of glycine (Table IV). Thus the γ turn may be equivalent to or even more favorable than the β turn in all-L sequences not containing glycine.

While the two hydrogen bonds in the β turn are linear and hence presumably of maximal strength, they are not strongly shielded from the solvent by the side chains in a hairpinlike structure. The same is true about the linear i to $i + 2$ hydrogen bond in the γ turn. While the $i + 2$ to i hydrogen bond of the latter is bent, and hence intrinsically weaker (Table III), it is considerably more shielded by the backbone and the side chains.[11,12] Thus, both structures can explain an observed reduction of amide–water proton exchange rates.

A criterion for distinguishing between the γ turn and the β turn can be furnished by nuclear magnetic resonance spectroscopy, *viz.*, the determination of the $^3J_{\mathrm{NC}}$ coupling constant.[29] From Figure 1 (A and B) of ref 29, the following values of $^3J_{\mathrm{NC}}$ can be estimated for L sequences in each of the turns:[30] for the γ turn, about 2.3, 7.9, and 9.7 Hz; for the β-I turn, 8.8, 7.9, 8.7, and 8.9 Hz; for the β-II turn, 8.9, 4.0, 6.6, and 8.9 Hz. If positions $i + 1$ or $i + 2$, respectively, of the two forms of the β turn were occupied by a D residue, corresponding to the most stable conformations, the sequences of coupling constants would become about 8.9, 2.6, 8.7, and 8.9 Hz for the β-I turn and 8.9, 4.0, 7.1, and 8.9 Hz for the β-II turn. In the γ turn, D substitution in position $i + 1$ would result in the sequence 2.3, 4.4, and 9.7 Hz. Thus, within the limitations of the method, the coupling constants can be used to distinguish uniquely between the various turns for a known amino acid sequence. Nmr studies are in progress in angiotensin II.

After submission of this manuscript, we obtained from Dr. B. W. Mathews details of the electron density map of thermolysin. These indicate the presence of a γ turn, with dihedral angles very similar to those proposed in this paper, occurring as residues 25–27 of thermolysin. A description of this structure, as well as a comparison with the present predictions, is being published.[32] Dr. Matthews also points out[32] the possibility of another form of the γ turn, based on the alternate form of the seven-membered hydrogen-bonded ring.[23]

Acknowledgment. We thank Dr. B. W. Matthews for making available to us his data on the thermolysin structure, and for sending us a preprint of his paper on the γ turn.

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(30) Recently, Ramachandran, *et al.*, presented[31] a revised equation for $^3J_{\mathrm{NC}}$ as a function of the N–C$^\alpha$ dihedral angle. With that equation, similar sequences of the coupling constants for the three postulated turns are obtained as shown in the text. Using the equation in ref 31, the differences between the high and low values of $^3J_{\mathrm{NC}}$ are smaller than listed here; however, the sequences of values are still characteristically different for the various conformations.

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Equation-of-State Parameters for Poly(dimethylsiloxane)

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ABSTRACT: The thermal expansivity $\alpha = V^{-1}(\partial V/\partial T)_{\mathrm{p}}$ and thermal pressure coefficient $\gamma = (\partial p/\partial T)_{\mathrm{V}}$ for poly(dimethylsiloxane) (PDMS), mol wt $\approx 10^5$, have been determined accurately over the temperature ranges 20–207 and 24–161°, respectively. Characteristic parameters v^*, T^*, and p^* calculated from these results are compared with those for other polymers and for low molecular weight liquids. For PDMS, α is much larger and γ much smaller than for any other polymer. The characteristic pressure p^* appears to be a more reliable index of the intermolecular energy than the cohesive energy density for this purpose. It is approximately the same for a polymer as for corresponding low molecular weight liquids. For PDMS and HMDS (hexamethyldisiloxane) p^* assumes exceptionally low values of 341 and 358 J cm^{-3}, respectively, which are duplicated only by the fluorocarbons ($p^* \approx 360$ J cm^{-3}).

The investigations reported here were carried out with the objective of determining the density ρ, the thermal expansivity $\alpha = V^{-1}(\partial V/\partial T)_{\mathrm{p}}$, and the thermal pressure coefficient $\gamma = (\partial p/\partial T)_{\mathrm{V}}$ for PDMS [poly(dimethylsiloxane)] over a wide range of temperature and with the accuracy required for evaluation of the reduction parameters needed for the treatment of solutions of this polymer. Results reported previously are limited in scope and in some instances are of uncertain accuracy. Comprehensive measurements of the equation-of-state parameters appear not to have been carried out heretofore on PDMS of high molecular weight.

Experimental Section

A sample of PDMS having a viscosity-average molecular weight of about 10^5 was obtained from the General Electric Co. Low molecular weight constituents were removed by fractional precipitation from a 0.5% solution in ethyl acetate using methanol as precipitant according to the procedure described previously.[1] Addition of methanol to the solution in the ratio of one to three parts by volume served to precipitate *ca.* 55% of the polymer at 30°. After addition of the precipitant, the temperature was raised to 50° to restore homogeneity, whereupon the solution was allowed to cool to 30° with gentle stirring. Separation of the precipitated phase and recovery of the polymer therein was carried out in the usual manner.[1]

Apparatus and procedures used for determination of the equation-of-state parameters have been described.[2,3] The cells used

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(2) R. A. Orwoll and P. J. Flory, *ibid.*, **89**, 6814 (1967).

(3) H. Höcker, G. J. Blake, and P. J. Flory, *Trans. Faraday Soc.*, **67**, 2251 (1971).

for dilatometric measurements and for determination of γ were charged with polymer. Owing to the fluidity of PDMS compared to that of other polymers of comparable molecular weight, it was necessary to chill the cell and contents with Dry Ice in order to solidify the polymer before evacuating the cell and introducing mercury.

Temperatures were controlled to ±0.001°. They were measured using a calibrated (±0.01°) Dymec quartz crystal thermometer (Hewlett-Packard DY-2801A). Corrections were applied for the thermal expansion of Pyrex glass comprising the cells.

Results

Determination of the density of PDMS using two pycnometers having capacities of *ca.* 5 and 10 cm^3, respectively, yielded $\rho = 0.9699$ (± 0.0001) g cm^{-3} at 25.0°. This result is consistent with the value 0.970 g cm^{-1} obtained[4] by extrapolation of the specific volumes of oligomers determined by Hurd:[5] it exceeds somewhat the value 0.9691 g cm^{-3} reported by Morimoto[6] for a sample of the high polymer. The result obtained by Weissler[7] for a polymer of molecular weight 26,500 at 30.0°, when corrected to 25.0°, is $\rho_{25°} = 0.9682$ g cm^{-3}, which is substantially lower than the other results quoted.

Relative densities were determined dilatometrically at intervals of about 2.5° throughout the temperature range 20–207°. Three runs carried out on different samples of the polymer in different dilatometers yielded closely agreeing results. Readings for ascending and descending temperatures were indistinguishable. The relative densities were converted to absolute values on the basis of the density at 25° given above. The following cubic equation in the Centigrade temperature t, obtained by the method of least squares, reproduces the measurements from 20 to 207° with a mean deviation of 0.53×10^{-4} g cm^{-3}.

$$\rho\ (\text{g cm}^{-3}) = 0.9919 - 8.92_5 \times 10^{-4}t + 2.65 \times 10^{-7}t^2 - 3._0 \times 10^{-11}t^3 \quad (1)$$

It follows from this expression that the thermal expansivity is given by

$$\alpha\ (\text{deg}^{-1}) = 0.900 \times 10^{-3} + 2.7_6 \times 10^{-7}t + 1._0 \times 10^{-10}t^2 \quad (2)$$

At 25° $\alpha = 0.907 \times 10^{-3}$ deg^{-1} according to eq 2. Morimoto[6] has reported a somewhat lower value of 0.887×10^{-3} deg^{-1}. Allen, *et al.*,[8] found $\alpha = 0.90 \times 10^{-3}$ deg^{-1} at 20° for a polymer of mol wt ≈15,000.

Thermal pressure coefficients were determined at intervals of *ca.* 20–25° from 24 to 161°. About 27 g of polymer was used. Each series of measurements at fixed volume (uncorrected; see below) was conducted over a range of about 5°, with the pressure increasing concomitantly from atmospheric to about 35 bars. The increase in pressure with temperature was accurately linear in every instance. The slope of this relationship, after correction for the thermal expansivities and compressibilities of mercury and glass,[2,8,9] yielded a value of γ which was identified with $(\partial p/\partial T)_V$ at the temperature at which $p = 0$. The results are summarized in the third column of Table I. From them we obtain the following relation by the method of least squares.

TABLE I
THERMAL PRESSURE COEFFICIENTS FOR PDMS

Temp, °C	No. of expt	—γ at $p = 0$, bar deg^{-1}— Obsd	Calcd from eq 3
24.90	6	7.612	7.587
49.81	4	6.553	6.580
70.77	5	5.769	5.821
86.45	4	5.340	5.307
106.31	4	4.750	4.722
132.29	4	4.072	4.067
161.64	4	3.471	3.478

$$\gamma\ (\text{bar deg}^{-1}) = 8.71 - 4.74 \times 10^{-2}t + 0.93 \times 10^{-4}t^2 \quad (3)$$

Values calculated according to this equation are given in the last column of Table I. The mean deviation of an individual observed value of γ from the result calculated from this equation is 0.025 bar deg^{-1}.

Weissler[7] measured adiabatic compressibilities of oligomers and low polymers of PDMS up to a molecular weight of 26,500. From the measured ratio of specific heats he calculated the isothermal compressibilities κ for oligomers and polymers up to mol wt = 3900. His results plotted against (molecular weight)$^{-1}$ lend themselves readily to extrapolation to the limiting values for mol wt = ∞. We thus obtain from Weissler's results $\kappa_{30°} = 1.238 \times 10^{-3}$ cm^3 J^{-1} at 30°. In combination with our expansion coefficient, this yields $\gamma_{30°} = 7.33$ bar deg^{-1}, in good agreement with the value, 7.37 bar deg^{-1}, given by eq 3.

Allen, *et al.*,[8] measured γ from −20 to 50° for an unfractionated commercial PDMS having a molecular weight of *ca.* 15,000. Within the range of our measurements, their results for γ are 2.0–2.4% greater than ours and the datum above from Weissler.[7] At 30°, for example, they obtain $\gamma_{30°} = 7.53$ bar deg^{-1}. Price, *et al.*,[10] found $\gamma_{31°} = 7.58$ bar deg^{-1}, corresponding to $\gamma_{30°}$, 7.54 deg^{-1}, for a sample of high molecular weight that had been cross-linked with benzoyl peroxide.

Values of the specific volume, of α and of γ calculated from eq 1, 2, and 3, respectively, for selected temperatures within the ranges of the present determinations are given in the second, third, and fourth columns of Table II. Characteristic parameters v^*, T^*, and p^* for use in the treatment of solutions are given in following columns of the table. They have been calculated from the relations[11]

$$\tilde{v}^{1/3} - 1 = \alpha T/3(1 + \alpha T) \quad (4)$$

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \quad (5)$$

$$p^* = T\tilde{v}^2\gamma \quad (6)$$

where $\tilde{v}$ and $\tilde{T}$ are the reduced volume and temperature defined respectively by $\tilde{v} = v/v^*$ and $\tilde{T} = T/T^*$. The parameters v^*, T^*, and p^* display changes with temperature that resemble those observed for other liquids, including both low molecular weight substances[12] and polymers.[2,3,13]

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Table II

Equation-of-State Data and Characteristic Parameters for PDMS at Selected Temperatures

Temp, °C	v_{sp}, cm^3 g^{-1}	$\alpha \times 10^3$, deg^{-1}	γ, bar deg^{-1}	$\tilde{v}$	v^*, cm^3 g^{-1}	T^*, °K	p^*, J cm^{-3}
20	1.0265	0.905_4	7.80	1.2248	0.8381	5494	343
25	1.0312	0.906_8	7.58	1.2283	0.8395	5528	341
30	1.0359	0.908_2	7.37	1.2318	0.8410	5563	339
40	1.0453	0.911_1	6.96	1.2388	0.8438	5631	335
50	1.0549	0.913_9	6.57	1.2458	0.8468	5700	330
60	1.0646	0.915_8	6.20	1.2525	0.8500	5772	324
80	1.0844	0.922_6	5.51	1.2664	0.8563	5907	312
100	1.1046	0.928_5	4.90	1.2800	0.8630	6046	300
120	1.1254	0.934_5	4.36	1.2935	0.8701	6187	287
140	1.1467	0.940_6	3.90	1.3068	0.8775	6328	275
160	1.1686	0.946_8	3.51	1.3199	0.8853	6469	265
180	1.1910	0.953_1	3.20	1.3330	0.8935	6612	257
200	1.2140	0.959_4	2.95	1.3458	0.9020	6756	253

Table III

Comparison of Equation-of-State Parameters for Amorphous Polymers and Representative Low Molecular Weight Liquids

Liquid[a]	Temp, °C	$\alpha \times 10^3$, deg^{-1}	γ, J cm^{-3} deg^{-1}	$\kappa \times 10^3$, cm^3 J^{-1}	$\tilde{v}$	$\tilde{T}$	v^*, cm^3 g^{-1}	T^*, °K	p^*, J cm^{-3}	Ref
PDMS	25	0.907	0.758	1.197	1.2283	0.0539	0.8395	5530	341	*c, d*
PM[b]	25	0.70	1.17	0.60	1.182	0.0459	1.000	6500	485	*c, d*
PIB	25	0.555	1.136	0.489	1.1488	0.0393	0.9493	7580	448	*e*
NR	25	0.654	1.271	0.515	1.1722	0.0440	0.9432	6775	519	*f*
PS	25	0.57	1.38	0.41_5	1.153	0.0402	0.810	7420	547	*g*
POE	57.9	0.75	1.38	0.54_5	1.204	0.0512	0.753	6460	670	*h*
PM	150	0.720	0.69_0	1.04_3	1.2510	0.0576	1.026	7345	460	*c*
PIB	150	0.577	0.678	0.851	1.2092	0.0508	0.9681	8340	419	*e*
$[(CH_3)_3Si]_2O$	25	1.398	0.685	2.012	1.3240	0.0675	0.9945	4420	358	*i*
c-C_6H_{12}	25	1.217	1.067	1.140	1.2906	0.0632	1.0012	4720	432	*j*
$C_2H_5C_6H_5$	25	1.019	1.181	0.863	1.2515	0.0576	0.9262	5175	551	*k*
$CH_3COC_2H_5$	25	1.308	1.142	1.145	1.3075	0.0654	0.9561	4555	582	*l*
n-C_6F_{14}	25	1.802	0.627	2.87	1.3917	0.0750	0.4300	3975	362	*m*

[a] Abbreviations introduced in this table are as follows: PM = poly(methylene), PIB = poly(isobutylene), NR = poly(*cis*-1,4-isoprene) (natural rubber), PS = polystyrene, and POE = poly(oxyethylene). [b] Values for PM at 25° have been extrapolated from measurements on *n*-alkanes[2] and hence are subject to somewhat greater errors than in other cases. [c] Reference 2. [d] P. J. Flory, B. E. Eichinger, and R. A. Orwoll, *Macromolecules*, **1**, 287 (1968). [e] Reference 13. [f] L. A. Wood and G. M. Martin, *J. Res. Nat. Bur. Stand. A*, **68**, 259 (1964); B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, **64**, 2035 (1968). [g] Reference 3. [h] C. Booth and C. J. Devoy, *Polymer*, **12**, 309 (1971). [i] V. Chang, unpublished results from this laboratory. [j] Reference 12. [k] H. Höcker and P. J. Flory, *Trans. Faraday Soc.*, **67**, 2270 (1971). [l] P. J. Flory and H. Höcker, *ibid.*, **67**, 2258 (1971). [m] A. Abe and P. J. Flory, *J. Amer. Chem. Soc.*, **88**, 2887 (1966).

Discussion

Equation-of-state parameters are assembled in Table III for those polymers for which the required data have been reliably determined. Included for comparison are similar data for several representative simple liquids. Considering first the polymers at ordinary temperatures, we observe that values of the equation-of-state coefficients α and γ for PDMS differ notably from those for the other polymers: α is larger and γ is much smaller than for any of the other polymers at the same temperature. The contrast between values of the isothermal compressibility $\kappa = \alpha/\gamma$, consequently, is even more marked. If the comparisons are made at comparable reduced temperatures $\tilde{T} = T/T^*$, *e.g.*, if PDMS at 25° is compared with PM and PIB at 150° (see Table III), the disparities are diminished; γ and κ take on similar values, but the α's for PM and PIB remain considerably lower than that for PDMS. Values of γ for the several polymers compare, roughly, with those for small molecules of corresponding constitution at the same temperature (25°); those for PM, PIB, NR, PS, and POE are in the same range as for typical organic compounds[12] exemplified in Table III by cyclohexane, ethylbenzene, and methyl ethyl ketone. Interestingly, γ for HMDS (*i.e.*, hexamethyldisiloxane) is only a little lower than γ for PDMS. The expansivities α and the isothermal compressibilities κ for the polymers are uniformly smaller than those for the corresponding low molecular weight liquids.

The characteristic parameters T^* and p^* afford a more meaningful basis than α and γ for comparisons between the various materials. The larger values of T^* for the polymers than for the analogous low molecular weight liquids reflect, according to theory,[11] the smaller number of intermolecular degrees of freedom (per unit volume) for the polymers.

The characteristic pressure p^* is closely related to the internal pressure defined by

$$p_i \equiv (\partial E/\partial V)_T = \gamma T$$

where E is the internal energy and γ is the thermal pressure coefficient at $p = 0$. According to the theory used to formulate the characteristic parameters

$$p^* = \gamma T \tilde{v}^2 = \tilde{v}^2 p_i \tag{7}$$

Thus, p^* differs from the internal pressure p_i, often used[8,14,15]

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to characterize the intermolecular energy in liquids, only through the factor $\tilde{v}^2$. We take p^* to be a measure of the mean intermolecular energy per unit volume corrected for the density of packing in the liquid. Values of p^* correlate favorably with the chemical nature of the liquid (see Table III and ref 2). For polystyrene (PS) and ethylbenzene, they are virtually coincident. We observe in particular the low values of p^* for PDMS and for HMDS and their similarity. They are much smaller than for organic liquids in general; comparable values are found only for the fluorocarbons.[16] Thus, the intermolecular energies for the methylsiloxanes are extraordinarily low. Although the origins of this peculiarity are obscure, it obviously underlies many of the properties of polymers in this series, *e.g.*, their low viscosities and the low temperature coefficients of their viscosities.

On the other hand, the indicated low value of the intermolecular energy density is not reflected in the interactions between PDMS and various solvents. Cohesive energy densities (ced) estimated from "solubility" or swelling measurements[15] indicate a value on the order of that found for aliphatic hydrocarbons and certainly greater than the ced for fluorocarbons, in which PDMS is insoluble. The large discrepancy between ced and p_{i} (and hence p^*) for PDMS has been pointed out by Allen, Gee, and coworkers.[8,15]

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Thermodynamics of Solutions of Poly(dimethylsiloxane) in Benzene, Cyclohexane, and Chlorobenzene

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ABSTRACT: Excess volumes have been measured at 25° for mixtures of poly(dimethylsiloxane) (PDMS) of high molecular weight with each of three solvents: benzene, cyclohexane, and chlorobenzene. Chemical potentials have been determined for solutions in the first two of these solvents by high-pressure osmometry and by vapor sorption. These results, in conjunction with osmotic measurements by Kuwahara, *et al.*, in chlorobenzene at 20 and 60°, and the heats of mixing determined by Delmas, *et al.*, for each of these systems permit a comprehensive analysis of the thermodynamic properties of the PDMS mixtures. They are characterized by entropies of dilution and excess volumes that are abnormally low compared with theoretical calculations.

A number of investigations have been reported on the thermodynamic properties of mixtures of poly(dimethylsiloxane) (PDMS) and its oligomers with various organic solvents. Most of these studies have dealt primarily with the heats of mixing. Delmas, Patterson, and Bhattacharyya[1] determined heats of mixing $\Delta H_{\mathrm{M}}^{\infty}$ to infinite dilution for PDMS in various solvents including benzene, cyclohexane, and chlorobenzene, and in mixtures of these solvents. Patterson, Bhattarcharyya, and Picker[2] carried out similar calorimetric measurements on binary mixtures of several oligomers of PDMS and of the dimer with PDMS itself. Morimoto[3] summarized and discussed calorimetric results for mixtures of PDMS with a large number of organic solvents. Dreifus and Patterson[4] reported heats of mixing for PDMS with *n*-alkanes and with several of its oligomers. Kuwahara, Okazawa, and Kaneko[5] have reported osmotic pressures of PDMS solutions in cyclohexane, toluene, and chlorobenzene at concentrations ranging from volume fractions of 0.07 to 0.25, *i.e.*, well above the usual dilute range. Malcolm and Koh[6] investigated the thermodynamic properties of chloroform and carbon tetrachloride solutions of a low molecular weight PDMS, covering the entire concentration range, and measured excess volumes as well. Recently Summers, Tewari, and Schreiber[7] have determined the activities of a number of hydrocarbons in PDMS in the "Henry's law" range of high concentration of polymer by use of gas–liquid chromatography.

Interpretation of the results of these investigations has been hampered by lack of reliable equation-of-state data for the polymer, a deficiency remedied by the results offered in the preceding paper.[8] Most of the investigations cited have been restricted in scope, being concerned with only one of the properties of the mixture, *i.e.*, with its excess enthalpy, or the chemical potential. Only the work of Malcolm and Koh[6] included determinations of both of these properties and the excess volume as well. The latter property is an important one with respect to the interpretation of interactions in mixtures.[9,10]

In this paper we present experimental measurements of excess volumes for mixtures of PDMS with three solvents: benzene, cyclohexane, and chlorobenzene. Chemical potentials in the former two solvents are reported, these being determined by osmometry and vapor sorption; the work of Kuwahara, *et al.*,[5] on chlorobenzene solutions obviated os-

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