heptanes but some fitting is necessary between eq 1 and the experimental $[\eta]$.

Solvent Quality for the Different Classes. For each sample the solvents are listed below in decreasing order of solvent quality: (75%) *trans*-decalin > *cis*-decalin > c-C_6 > S.H. br-C_9 > cycloalkanes > S.H. br-C_7 > *n*-alkanes not S.H. br-C_9 > tetrahydronaphthalene > highly branched alkanes > toluene > tetrahydrofuran > $SnBut_4$; (63%) cyclopentane > *trans*-decalin > *cis*-decalin > methyl c-C_6 > cycloalkanes > S.H. br-C_9 > S.H. br-C_7 > not S.H. br-C_9 > *n*-alkanes > not S.H. br-C_7 > highly branched alkanes > toluene > tetrahydronaphthalene > tetrahydrofuran > $SnBut_4$; (33%) cyclopentane > methyl c-C_6 > *cis*-decalin > cycloalkanes > br-C_9 S.H. br-C_7 > highly branched alkanes > *n*-alkanes > toluene > tetrahydronaphthalene > tetrahydrofuran > *n*-C_{16}, *n*-C_{17} > $SnBut_4$. It is to be noted that for two samples, cyclopentane is by far the best solvent. The order of the solvent quality is about the same for the three samples except for *cis*- and *trans*-decalin, tetrahydronaphthalene, and for the linear and branched alkanes where correlations of orientations between solvent and polymer are important.

This work illustrates the importance of the shape of the polymer and that of the solvent on the free energy of mixing. Large variations in $[\eta]$ may be found in systems where the usual parameters influencing the solvent quality and chemical and free volume differences are apparently negligible.

Acknowledgment. We acknowledge the support of the Imperial Oil Company and of the Ministère de l'Education (Québec) for this work.

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Pressure Dependence of the Intrinsic Viscosity of Poly(dimethylsiloxane)–Cyclohexyl Bromide Solution

Kenji Kubota* and Kazuyoshi Ogino

Department of Pure and Applied Sciences, College of General Education,
University of Tokyo, Komaba, Meguro-ku, Tokyo, 153, Japan. Received May 15, 1978

ABSTRACT: The pressure dependence of the viscosity of solutions of poly(dimethylsiloxane) in cyclohexyl bromide was measured over the pressure range of 1 to 400 kg/cm^2 and the temperature range of 25 to 45 °C. The viscosity measurements at elevated pressure were carried out using the rolling-ball type viscometer, and the validity of this method was examined by comparison with the measurements by the Ubbelohde viscometer at atmospheric pressure. The intrinsic viscosity and the chain dimension increase with the increase of pressure. The interaction parameter, χ_1, was deduced from the coil expansion coefficients on the assumption of the fifth power rule for the expansion of the polymer molecules in the solution. χ_1 decreases with increasing pressure and in this system the solvent becomes better near the Θ temperature. The pressure coefficient of the Θ temperature calculated from the pressure and the temperature dependence of χ_1 agreed with the results obtained by high-pressure light-scattering measurement. Values of χ_1 were compared with those predicted from the Patterson theory and the new Flory theory for polymer solutions.

The importance of the effect of pressure on solution thermodynamics has been recognized by recent investigations,[1–12] and many interesting characteristics of the pressure effect have become evident. The new Flory theory[13,14] of polymer solutions based on the principle of corresponding states[15] emphasizes the importance of the free volume effect, and the pressure effect on the solution thermodynamic properties is of great interest. The

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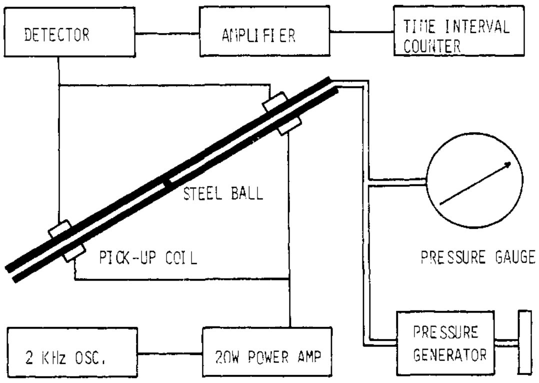

Figure 1. Block diagram of the rolling-ball viscometer and the detection system. Details are given in the text.

pressure effect has been examined mainly by light scattering,[1-4] the second virial coefficient and the radii of gyration of the polymer chain in dilute solution, the phase diagram,[5-12] and the upper and lower critical solution temperatures. The hydrodynamic properties of the polymer solution are affected by the pressure through the interaction parameter and the coil expansion. Until now, viscosity measurements under high pressure of low molecular weight liquids were reported in several studies,[16-18] but those for polymer solutions are scarce.

In this work, the pressure dependence of the viscosity of solutions of poly(dimethylsiloxane) and cyclohexyl bromide (Θ solvent) was examined and the interaction parameter was derived. The intrinsic viscosity at the Θ temperature was determined using the pressure dependence of the second virial coefficient obtained by light-scattering measurements under high pressure.[4]

Poly(dimethylsiloxane) has a very large thermal expansion coefficient and isothermal compressibility, close to those of low molecular weight liquids.[19,20] Therefore, for PDMS solutions, the equation-of-state term contribution of either the Flory or the Patterson theory[21] is very small and the theories give poor predictions of the behavior of the interaction parameter or the volume change on mixing.[22,23] The pressure and the temperature dependence of the interaction parameter derived from the intrinsic viscosity for PDMS–cyclohexyl bromide solution were compared with the new Flory and Patterson theories.

Experimental Section

The poly(dimethylsiloxane) used was from Shin-Etsu Chemical Co., with a bulk viscosity of 50 × 10^4 cSt, and was fractionated by means of the fractional solution method using benzene as a solvent and methanol as a precipitant. The viscosity average molecular weight of the fraction used for this work was 29.7 × 10^4. Cyclohexyl bromide was reagent grade and was further purified before use by vacuum distillation.

The density of PDMS and cyclohexyl bromide under high pressure was measured by use of a piston-cylinder type high-pressure cell, the details of which are described elsewhere.[20] The concentration of the solution was calculated from these densities.

The viscosities of PDMS–cyclohexyl bromide solutions were measured at pressures to 400 kg/cm^2 by use of a self-made rolling-ball viscometer.[16-18] The viscometer[24] was constructed of high-pressure tubing (304SS, Autoclave Engineers, Inc.) of 0.083 in. i.d. and 0.25 in. o.d. The block diagram of the apparatus is shown in Figure 1. The tube was inclined at about 25° to the horizontal and a steel ball (2 mm diameter) was rolled down the tube. The viscosity is determined from the time interval between two pick-up coils, arranged at a fixed distance apart (about 25 cm) along the tube. The rolling time was read to 0.01 s.

In the present work, the simplified relation developed by Sage[25] for limiting Reynolds number was used,

$$\eta = kt(\rho_F - \rho_{soln}) \qquad (1)$$

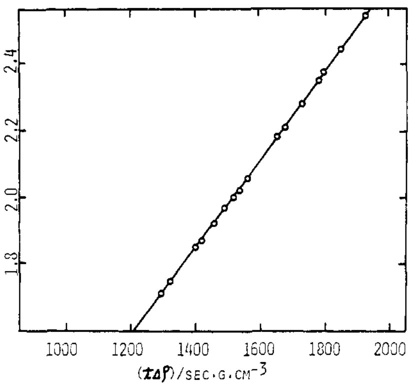

Figure 2. The calibration curve of the rolling-ball viscometer. t is the rolling time of the steel ball and $\Delta\rho$ is the difference of the densities between the steel ball and the solution.

where η is the viscosity, k is a constant, t is the rolling time, and ρ_F and ρ_{soln} are the density of the steel ball and the solution, respectively. ρ_F was calculated from the expression in degrees Celsius and kg/cm^2,[26]

$$\rho_F = 7.8835/(1 + 3.5 \times 10^{-5}T)(1 - 6.3 \times 10^{-7}[P - 1]) \qquad (2)$$

The relation of eq 1 was examined by measuring the rolling time for liquids of known viscosity. The specific viscosity of the solution at elevated pressure was determined by the following equation

$$\eta_{sp} = \eta_{rel}{}^{1\ atm}[(t\Delta\rho)^P/(t\Delta\rho)^{1\ atm}]_{soln}/[(t\Delta\rho)^P/(t\Delta\rho)^{1\ atm}]_{solv} - 1 \qquad (3)$$

$\eta_{rel}{}^{1\ atm}$ is the relative viscosity of the solution at atmospheric pressure and $\Delta\rho$ is the difference of the density between the steel ball and the solution. The pressure was generated by compressing the solution directly. The viscometer was located in a water bath regulated within ±0.1 °C. The pressure was determined by a calibrated Bourdon pressure gauge and controlled within ±2 kg/cm^2.

Excess volumes for mixtures of PDMS were measured directly by observation of the change in volume upon dissolution. Polymer (4–6 g) and solvent were placed in separate bulbs of a glass cell of the design described by Flory.[26] The difference between the positions of the liquid meniscus in a calibrated capillary before and after mixing at 30 °C yielded the volume change.

Results and Discussion

The rolling time ranged from 150 to 450 s. Repeatability of the rolling time was found to be within 0.1% over the whole range. The viscometer was calibrated at atmospheric pressure using a solution, the viscosity of which was determined by a calibrated Ubbelohde viscometer. The calibration curve is shown in Figure 2. The constant k was found to be 1.32 × 10^{-3} cP/s g cm^{-3}. The relation of eq 1 is well reproduced. In Figure 3 $t\Delta\rho$ plotted against pressure for one solution (weight fraction is 0.00268) is shown. The intrinsic viscosity was obtained by the conventional method, and those at various pressures and temperatures are tabulated in Table I (see Figure 4).

The intrinsic viscosity is related to the molecular weight and expansion of a polymer molecule. Flory showed that the expansion of the polymer molecule in the solution could be expressed by

$$[\eta] = KM^{1/2}\alpha_\eta{}^3 \qquad K = 6^{3/2}\Phi(\langle S^2\rangle_0/M)^{3/2} \qquad (4)$$

and

$$\alpha^5 - \alpha^3 = 2Cf(1/2 - \chi_1)M^{1/2} \qquad (5)$$

$$C = 9.682 \times 10^{-26}(\bar{v}^2/V_1)(\langle S^2\rangle_0/M)^{-3/2}$$

where α is the expansion factor arising from intramolecular interaction, Φ is a universal constant, $\bar{v}$ is the specific volume of polymer, V_1 is the molar volume of the solvent,

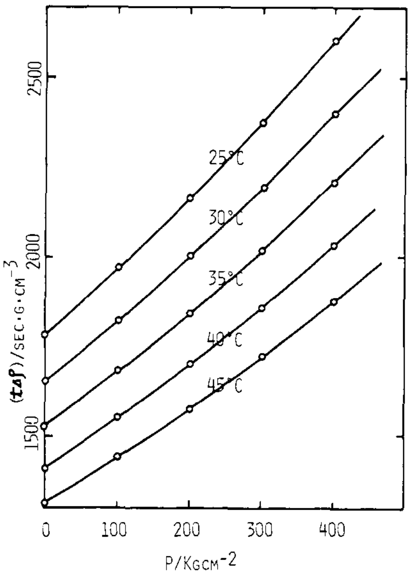

Figure 3. $t\Delta\rho$ of the solution (weight fraction = 0.00268) as a function of pressure at various temperatures.

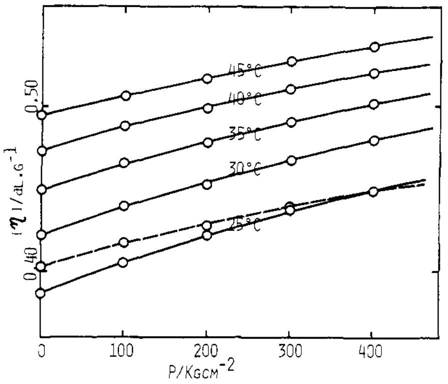

Figure 4. The intrinsic viscosity as a function of pressure at various temperatures. The dashed curve is that at the Θ temperature.

and $\langle S^2\rangle_0$ is the unperturbed mean-square radius of gyration of the polymer. In the original derivation of Flory and Fox,[27] the factor f is unity, but Stockmayer[28] suggested that a value of 0.4913 is preferable. In the present work, Stockmayer's theoretical value was used. Concerning eq 4, in the original theory of Flory,[27] there is no distinction made between the radius expansion factor, α_η, for the viscosity and the statistical expansion factor, α, for radius of gyration. Yamakawa and Kurata[29] developed an approximate first-order perturbation theory of the intrinsic viscosity on the basis of the Kirkwood-Riseman theory,[30] emphasized the difference between α_η and α, and proposed a semiempirical expression for α_η, $\alpha_\eta^3 = \alpha^{2.43}$. Therefore, in this work, the expansion factor was obtained by use of the expression of the Yamakawa theory and using this value, the interaction parameter, χ_1, was calculated from eq 5. Values of K or $[\eta]_\Theta/M^{1/2}$ calculated from the intrinsic viscosity at the Θ temperature increase with increase of pressure as is shown in Figure 4. The change is 11.4% at 400 kg/cm^2 relative to atmosphere pressure. This suggests that the unperturbed chain dimensions increase with pressure assuming that Φ is independent of pressure. The fact that the unperturbed chain dimensions are influenced by pressure is also observed by Schulz and Lechner.[1] As is pointed out by Gaeckle and Patterson,[2] this result may indicate an effect of the solvent packing on the population of conformations or rotational isomers of polymer. In order to calculate the value of α, K was assumed to be independent of temperature, and the relation of $\alpha^{2.43} = [\eta]/[\eta]_\Theta$, where $[\eta]_\Theta$ is the intrinsic viscosity at the Θ temperature, was used. The pressure and the temperature dependence of the interaction parameter χ_1 were obtained from eq 5. In Figure 5 the pressure dependence of χ_1 is shown. χ_1 decreases with increasing pressure and compatibility becomes better near the Θ temperature.

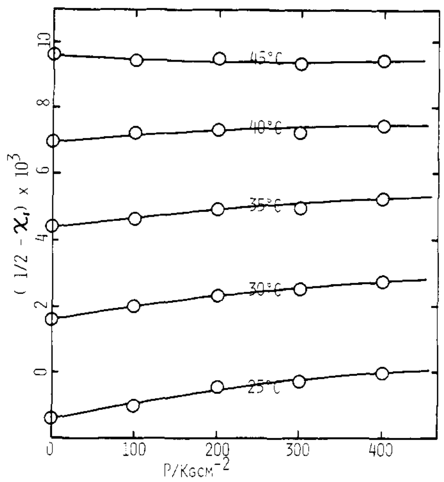

Figure 5. Plots of $(1/2 - \chi_1)$ vs. pressure at various temperatures for poly(dimethylsiloxane) in cyclohexyl bromide.

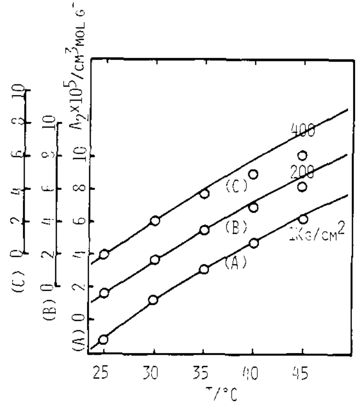

Figure 6. The comparison of the second virial coefficient calculated from intrinsic viscosity data (O) with those from the light-scattering measurements (solid curve).

χ_1 is related to the second virial coefficient through the following relation,[31]

$$A_2 = (\bar{v}^2/V_1)(1/2 - \chi_1)h(z/\alpha^3) \qquad (6)$$

where the function $h(z/\alpha^3)$ expresses the intermolecular interaction, and according to the modified Orofino and Flory theory,[32] $h(z/\alpha^3)$ is expressed by

$$h(z/\alpha^3) = \ln(1 + 5.73z/\alpha^3)/5.73z/\alpha^3 \qquad (7)$$

where $\alpha^5 - \alpha^3 = 1.28z$. Applying these relations the second virial coefficients were calculated by use of intrinsic viscosity data and compared with the results obtained from light-scattering measurements. The comparison is shown in Figure 6. The pressure and temperature derivatives of A_2 at the Θ temperature at atmospheric pressure are 4.7 × 10^{-8} cm^3 mol g^{-2}/kg cm^{-2} and 5.0 × 10^{-6} cm^3 mol g^{-2}/deg, respectively, from the intrinsic viscosity and eq 4–7 and 4.5 × 10^{-8} and 4.7 × 10^{-6}, respectively, from light scattering. Values from the intrinsic viscosity are slightly larger than those from light scattering. As is shown in Figure 6, the agreement is good near the Θ temperature, but discrepancy was observed away from the Θ temperature. This discrepancy would be due to the fact that the relations used

Table I
Intrinsic Viscosity of Poly(dimethylsiloxane) (M_v = 29.7 × 10^4) in Cyclohexyl Bromide at several Pressures and Temperatures ([η], dL g^{-1})

temp, °C	pressure, kg/cm² 0	100	200	300	400
25.0	0.386	0.405	0.422	0.437	0.449
30.0	0.421	0.439	0.452	0.467	0.478
35.0	0.449	0.465	0.477	0.490	0.501
40.0	0.472	0.488	0.498	0.510	0.520
45.0	0.494	0.506	0.516	0.527	0.536

Table II
Characteristic Parameters for Poly(dimethylsiloxane) and Cyclohexyl Bromide at 30 °C and Atmospheric Pressure

	P^*, kg cm^{-2}	V^*, cm^3 g^{-1}	T^*, K	$\tilde{V}$	$10^3\alpha$, deg^{-1}
PDMS[a]	3457	0.8410	5563	1.2318	0.908
cyclohexyl bromide	4641	0.6176	5529	1.2339	0.918

[a] Reference 19.

Table III
Excess Volume of PDMS-Cyclohexyl Bromide Mixtures at 30 °C

	volume fraction 0.20	0.40	0.51	0.64	0.79
$(V^E/V^0) \times 10^3$	−2.35	−3.07	−3.61	−2.77	−2.43

for calculating A_2 from the intrinsic viscosity are valid strictly near the Θ temperature but become invalid away from the Θ temperature. This is especially so for the Yamakawa theory, which is based on a first-order perturbation; the further from the Θ temperature the worse its prediction becomes.

At the Θ temperature, χ_1 is 0.5 and the pressure derivative of the Θ temperature is expressed by the following relation

$$d\Theta/dP = (\partial T/\partial P)_{\chi_1} = -(\partial\chi_1/\partial P)_T/(\partial\chi_1/\partial T)_P \qquad (8)$$

The Θ temperature corresponds to the critical temperature for infinite molecular weight of polymer and the corresponding critical concentration is the limit of zero polymer concentration. $(\partial\chi_1/\partial P)_T$ and $(\partial\chi_1/\partial T)_P$ are related to $\Delta\bar{V}_1$ and $\Delta\bar{H}_1$, respectively, by thermodynamic relations. At the Θ temperature,

$$\Delta\bar{V}_1 = \phi^2RT(\partial\chi_1/\partial P)_T$$
$$\Delta\bar{H}_1 = -\phi^2RT^2(\partial\chi_1/\partial T)_P \qquad (9)$$

where ϕ is the volume fraction of the polymer and R is the gas constant. Equation 8 expresses the pressure derivative of the critical temperature. In the vicinity of the upper critical solution temperature and the corresponding Θ temperature, the process of mixing is endothermal and the sign of the pressure coefficient of the critical temperature and the Θ temperature is the same as that of the volume change on mixing. For PDMS-cyclohexyl bromide, the volume change on mixing is negative as is shown in Table III. Therefore, the pressure coefficient of the Θ temperature should be negative.

In the previous work for this system,[4] the pressure dependence of the Θ temperature was obtained. Values are 27.6, 26.6, 25.8, 25.4, and 25.0 °C for 1, 100, 200, 300, and 400 kg/cm², respectively; $d\Theta/dP$ at atmospheric pressure is -0.96×10^{-2} deg/kg cm^{-2}.

From the data obtained for χ_1, the pressure and the temperature derivatives of χ_1 were calculated to be -5.5×10^{-6} cm²/kg and -5.8×10^{-4} deg^{-1}. These give $d\Theta/dP = -0.95 \times 10^{-2}$ deg/kg cm^{-2} from eq 8. Good agreement with the results of light scattering was obtained. This corresponds to the fact that A_2 calculated from the intrinsic viscosity agrees with A_2 from light scattering near the Θ temperature.

In order to investigate the pressure and temperature dependence of χ_1, the value of χ_1 predicted by the Patterson theory[21] was obtained using the characteristic parameters listed in Table II. Those for PDMS were obtained from Shih and Flory,[19] and those for cyclohexyl bromide were obtained from the density, thermal expansion coefficient, and isothermal compressibility.

According to the Patterson theory, χ_1 at atmospheric pressure is given by the following equation

$$\chi_1 = c_1\nu^2/\tilde{V}_1\tilde{T}_1 + \tfrac{1}{2}c_1\tau^2/([4/3]\tilde{V}_1^{-1/3} - 1) \qquad (10)$$

where $\tilde{V}_1$ and $\tilde{T}_1$ are the reduced volume and temperature of the solvent and c_1 is the external degree of freedom of the solvent, and is equal to $P_1^*V_1^*/RT_1^*$. τ is related to the difference between the thermal expansion of the solvent and the polymer and is defined by

$$\tau = 1 - T_1^*/T_2^* \qquad (11)$$

The parameter ν^2 represents the difference in the chemical nature of the components and was determined so that the value of χ, predicted by eq 10, gives the experimental value of χ_1 at atmospheric pressure and 30 °C, which is 0.338. The first term of eq 10 is the interaction contribution and the second term is the equation-of-state contribution. As Patterson pointed out,[23] PDMS has a large thermal expansion coefficient, and the τ parameter is small. Therefore the equation-of-state contribution is very small in this system, in contrast to other polymer solutions, e.g., polystyrene.

Using the parameters determined above, the pressure and the temperature derivatives of χ_1 were calculated at atmospheric pressure and 27.6 °C (Θ temperature). Those were 2.11×10^{-4} cm²/kg and -21.2×10^{-4} deg^{-1}, respectively. The predicted pressure coefficient of the Θ temperature was 9.95×10^{-2} deg/kg cm^{-2} and is positive and too large compared with the result from light scattering. The predicted value of $(\partial\chi_1/\partial P)_T$ is about 40 times larger in absolute value as the experimental and is positive. On the other hand, the predicted value of $(\partial\chi_1/\partial T)_P$ is about four times as large as the experimental. The poor prediction of the pressure dependence of the Θ temperature also appears in the prediction of the excess volume on mixing. The excess volume for PDMS-cyclohexyl bromide is negative, as is shown in Table III. By use of the above parameters, the theoretical value of V^E/V^0, calculated for volume fraction = 0.50 and s_2/s_1 = 2/3, was 1.42×10^{-3} and positive. V^0 would be the volume of the mixture if no volume change occurred on mixing. The value of s_2/s_1, the ratio of the (surface/volume) ratio of the polymer to that of the solvent, is obtained assuming that the solvent molecule is a sphere and the PDMS molecule has a cylindrical shape of diameter equal to that of the solvent. This prediction of positive volume change on mixing could be made negative if ν^2 had an unrealistic negative value. For PDMS solutions, as is pointed out by Flory[22] and Patterson,[23] the theoretical values of the excess volume, e.g., benzene, toluene, chlorobenzene, and ethylbenzene, are positive in contrast to the negative experimental value. This discrepancy is unexplained.

According to the new Flory theory,[13] χ_1 is expressed by

$$\chi_1 = (c_1/\tilde{V}_1\tilde{T}_1)(X_{12}/P_1^*[s_1/s_2]^2 + \tfrac{1}{2}\alpha_1TA^2) - V_1^*Q_{12}/R[s_1/s_2]^2 \qquad (12)$$

where X_{12} is the exchange interaction parameter for the enthalpy, exclusively, and Q_{12} is the corresponding parameter for the exchange entropy. A is defined as

$$A = (1 - T_1^*/T_2^*)(P_2^*/P_1^*) - (X_{12}/P_1^*)(s_2/s_1) \qquad (13)$$

The reduced residual partial molar enthalpy $\chi_{\mathrm{H},1}$ is

$$\chi_{\mathrm{H},1} = (c_1/\tilde{V}_1\tilde{T}_1)(1 + \alpha_1 T)(X_{12}/P_1^*[s_1/s_2]^2 - \tfrac{2}{3}[A\alpha_1 T]^2) \qquad (14)$$

In these expressions X_{12} should be determined from the heat of mixing, but in this work X_{12} was determined from the relation of $\chi_{\mathrm{H},1} = -T(\partial\chi_1/\partial T)$. Since eq 4–7 are valid near the Θ temperature, $\chi_{\mathrm{H},1}$ was calculated from χ_1 determined from the intrinsic viscosity at 30 °C and atmospheric pressure. X_{12} is found to be 95.7 kg/cm^2. Q_{12} was determined by use of this X_{12} and the experimental χ_1 at 30 °C and atmospheric pressure to be –0.688 kg/cm^2 deg. These values are comparable with the values which Flory and Shih obtained, 81.6 kg/cm^2 and –0.398 kg/cm^2 deg for PDMS–cyclohexane and 112 kg/cm^2 and –0.653 kg/cm^2 deg for PDMS–chlorobenzene. A large negative value of Q_{12} is characteristic of PDMS solutions. Calculated pressure and temperature dependence of χ_1 at the Θ temperature and atmospheric pressure using the above values of X_{12} and Q_{12} and eq 12 are 1.23×10^{-5} cm^2/kg and -5.69×10^{-4} deg^{-1}, respectively. The contribution of the equation-of-state term containing A^2 in eq 12 to these values is very small. The predicted value of $(\partial\chi_1/\partial T)_P$ is in agreement with the value determined from the intrinsic viscosity, but predicted $(\partial\chi_1/\partial P)_T$ is positive, as in the case of the Patterson theory. These give positive $\mathrm{d}\Theta/\mathrm{d}P$, 2.16×10^{-2} deg/kg cm^{-2}. These deficiencies of the theoretical predictions, as pointed out by Patterson,[23] are unexplained.

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Calculated and Measured ^{13}C NMR Chemical Shifts of the 2,4,6-Trichloroheptanes and Their Implications for the ^{13}C NMR Spectra of Poly(vinyl chloride)

A. E. Tonelli,* F. C. Schilling, W. H. Starnes, Jr., L. Shepherd, and I. M. Plitz

Bell Laboratories, Murray Hill, New Jersey 07974. *Received October 4, 1978*

ABSTRACT: ^{13}C NMR chemical shifts are measured for each of the carbon atoms in the three stereoisomers of 2,4,6-trichloroheptane (TCH). Spectra are recorded from solutions employing a broad range of solvents, as well as the neat liquids, over the temperature range of 25–140 °C. The differences in chemical shifts observed between the carbon atoms of the three TCH isomers are virtually independent of solvent for the methine carbons, only slightly solvent dependent for the methyl carbons, and extremely sensitive to solvent for the methylene carbons. The ^{13}C chemical shifts observed for TCH can be predicted, with the exception of those of the solvent-sensitive methylene carbons, by quantitatively calculating the number of three-bond gauche or γ interactions between carbon atoms and between carbon and chlorine atoms. The following γ effects are required to achieve this agreement: $\gamma_{\mathrm{CH_2\ or\ CH_3,CH}} = -2.5$ ppm, $\gamma_{\mathrm{CH,CH_2\ or\ CH_3}} = -5.0$ ppm, and $\gamma_{\mathrm{CH,Cl}} = -3.0$ ppm, where $\gamma_{\mathrm{a,b}}$ is the upfield shift observed at carbon a due to atom b, which is γ to a and in the gauche conformation. In addition to the ^{13}C chemical shifts of TCH and their temperature dependence, these γ effects correctly predict the chemical shift differences observed for the methyl and methine carbons between the meso and racemic isomers of 2,4-dichloropentane and the chemical shift pattern of the methine region in the ^{13}C NMR spectra of poly(vinyl chloride).

The most detailed information concerning the stereoconfiguration and/or sequence distribution of monomer units constituting vinyl homo- and copolymers is provided by ^{13}C NMR spectroscopy.[1-3] Recently one of the present

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