however, suggests that the roles may be reversed (i.e., sorption of tetrasubstituted olefins may be sterically easier if it involves the hydrogen atom on the phenyl



Figure 8 Suggested modes of adsorption for tetrasubstituted and functionally substituted ethylenes: as described in the text.

ring projecting into the π orbital system of the olefinic bond) as suggested in Figure 8(a). This alternate possibility will have to remain a most consideration, however, until more liquid samples of tetrasubstituted olefins become available to us for evaluation.

Meanwhile, we can only indicate the possible complexity of the rigidly interconnected network of log α versus N linear relationships expected for the trisubstituted ethylenes based on the α values observed for the three samples obtained thus far in this classification (olefins 28–30 in Table III). The trimethyl-substituted ethylene (no. 28 in Table III) is the first member of three homologous subseries in which one alkyl substituent is incremented from 1 to 8 while the other two are held constant. In addition, it is also the first member of three homologous subseries in which two alkyl subseries are incremented simultaneously while the third is held constant, and it is the first member of the series in which all three alkyl substituents are incremented simultaneously. Each pairing of the appropriate single and double incrementations will produce triangular arrays of rigidly interconnected log α versus N linear relationships in a given plane of multidimensional space. The log α versus N linear relationships in these planes in multidimensional space are rigidly interconnected such that the data may be

projected onto a reference plane (Figs. 3, 4). The 2-dimensional pattern obtained thereby should evoke in the mind of the observer a 3-dimensional image (see examples recorded in figs. 10, 13, and 14 in Errede¹¹). It is conceivable that one can establish the rigidly interconnected network of log α versus N linear relationships in multidimentional space, but it will require additional samples of key members of the subseries that comprise this GMS classification.

The treatment becomes even more complex when one attempts to consider the tetrasubstituted olefins. Nevertheless, it can be done, but it involves a few more dimensions because of the added variable and combinations thereof. Unfortunately, the samples of two or more members of each series, which are needed to establish such a rigidly interconnected network of the respective log α versus N linear relationships, are not yet available to us.

Miscellaneous Olefins Having Other Functional Groups

The results observed in the study involving sorption of α, ω -divinyl-substituted polymethylenes (nos. 15–17 in Table II and series 4 in Table V) reconfirm that the mode of adsorption of polyfunctional molecules to poly(Sty-co-DVB) at liquidsaturation is monodentate: one functional group is immobilized by a liaison with the pendent phenyl group of the polymer while the others on the nonadsorbed portion extend away from this site where they are involved in dynamic associative interactions with the mobile sorbed but not adsorbed molecules of their own kind. Thus, the α values for such polyfunctional molecules are affected not only by the electronic and steric contributions of the nonadsorbed functional groups, but also by these dynamic associative interactions.

In the cases of α, ω -disubstituted polymethylenes having the GMS $A(CH_2)_n R$, where A and R are the adsorbed and nonadsorbed functionalities, respectively, the manner in which the mode of adsorption can be affected by R at the other extremity is limited to how well it participates in dynamic associative interactions with the mobile sorbed-but-not-adsorbed molecules in the polymer-liquid system at saturation. The magnitude of this interaction affects the attitudinal angle (ϕ) at which the nonadsorbed portion $[(CH_2)_n R]$ projects away from the adsorption site^{8,13,15}; and, because the magnitude of steric hindrance to further adsoption in a given $A(CH_2)_n R$ series varies inversely with ϕ , the D_s for that series varies accordingly. Hence, D_{\circ} reflects the relative ability of R to participate in such dynamic associative interactions, which alter ϕ positively. The difference ΔD_s [= D_s for A(CH₂)_nH – D_s for A(CH₂)_nR], therefore, is a measure of how well the group R in the ω position can alleviate steric hindrance to further adsorption, as noted earlier,^{8,13,15} and again here (Fig. 1) in the case of $CH_2 = CH(CH_2)_n CH = CH_2$. For the sake of brevity and convenience, the above ameliorating effect on steric hindrance in such series will be referred to descriptively as a "desteric" effect.¹⁵

The relative ability of the R group to exhibit a desteric effect depends on its molecular structure.^{8,11–15} Although the results observed thus far in this ongoing investigation do not yet enable one to make hard quantitative comparisons because the A and R pairings are not the same, the efficacy for the incomplete compilation appears to be in the following approximate order: $C(OCH_3)_3 > CH(OCH_3)_2 > CH_2OCH_3 > CCl_3 \cong CBr_3 > CHCl_2 \cong CHBr_2 > CH_2Cl \cong CH_2Br > C(CH_3)_3 > CH(CH_3)_2 > CH_2CH_3.$

In those cases for which the terminal groups A and R are the same, it is not necessary to indicate the adsorption preference; but when this is not the case, the adsorption selectivity depends upon the relative affinities of the functional groups A and R for the adsorption site. The sorption preference in such cases is manifested in the constants α_i and D_s that characterize the log α versus N linear relationship for the $A(CH_2)_n R$ series, which in most cases permits one to adjudicate between the options when the observed results are compared with those exhibited by the corresponding series having only one of the functional groups in the difunctional series being considered. In some cases, such adjudications can be made even on the bases of comparisons involving only a single set of equivalent structures in each of the three homologous series involved. There is a caveat here that the mode of adsorption for the series being compared must be the same to ensure valid comparison, which is indicated by the examples that follow.

To this end, the adsorption data for a set of 14 olefins that carry a second functional group are collected in Table IV. The entries are listed in the approximate descending order of their respective α values. These data show that all except that for CH₂=CHCH₂C₆F₅ ($\alpha = 0.38$) are considerably higher than the highest α value deduced for an α

olefin, which is the phantom value ($\alpha = 0.49$; series 1 in Table I) for propylene.

This is consistent with the point of view that the relative affinities of acyclic monoolefins are markedly less than those for the corresponding structures having a phenyl,² ether,¹⁰⁻¹⁴ thioether,¹⁴ or ester group. Thus, in the cases of liquid molecules having an olefinic double bond and one of the other functional groups noted above, the adsorption preference will usually favor the latter, leaving the olefinic group free in the nonadsorbed portion where it can affect the α value of the adsorbed molecule by electronic contribution to the adsorption site and/or by dynamic associative interactions with the mobile molecules. As stated above, the constants α_i and D_s that characterize the log α versus N linear relationship of the series being considered can be used as criteria for adjudicating the adsorption selectivity. Examples of such adjudications involving the list of olefins having a second functional group (Table IV) are given in the following paragraphs.

As noted earlier in the comparative studies involving sorption of $\rm C_6H_5SCH_3$ and $\rm C_6H_5OCH_3$ (see table 4 in Errede and $Tiers^{15}$), it is the phenyl group of such molecules that is involved in a direct liaison with the adsorption site, not the heteroatoms. However, the latter affect the magnitude of α for these molecules by their electronic contribution to the adsorption site via inductive or resonance contributions to the phenyl group adsorbed thereto. The same is true for vinyl benzene (i.e., styrene) and allyl benzene (olefins 33 and 34, respectively, in Table IV): it is the phenyl group that makes the liaison with the adsorption site whereas the olefinic group is part of the nonadsorbed portion of the molecule that extends away from the adsorption site, and it can affect the magnitude of α via electronic interaction with the phenyl group, as described above.

The ratio of the α value for styrene (1.91) to that for allyl benzene (1.51) is consistent with the expectation based on electronic resonance theories. Table VI compares the α values observed for such difunctional molecules (column A) with those for the corresponding molecular structures in which the olefinic unsaturation had been elimininated (column B) and with those for the corresponding molecular structures in which the aromatic group was replaced by the equivalent number (six) of linear polymethylene groups (column C). As expected, the α values for these two aromatic compounds (column A) are slightly

A	В	С
$\begin{array}{l} C_{6}H_{5}CH &= CH_{2} \ 1.91 \\ C_{6}H_{5}CH_{2}CH &= CH_{2} \ 1.51 \\ C_{6}F_{5}CH_{2}CH &= CH_{2} \ 0.38 \\ cyclo \ C_{6}H_{11}CH &= CH_{2} \ 0.79 \\ CH_{3}SCH &= CH_{2} \ 1.94 \\ trans \ CH_{3}CH &= CHCO_{2}CH_{3} \ 1.46 \\ trans \ CH_{3}CH &= CHCO_{2}CH_{2}CH_{3} \ 1.26 \\ CH_{3}CO_{2}CH_{2}CH &= CH_{2} \ 0.86 \\ H(CH_{2})CO_{2}CH_{2}CH &= CH_{2} \ 0.90 \\ O(CH_{2}CH &= CH_{2})_{2} \ 1.17 \end{array}$	$\begin{array}{c} \mathbf{C_6H_5CH_2CH_3 \ 1.55} \\ \mathbf{C_6H_5(CH_2)_3H \ 1.33} \\ \mathbf{C_6F_5(CH_2)_3H \ ca. \ 0.22} \\ cyclo \ \mathbf{C_6H_{11}(CH_2)_3H \ 0.18} \\ CH_3\mathbf{S}(CH_2)_3H \ 1.80 \\ H(CH_2)_3\mathbf{CO_2CH_3 \ 1.22} \\ H(CH_2)_3\mathbf{CO_2CH_2CH_3 \ 1.01} \\ CH_3\mathbf{CO_2(CH_2)_3H \ 1.20} \\ H(CH_2)_3\mathbf{CO_2(CH_2)_3H \ 1.20} \\ H(CH_2)_3\mathbf{CO_2(CH_2)_3H \ 0.89} \\ \mathbf{O}(CH_2CH_2CH_3)_2 \ 0.48 \ or \\ \mathbf{O}(CH_2CH_2OCH_3)_2 \ 1.02 \end{array}$	$\begin{array}{l} \mathbf{CH_2} &= \mathbf{CH}(\mathrm{CH_2})_6\mathrm{H} \ 0.23 \\ \mathbf{CH_2} &= \mathbf{CH}(\mathrm{CH_2})_7\mathrm{H} \ 0.20 \\ \mathbf{CH_2} &= \mathbf{CH}(\mathrm{CH_2})_7\mathrm{H} \ 0.20 \\ \mathbf{CH_2} &= \mathbf{CH}(\mathrm{CH_2})_6\mathrm{H} \ 0.23 \\ \mathbf{CH_2} &= \mathbf{CH}(\mathrm{CH_2})_4\mathrm{H} \ 0.31 \\ trans \ \mathrm{CH_3}\mathbf{CH} &= \mathbf{CH}(\mathrm{CH_2})_3\mathrm{H} \ 0.29 \\ trans \ \mathrm{CH_3}\mathbf{CH} &= \mathbf{CH}(\mathrm{CH_2})_4\mathrm{H} \ 0.31 \\ \mathbf{CH_2} &= \mathbf{CH}(\mathrm{CH_2})_4\mathrm{H} \ 0.31 \\ \mathbf{CH_2} &= \mathbf{CH}(\mathrm{CH_2})_4\mathrm{H} \ 0.31 \\ \mathbf{CH_2} &= \mathbf{CH}(\mathrm{CH_2})_6\mathrm{H} \ 0.23 \\ \mathbf{CH_2} &= \mathbf{CH}(\mathrm{CH_2})_4\mathrm{H} \ 0.31 \end{array}$

Table VI Comparisons Indicating Mode of Adsorption on Basis of α Values

The functional group making a liaison with the adsorption site is indicated in bold.

greater than those for the corresponding structures in column B, but they are considerably greater than those for the corresponding structures in column C. This is interpreted to mean that the adsorption preference is greatly in favor of the phenyl group over the olefinic group.

Adjudication of the adsorption preference using the above criterion, however, is much more difficult in the case of allyl-pentafluorobenzene (α = 0.38; olefin 45 in Table IV), because the α value for the reference molecule (ca. 0.22) in column B is about the same as that (0.20) observed for the reference molecule in column C. The small differences in these two cases is not sufficient to permit one to choose between the two alternatives. The possibility that the pentafluorobenzene is making a liaison with the adsorption site while the allyl group is serving to raise the attitudinal angle of projection away from the adsorption site is just as probable as the alternate possibility that the olefin group is liaising with the adsorption site while the pentafluorobenzyl group is serving to increase the angle of projection away from the adsorption site.

Adjudication of the adsorption preference in the case of vinylcyclohexane ($\alpha = 0.79$; olefin 44 in Table IV) is also uncertain for essentially the same reasons: the α values for the reference compounds in column B (ethylcyclohexane; $\alpha = 0.18$) and in column C (1-heptene; $\alpha = 0.23$) are approximately equivalent. It is suspected that the adsorption preference favors cyclohexyl over the vinyl group for reasons to be offered after we have had the opportunity to present the data accumulated in our studies involving sorption of cyclic olefins, which will be the subject of our next publication.

In contrast to the above uncertainties, the comparison data in Table VI for methyl allyl sulfide (olefin 32 in Table IV) unequivocally shows that the adsorption mode involves a liaison with the sulfur atom rather than with the olefin group. In the study involving sorption of thioethers bearing a methyl substituent and a group that can participate well in dynamic associative interactions with the mobile sorbed molecule, we suggested that such molecules are tilted to one side so that the methyl substituent attached to the sulfur atom is pressed against the adsorption site and the rest of the molecule extends away from that site [see fig. 3(a) in Errede and Tiers¹⁵]. Consistent with this suggestion, the mode of adsorption for methyl allyl sulfide is believed to be as shown schematically in Figure 8(b).

The adsorption preference in the cases of the ester olefins (olefins 36-40 in Table IV) is also unmistakably in favor of the ester group rather than the olefinic double bond. In each case, the difference between the α value observed for the difunctional molecule (column A in Table VI) and the reference structure in column B is much smaller than the corresponding difference between column A and column C. These comparisons are interpreted to mean that the mode of adsorption of ester-olefin molecules involves a liaison with the ester group while the rest of the molecule extends away from that site as shown in Figure 8(c). Our studies involving sorption of monoesters and diesters, which will soon be submitted for publication, have shown that the mode of adsorption for such molecules depends on the numbers of methylene groups on both sides of the ester group. Although these factors complicate the adsorption picture somewhat, the magnitude

of such complications in this case is not sufficient to alter the conclusion stated above, as will be made clear after it has been possible to present all the adsorption data for this classification.

Adjudication of the adsorption preference for diallyl ether ($\alpha = 1.17$; olefin 40 in Table IV) is complicated by its unusual mode of adsorption due to the dynamic associative interaction of both diallyl groups with the mobile sorbed-but-not-adsorbed molecules. This causes both of the attached substituents to extend away from the adsorption site at relatively sharp angles as shown in Figure 8(d), which serves to decrease the magnitude of steric hindrance to further adsorption. When these centers of unsaturation are eliminated to produce the reference molecule di-*n*-propyl ether (column B; $\alpha = 0.48$), one *n*-propyl substituent lies over the adsorption site while the other extends away from that site at a relatively low angle of projection [fig. 4(b) of Errede and Tiers¹²], which results in considerable increased steric hindrance to further adsorption. The modes of adsorption in these two cases are obviously very different, and therefore this precludes making a valid comparison in accordance with the caveat mentioned above. In this case, a much more appropriate reference compound is di-(2-methoxy)ethyl ether ($\alpha = 1.02$; the alternate reference compound listed in column B of Table VI), which is held to the adsorption site in essentially the same way [see fig. 4(b) of Errede and Tiers¹³] as that shown here for diallyl ether [Fig. 8(d)]. Because the α value for diallyl ether (1.17) is greater than that for di-(2-methoxy)ethyl ether, we concluded that the ability to increase the angle of projection of the nonadsorbed portion away from the adsorption site (i.e., the desteric effect) may be greater when the terminal substituent is a vinyl group than when it is a methoxy group, despite that the latter is rated relatively high in the partial list of substituents identified thus far that can induce a desteric effect.

The set of three allyl ethers (nos. 41–43 in Table IV) are members of the homologous series having the GMS $H(CH_2)_mOCH_2CH=CH_2$ (i.e., series 13 in Table VII). Hence, adjudication of the adsorption preference in this case can be done more effectively by comparing the log α versus N linear relationship for this series with those for $H(CH_2)_mO(CH_2)_3H$ and for $CH_2=CH(CH_2)_{n+2}H$. This comparison (Fig. 9) shows that the log α versus N linear relationship for $H(CH_2)_mO(CH_2)_3H$ and for $H(CH_2)_mO(CH_2)_{n+2}H$. This comparison (Fig. 9) shows that the log α versus N linear relationship for $H(CH_2)_mO(CH_2)_3H$ and for $H(CH_2)_mO(CH_2)_3H$ than it is to that for $CH_2=CH(CH_2)_{n+2}H$. This is

interpreted to mean that a liaison of $H(CH_2)_m$ - $OCH_2CH = CH_2$ (i.e., series 13 in Table VII) with the adsorption site involves the oxygen atom of the H(CH₂)_mO group. The fact that the log α versus N linear relationship for $H(CH_2)_m OCH_2 CH$ =CH₂ is uniformly above that for H(CH₂)_mO-(CH₂)₃H reflects the relative desteric contributions of the allyl and *n*-propyl groups, which are kept constant in their respective series while *n* is incremented from 1 to 3. In the allyl ethers the desteric contribution on the part of the allyl groups may be sufficiently great that inversion of the preference [of the sort noted for the $H(CH_2)_m O(CH_2)_n H$ ethers when *m* becomes larger than n (see figs. 3, 7, 11, and 12 in Errede and Tiers¹¹ for examples)] may not occur in series $H(CH_2)_m OCH_2 CH = CH_2$ until *m* is incremented to some critical value m' even larger than 4 (but<8).

Because series 14 in Table VII is an α, ω difunctionally substituted polymethylene [i.e., $CH_3O(CH_2)_nCH=CH_2$, the critical value n' at which the higher members of the series begin to deviate from the linearity expressed by eq. (1), due to correlated molecular orientation, 1,17-19 does not occur until n > 12. Hence, it is interesting to note here that if it were possible to obtain one or more liquid samples of the members that comprise series 14, it would then be possible to deduce thereby the α values for almost all of the 96 permutations of the GMS $H(CH_2)_m O(CH_2)_n CH$ =CH₂ (in which *n* is incremented from 1 to 12 while *m* is kept constant at 1-8) in the manner used to deduce the planes of rigidly interconnected log α versus N linear relationships for the monoether series $H(CH_2)_m OCH(CH_3)(CH_2)_n H$ and H(CH₂)_mOC(CH₃)₂(CH₂)_nH (figs. 11 and 12, respectively, of Errede¹¹).

In the meantime, it is informative to indicate semiquantitatively the general shape of the 8 \times 12 array of data points that can be deduced on the basis of the log α versus N linear relationship already established for H(CH₂)_mOCH₂CH=CH₂ (series 13 in Table VII) and the comparison of the α values for O(CH₂CH=CH₂)₂ and O(CH₂CH₂-OCH₃)₂ noted in Table VI, which indicate that the decrementation constant (D_{14}) for the methoxy-olefins CH₃O(CH₂)_nCH=CH₂ should be somewhat less than that for the corresponding dimethoxy ether series CH₃O(CH₂)_{n+2}OCH₃ (0.0429; fig. 2 in Errede and Tiers¹³: the relative desteric influence of CH=CH₂ is somewhat greater than that for OCH₃.



Figure 9 The log α versus *N* relationships for alkoxysubstituted olefins. (•) Experimental data; (•) data obtained by extrapolation or interpolation; (•) phantom data.

For purposes of illustration, therefore, we assume that D_{14} has a value of 0.04 (i.e., slightly less than the 0.0429 observed for the α,ω -dimethoxypolymethylenes). This approximation, in conjunction with the α value ($\alpha_{1,1} = 1.29$) deduced for CH₃OCH₂CH=CH₂ (which is also the first member of series 14), enables one to calculate by means of eq. (1) the approximate $\alpha_{1,n}$ values for the n = 2-12 members of CH₃O(CH₂)_nCH=CH₂ in which n is incremented from 1 to about 12, as outlined for series 14 in Table VII and as shown in Figure 9.

Reasoning by analogy with the results observed in the studies recorded in figures 11 and 12 of Erede,¹¹ the log α versus N linear relationships for each of the subseries in the classification having the GMS $H(CH_2)_mO(CH_2)_nCH=CH_2$, in which n is held constant at 2–12 while m is incremented from 1 to (n + 3) < 9 (i.e., series 13a–13k in Table VII), should be parallel to that established for series 13 ($D_{13} = 0.1060$; n = 1 while m is incremented from 1 to 5 in Table VII). Simi-

larly, those for each of the subseries, in which *m* is held constant and n is incremented from 1 to 12 (series 14a–14g in Table VII), will be parallel to the log α versus N linear relationship for $CH_3O(CH_2)_nCH=CH_2$ ($D_{14} = ca. 0.04$; i.e., series 14 in Table VII) as shown in Figure 9. The intersections of these two sets of mutually parallel lines identify the $\alpha_{m,n}$ values for all 96 permutations of GMS H(CH₂)_mO(CH₂)_nCH=CH₂, except for the five data points (represented as empty squares) in the triangular area at the bottom-left corner of the array shown in Figure 9. These may be phantom values for the respective members, if indeed there is a change in the mode of adsorption at a critical value of m = m', where the forces owing to dynamic associative interaction on $H(CH_2)_m$ become greater than those on $(CH_2)_n CH = CH_2$, as described earlier for the saturated ethers (for examples see figs. 7, 11, and 12 in Errede¹¹).

The diagonal line drawn from the data point for $CH_3OCH_2CH=CH_2$ ($\alpha_{1,1} = 1.29$ at N = 5 in

GMS and Subseries	No.	$\alpha_i:N_i$	D_s	$\alpha_f:N_f$	r^2
H(CH ₂) O(CH ₂) ₋ CH=CH ₂					
m = 1-5, n = 1	13	1.29:5	0.1060	0.481:9	←0.9999
m = 1-6, n = 2	13a	1.18:6		0.348:11	
m = 1-7, n = 3	13b	1.07:7		0.247:13	
m = 1-8, n = 4	13c	0.979:8		0.177:15	
,				↑ Srs. 15a	
m = 1-8, n = 5	13d	0.892:9		0.161:16	
m = 1-8, n = 6	13e	0.814:10		0.147:17	
m = 1 - 8, n = 7	13f	0.742:11		0.134:18	
m = 1 - 8, n = 8	13g	0.677:12		0.123:19	
m = 1 - 8, n = 9	13h	0.617:13		0.112:20	
m = 1 - 8, n = 10	13i	0.563:14		0.102:21	
m = 1 - 8, n = 11	13j	0.513:15		0.0929:22	
m = 1-8, n = 12	13k	0.468:16		0.0847:23	
		\uparrow Srs. 14		\uparrow Srs. 14g	
m = 1, n = 1 - 12	14	1.29:5	ca. 0.04	0.468:16	
m = 2, n = 1 - 12	14a	1.01:6		0.367:17	
m = 3, n = 1 - 12	14b	0.79:7		0.286:18	
m = 4, n = 1 - 12	14c	0.62:8		0.225:19	
m = 5, n = 1 - 12	14d	0.481:9		0.176:20	
		\uparrow Srs. 13			
m = 6, n = 2 - 12	14e	0.348:11		0.138:21	
m = 7, n = 3-12	14f	0.247:13		0.108:22	
m = 8, n = 4-12	14g	0.177:15		0.0847:23	
		↑ Srs. 15a		↑ Srs. 13k	
$H(CH_2)_{m+a}O(CH_2)_{m+b}CH=CH_2$					
a = 1, b = 1, m = 0-7	15	1.29:5	$ca. \ 0.073$	0.123:19	
a = 5, b = 1, m = 0-3	15a	0.481:9		0.177:15	
a = 4, b = 1, m = 0-4	15b	0.62:8		0.161:16	
a = 3, b = 1, m = 0-5	15c	0.79:7		0.147:17	
a = 2, b = 1, m = 0-6	15d	1.01:6		0.134:18	
		Srs. $13\uparrow$			
a = 1, b = 2, m = 0-7	15e	1.18:6		0.112:20	
a = 1, b = 3, m = 0-7	15f	1.07:7		0.102:21	
a = 1, b = 4, m = 0-7	15g	0.979:8		0.0929:22	
a = 1, b = 5, m = 0-7	15h	0.892:9		0.0847:23	
				\uparrow Srs. 14g	
a = 1, b = 6, m = 0-6	15i	0.814:10		0.108:22	
a = 1, b = 7, m = 0-5	15j	0.742:11		0.138:21	
a = 1, b = 8, m = 0-4	15k	0.677:12		0.176:20	
a = 1, b = 9, m = 0-3	151	0.617:13		0.225:19	
a = 1, b = 10, m = 0-2	15m	0.563:14		0.287:18	
a = 1, b = 11, m = 0-1	15n	0.513:15		0.367:17	
		\uparrow Srs. 14		\uparrow Srs. 13k	

Table VII log $\alpha_f = \log \alpha_i - D_s (N_f - N_i)$ Relationships for $H(CH_2)_m O(CH_2)_n CH = CH_2$

See Table V footnote.

Fig. 9) to that $(\alpha_{8,8} = 0.123 \text{ at } N = 19)$ for $H(CH_2)_8O(CH_2)_8CH \longrightarrow CH_2$ identifies the log α versus N linear relationship for the subseries $H(CH_2)_mO(CH_2)_mCH \longrightarrow CH_2$ (series 15 in Table VII; m = 1-8). The decrementation constant for this subseries is $D_{15} = 0.073$ [i.e., $(D_{13} + D_{14})/2$].

The log α versus *N* linear relationship for series 15a in Table VII, which extends from the data point for H(CH₂)₅OCH₂CH=CH₂ ($\alpha_{5,1} = 0.481$ at N = 9) to that for H(CH₂)₈O(CH₂)₄CH=CH₂ ($\alpha_{8,4} = 0.175$ at N = 15), is parallel to the log α versus *N* linear relationship for series 15 as are those for

the three others (series 15d, 15c, and 15b) that extend diagonally from the data points for the m = 2, 3, and 4 members, respectively, of subseries $H(CH_2)_m OCHCH = CH_2$. Similarly, the lines that extend diagonally from the data points for the n= 2–12 members of $CH_3O(CH_2)_nCH=CH_2$ (i.e., series 15e-15h in Table VII) are parallel to the log α versus N linear relationship for series 15 [i.e., $H(CH_2)_m O(CH_2)_m CH = CH_2]$. Thus, this set of 12 mutually parallel diagonal lines also passes through the intersection of the other two sets of mutually parallel lines that approximately identify the $\alpha_{m,n}$ values for 91 of the 96 permutations the classification having the of GMS $H(CH_2)_m O(CH_2)_n CH = CH_2.$

It is also of interest to note that the set of 17 vertical lines that extend upward from N = 6-22 scaled on the abscissa identify 17 vectors for a homologous series of the type $H(CH_2)_{m+a}O(CH_2)_{n-a}CH=CH_2$ in which 1 to a methylene units are transferred systematically at constant N from the nonadsorbed portion to the adsorbed portion of the molecules that comprise these homologous series within the bounds indicated by the perimeter of the rhomboid-shaped data area identified in Figure 9.

Perhaps liquid samples of one or more members in this classification having the GMS $H(CH_2)_mO(CH_2)_nCH=CH_2$ will become available, enabling the quantitative establishment of the data array shown in Figure 9 in the manner described above.

Moreover, if it were possible to obtain one or more members of the branched series H(CH₂)_m- $OCH_{2-q}(CH_3)_q(CH_2)_{n-1}CH = CH_2$ in which q is 1 or 2, it would then be possible to deduce the multidimensional rigidly interconnected network of log α versus N linear relationships contained within a rhombohedron-shaped volume domain. The rhomboid planes that contain the log α versus N linear relationships in which q is incremented from 0 to 2 at constant m and n (see, e.g., Fig. 5) would extend downward from each of the log α versus N linear relationships for those parallel to that for series 13 (q = 0, m = 1-8, n = 1), series 14 (q = 0, m = 1, n = 1-12), and series 15 (q = 0, n = 1, n =m = n = 1-8). The points of intersections for the three sets of mutually parallel rhomboid planes within this rhombohedron domain identify the $\alpha_{m,n,q}$ values for all the permutations contained in the universe having the GMS $H(CH_2)_m OCH_{2-q}$ - $(CH_3)_a(CH_2)_{n-1}CH = CH_2.$

The universe of data points would be more than doubled if it were possible to obtain a few additional samples in which both substituents attached to the ether oxygen atom have branched methyl groups [i.e., members with q' = 1 or 2 in the classification having the GMS $H(CH_2)_{m-1}$ - $(CH_3)_{q'}CH_{2-q'}OCH_{2-q}(CH_3)_{q}(CH_2)_{n-1}CH = CH_2].$ This would enable one to deduce a threefold greater array of $\alpha_{m,n,q,q'}$ values contained within a rhombohedron of space that extends sharply downward from the face of the original rhomboid area. This would be done in the manner used to deduce the cluster of tetrahedron-like structures that represent the rigidly interconnected network of log α versus N linear relationships for $\mathrm{H(CH}_2)_{m-1}(\mathrm{CH}_3)_{a'}\mathrm{CH}_{2-a'}\mathrm{OCH}_{2-a}(\mathrm{CH}_3)_{a}(\mathrm{CH}_2)_{n-1}\mathrm{H}$ (see figs. 10, 13, and 14 of $Errede^{11}$).

It is interesting to note here that the log α versus N linear relationships calculated for the subseries of the above GMS for the ether-olefins lie well above those for the corresponding subseries that does not carry an ω -olefin group. This difference reflects the desteric influence of the olefin group when located at the ω position of the nonadsorbed portion of the adsorbed molecule.

The above suggested research efforts represent more than just an academic exercise in extension for extension's sake. Admittedly, the extrapolations that would follow from the above suggested measurements for the above complex olefin-ether GMS project steeply downward to well below the lowest level of α that can be measured by the present experimental procedure. Nevertheless, these extrapolation values have significant meaning because they enable one to identify a homologous series, the log α versus N linear relationship of which begins in this domain of nonmeasurable values and extends upward to a domain that does contain molecular structures having measurable α values. Procurement of the identified structures would permit one to compare the observed value with the predicted value deduced via upward extrapolation. Such identifications might justify the time and effort needed to prepare samples of these molecular structures via synthetic organic chemistry procedures.

This philosophical approach has been used to test the validity of the rigidly interconnected network of log α versus N linear relationships in multidimensional space¹¹ for the ethers having the GMS $H(CH_2)_{m-1}(CH_3)_{q'}CH_{2-q'}OCH_{2-q}(CH_3)_q(CH_2)_{n-1}H$. The relatively good agreement between predicted and observed values in the two comparisons completed thus far was most gratifying. The results observed in these preliminary comparisons will be reported after we have had the opportunity to test whether or not such predictive mathematical procedures are also valid in other more complicated functional classifications, such as ketones and esters. The data accumulated in those studies are being organized for interpretation and preparation in a form suitable for publication.

REFERENCES

- 1. Errede, L. A. Adv Polym Sci 1991, 99.
- 2. Errede, L. A. Macromolecules 1986, 19, 1525.
- 3. Errede, L. A. J Phys Chem 1989, 93, 2668.
- 4. Errede, L. A. J Phys Chem 1990, 94, 466.
- 5. Errede, L. A. J Phys Chem 1990, 94, 3851.
- 6. Errede, L. A. J Phys Chem 1990, 94, 4338.
- 7. Errede, L. A. J Phys Chem 1991, 95, 1836.
- 8. Errede, L. A. J Phys Chem 1992, 96, 3537.
- Errede, L. A.; Hanson, S. C. J Appl Polym Sci 1994, 54, 619.
- 10. Errede, L. A. J Phys Chem 1994, 98, 8580.
- Errede, L. A. Adv Colloid Interface Sci 1995, 61, 119–198.

- Errede, L. A.; Tiers, G. V. D. J Phys Chem 1996, 100, 9918.
- Errede, L. A.; Tiers, G.V.D. J Phys Chem B 1997, 101, 3333.
- Errede, L. A.; Tiers, G. V. D. J Phys Chem B 1997, 101, 7794.
- Errede, L. A.; Tiers, G. V. D. Adv Colloid Interface Sci 1998, 74, 31.
- Errede, L. A.; Tiers, G. V. D. Polymer 1999, 40, 1567.
- 17. Fowkes, F. W. J Phys Chem 1980, 84, 510.
- 18. Botherel, P. J. J Colloid Sci 1968, 27, 529.
- 19. Tancrede, P.; Patterson, D.; Botherel, P. J. J Chem Soc Faraday Trans 2 1977, 73, 29.
- 20. Errede, L. A. J Appl Polym Sci 1992, 45, 619.
- 21. Guenet, J. M.; Lotz, B.; Wittmann, J.-C. Macromolecules 1985, 18, 420.
- Guenet, J. M.; Gan, J. Y. S.; Français, J. Macromolecules 1986, 19, 173.
- 23. Guenet, J. M. Macromolecules 1986, 19, 1961.
- 24. Guenet, J. M.; McKenna, G. B. Macromolecules 1988, 21, 1752.
- Guenet, J. M.; Heyz, J.; He, X. Macromolecules 1988, 21, 1757.
- Guenet, J. M.; Klein, M. Macromolecules 1989, 22, 3716.