Notes

Interlaboratory Comparison of Gas–Liquid Chromatographic Data for Polydimethylsiloxane–Hydrocarbon Systems

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The systems (PDMS)-hydrocarbons have been examined independently by two groups of workers[2a,b] using the gas-liquid chromatographic (glc) technique. In the initial publication from the McGill laboratory,[2a] it was shown that thermodynamic interaction parameters χ^* calculated from the $V_g{}^0$ values were in good agreement with values[3] obtained from the conventional, equilibrium sorption method. The $V_g{}^0$ values obtained in the Berkeley laboratory for PDMS interacting with n-C$_5$, n-C$_6$, benzene, and toluene at 25, 40, and 55° are higher than the McGill data, the difference varying from 6.1 to 11.6%. The higher $V_g{}^0$ values would result in χ^* being some 0.06–0.11 lower than the sorption-derived values, and therefore outside the range of combined experimental errors claimed for these techniques. As a result of these discrepancies we have carried out an interlaboratory comparison of $V_g{}^0$ data, in which polymer samples were exchanged, packed columns were interchanged, and implicitly the performances of the two sets of apparatus and their operators have been compared. Here, we briefly comment upon the results of this intercomparison shown in Table I.

Table I
Interlaboratory Comparison of $V_g{}^0$ Data for PDMS

°C	A[a]	B	C	D	E	F
25 (1)[b]	74.76	76.8–78.8	75.2–77.1	77.8–79.5	79.9–81.0	77.2
(2)	211.1	214.8-220.6	210.5–217.4	219.2–224.2	226.4–230.4	219.9
(6)	340.4	348.4–356.7	342.0–353.6	353.3–372.0	366.8–380.0	354.1
40 (1)	43.65	46.6–47.1	45.8–46.5	47.3–48.1	47.1–48.6	46.1
(2)	114.8	119.2–120.2	118.9–120.0	123.2–123.9	123.0–126.8	120.0
(3)	290.8	305.0–307.0	303.7–308.3	312.8–318.2	316.7	307.6
(5)	463.7	493.3–494.4	492.4–504.9	508.5–520.8	504.8–525.1	494.1
(6)	181.2	191.1–191.9	190.1–192.5	197.3–198.2	196.2–203.3	192.9
55 (1)	27.43	29.3–29.4	29.4–30.1	29.9	29.7–29.8	29.2
(2)	66.45	70.1–70.2	70.2–70.8	72.6	70.5–72.1	70.6
(3)	157.8	164.3–165.3	165.3–166.6	168.4	169.5	165.6
(4)	367.1	385.8–386.4	385.9–388.5	398.9	395.3	
(5)	251.4	263.0–263.5	264.0–266.0	267.3	268.4–269.2	264.6
(6)	105.4	110.0–110.1	110.7–111.0	113.1	111.6–112.5	110.1

[a] For columns, see A, results of Summers *et al.*;[2a] B, recent McGill results using samples of ref 1a; C, recent McGill results using PDMS sample of Berkeley group.[2b] Range indicates results obtained in repeated trials over a 2-month period; D, recent McGill results using column packed by the Berkeley group with their PDMS sample; E, results reported in ref 2b; F, results of Berkeley group using column packed by the McGill group. [b] For probes, see (1) n-C$_5$; (2) n-C$_6$; (3) n-C$_7$; (4) n-C$_8$; (5) toluene; (6) benzene.

The intercomparison of data, columns A–F, shows that apparently none of the variables involved, *viz.*, the polymer sample, exact apparatus-operator combination, or age of packed column seriously affects the $V_g{}^0$ data, except the coating and packing procedure. That is indicated by the agreement of the results in column D with those in column E and the agreement of those of columns B, C, and F with each other. Both groups obtain the same results (to within ±1.5% about a mean) using the same chromatographic column, whereas the results with the Berkeley column are always somewhat higher (about 2%) than those with the McGill column. However the study has not fully resolved the discrepancy with the results in column A. The bulk of the glc data remains higher than the results of Summers *et al.* by 3–5%. These earlier data at 25° are supported by χ^* data obtained through the apparently accurate vapor sorption method.[3] A choice of absolute $V_g{}^0$ values is for this reason difficult. It is possible that fuller comparison of glc-derived and equilibrium sorption-derived χ^* for PDMS-hydrocarbons would be useful.

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(1) (a) From the University of California at Berkeley; (b) from McGill University.

(2) (a) W. B. Summers, Y. B. Tewari, and H. P. Schreiber, *Macromolecules*, 5, 12 (1972). (b) R. N. Lichtenthaler, R. D. Newman, and J. M. Prausnitz, *Macromolecules*, 6, 650 (1973).

(3) R. S. Chahal, W. P. Kao, and D. Patterson, *J. Chem. Soc., Faraday Trans. 1*, 69, 1834 (1973). In this publication, the interaction parameter is written without an asterisk. In conformity with recent usage, it is obtained using segment fraction, not volume fraction, as the composition variable. Reference 2a uses both volume and segment fraction, employing χ and χ^* as the symbols for the parameters so derived.

Comments on the Paper "Nuclear Magnetic Resonance Studies on the Polymerization of Cyclic Ethers"[1] by G. Pruckmayr and T. K. Wu

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Recently Pruckmayr and Wu published a paper entitled "Nuclear Magnetic Resonance Studies on the Polymeriza-

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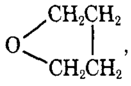
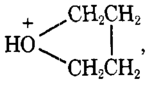
(1) G. Pruckmayr and T.-K. Wu, *Macromolecules*, 6, 33 (1973).

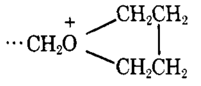
tion of Cyclic Ethers," describing the polymerization of tetrahydrofuran (1) with fluorosulfonic acid (FSO_2OH, 2) in benzene solvent over the temperature range 0–35°.[1]

These authors claim to be able to distinguish separately between 1 and 3 on the basis of ^1H nmr spectra and give assignments of the ^1H nmr chemical shifts for the H atoms of the following species coexisting in benzene solution.


1


3

and

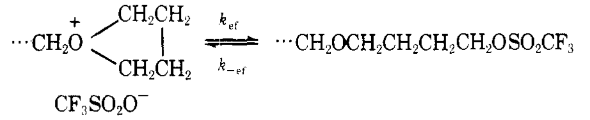

4

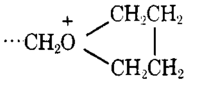
The possibility of determining 3 in the presence of an excess of 1 at room temperature seems to us to be very unlikely because the proton exchange between 1 and 3 is too fast to distinguish 1 and 3 on the nmr time scale. The chemical shifts of H bound to the α-carbon atoms in 1 and 3 cannot be observed separately and the measured chemical shift of these H atoms is a statistically weighed average of the instantaneous concentrations of 1 and 3 and the corresponding chemical shifts.

The band positions expressed in parts per million (δ) in the cited paper are probably also incorrect, since the authors have used the position of C_6H_6 solvent as the internal standard. However, due to the H^+ (solvated)–π interaction the position of C_6H_6 singlet should be dependent on the acid concentration. At the 12.5 mol % of 2 used the $\Delta\nu$ ($\nu(C_6H_6)_{obsd} - \nu(C_6H_6)_{neat}$) can be equal to several tenths of a ppm.

The error of the assignment given for 3 can also be seen on the basis of the following reasoning. The authors correctly assume the equilibrium $1 + 2 \rightleftarrows 3$ to be very rapidly established (Scheme I),[1] but in contrast to this assumption and according to the experimental data given in their Table II, the concentration of the species supposed 3 slowly within several hours increases.

According to the experimental evidence given in ref 1, there are indeed two different kinds of highly deshielded H atoms bound to the carbon atoms in the α position to the deshielding center (a positively charged oxygen atom). Since, according to our argument, one of these cannot be 3, and since it is known from our recent work, that in a similar system (with $CF_3SO_2O^-$ anion) 4 exists in equilibrium with a corresponding macroester,[2] we postulate that in reality the two different deshielded species observed by Pruckmayr and Wu are




4, FSO_2O^-

$\cdots CH_2CH_2OSO_2F$
5

Thus, we suppose that the assignment claimed for 3 corresponds in fact to 4 and the assignment attributed to 4 corresponds to 5.

In addition there are some inconsistencies within the data given in the paper under discussion. These are the results of the incorrect ^1H nmr assignments. In Figure 3 part of the ^1H nmr spectrum (220 MHz) of the polymerization mixture is given. The large triplet at δ 4.25 ppm is observed and assigned to six deshielded H atoms in 4. If this triplet were the spectrum of these H atoms in 4, then necessarily four less deshielded H atoms of 4 should also be seen. These four absorb, according to ref 1, at δ 2.19 ppm. However, there is practically no absorption at δ 2.19 ppm in Figure 3. This is in agreement with our assumption that the absorption due to the ester (5) had erroneously been taken for 4.

Our postulate is also in agreement with the value of $k_p^{\pm}$ (rate constant of 1 propagation involving the ion pairs 4) that we calculate using the experimental data given in the paper[1] and assuming that only the tertiary oxonium ions are able to propagate.[2] According to these calculations, $k_p^{\pm}$ (C_6H_6–1 mixture) $= 2.6 \times 10^{-2}\ M^{-1}\ sec^{-1}$, while the k_p^{app} (apparent, including $k_p^{\pm}$ and the equilibrium constant describing the ion pair $\rightleftarrows$ ester equilibrium) is equal under the same conditions to $2.0 \times 10^{-3}\ M^{-1}\ sec^{-1}$, close to the values determined by us elsewhere for the identical monomer-solvent mixture.[2] Otherwise, if Pruckmayr and Wu's assignments were correct, the $k_p^{\pm}$ would be very much lower (by almost two orders of magnitude) than determined by us as well as by the other authors for various initiators ($k_p^{\pm}$ was found to be independent on the anion structure[2]).

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(2) K. Matyjaszewski, P. Kubisa, and S. Penczek, International Symposium on Cationic Polymerization, Rouen, Sept 1973, Paper 25.

New Method for Calculating the Conformational Entropy of a Regular Helix[1]

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The conformational entropy plays an essential role in the conformational transitions of macromolecules. In a theoretical treatment in which bond lengths and bond angles are maintained fixed, the conformational entropy of a macromolecule can be obtained from the matrix **F** of second derivatives as $-(R/2)$ ln det **F**, where the elements $f_{i,j}$ of the matrix **F** are the second derivatives of the conformational energy with respect to the independent variables q_i and q_j calculated at the minimum point.[3,4] This method was applied previously[5] (see eq 12 of ref 5 in which g is $\exp(-S_h/R)$ and $\mathbf{A}_j$ is the matrix of second derivatives of a $j$mer corresponding to $\mathbf{F}_n$ below) to calculate the conformational entropy of a regular helix; *i.e.*, the conformational entropy per repeating unit, S_h, of a regular helix was obtained as a limit, given by

$$S_h = -\lim_{n\to\infty} (R/2) \ln (\det \mathbf{F}_{n+1}/\det \mathbf{F}_n) \qquad (1)$$

where $\mathbf{F}_n$ is the matrix of second derivatives at the energy

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(2) (a) Kyushu University; (b) Cornell University.

(3) N. Gō, M. Gō, and H. A. Scheraga, *Proc. Nat. Acad. Sci. U. S.*, **59**, 1030 (1968).

(4) N. Gō and H. A. Scheraga, *J. Chem. Phys.*, **51**, 4751 (1969).

(5) M. Gō, N. Gō, and H. A. Scheraga, *J. Chem. Phys.*, **52**, 2060 (1970).