abled by the mutual repulsion of the ionic head groups. This leads to the conclusion that the central part of the surfactant vesicle bilayers is significantly more polar than that of the phospholipid vesicles.

Regardless of our limited understanding of the mechanism of the thermally induced diffusion of the probe, the mere discovery of such a phenomenon in vesicles may have significant implications in various applications of vesicles. A variation of the polarity around a solubilizate (a reagent) with temperature may profoundly affect the results of photochemical, electrochemical, and other processes catalyzed or retarded in the heterogeneous vesicular media.

Acknowledgment. S. L. thanks Drs. R. O. Loutfy and K. Y. Law for helpful discussions and for providing the purified sample of **1**.

Registry No. 1, 74677-08-0; DPPC, 2644-64-6; DSPC, 4539-70-2; DODAB, 3700-67-2; DHP, 2197-63-9; ethylene glycol, 107-21-1.

Studies of Siloxane Oligomers by Depolarized Rayleigh Scattering

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Abstract: We have studied the depolarized Rayleigh scattering spectra and the total scattering intensities of four siloxane oligomers: (A) 1,3-diphenyl-1,1,3,3-tetramethyldisiloxane; (B) 1,1,3,3-tetraphenyl-1,3-dimethyldisiloxane; (C) 1,1,5,5-tetraphenyl-1,3,3,5-tetramethyltrisiloxane; (D) 1,1,3,5,5-pentaphenyl-1,3,5-trimethyltrisiloxane. Our objective was to examine the applicability of depolarized Rayleigh spectroscopy of nonrigid molecules with low symmetry. The shear viscosity and the Rayleigh relaxation time for each of the four oligomers have been determined as a function of temperature. The Arrhenius equation is found to be inadequate to describe the temperature dependence, but the Vogel–Fulcher–Tamman (VFT) equation fits well to the experimental data. The mechanism for the depolarized Rayleigh scattering spectrum of each oligomer is shown not due to the overall rotation of the molecule but to the rotation of the end groups. Concentration-dependent studies of oligomer A in CCl_4 have also been carried out. The results show that in these siloxane oligomers the intramolecular pair orientation correlation is operative but the intermolecular pair orientational correlation is absent, in contrast to the result of poly(phenylmethylsiloxane) polymer in which the depolarized Rayleigh spectrum is affected by the intra- and intermolecular pair orientational correlation.

Introduction

Depolarized Rayleigh scattering is a valuable technique for the study of molecular reorientation in the liquid state. When a molecular liquid consisting of optically anisotropic molecules is illuminated with monochromatic laser radiation, the depolarized component of the light Rayleigh scattered from the medium consists of a distribution of frequencies. The width of the frequency distribution directly reflects the rate of the molecular reorientation.

It is now well established that, for a system of symmetric top molecules, the characteristic feature of the depolarized Rayleigh spectrum, $I_{VH}(\omega)$, is a sharp central component of Lorentzian shape superimposed on a broad background. For molecular fluids of low viscosity (<1 cP), the width of the sharp component can be measured with a Fabry–Perot interferometer. For a system of rigid asymmetric top molecules, the sharp depolarized Rayleigh spectrum may consist of from two to five Lorentzians, depending on the symmetry of the asymmetric top. For example, the $I_{VH}(\omega)$ spectrum is predicted to consist of two Lorentzians if the principal symmetry axis of the asymmetric top molecule coincides with the rotational diffusion constant tensor.[1] However, the separation of Lorentzian components is difficult using the Fabry–Perot interferometer, unless the widths of the Lorentzians differ at least by a factor of 10. Thus, the line width of the depolarized Rayleigh spectrum of a system of asymmetric top molecules reflects the average rate of molecular reorientations about different principal axes.[2,3]

For polymeric liquids, Bauer et al.[4] have found that the $I_{VH}(\omega)$ spectra of polystyrene in solutions consist of a narrow molecular weight dependent and a broad molecular weight independent component. They interpret the narrow component to be associated with the long-wavelength mode of the Rouse–Zimm chain, and the broad component to be associated with the localized crankshaft type of motion involving the phenyl groups. Using a Fabry–Perot interferometer, Jones and Wang have studied the $I_{VH}(\omega)$ spectra of poly(propylene glycol) of varying molecular weights.[5] They have found only the molecular weight independent component, the narrow molecular weight dependent component being absent in the $I_{VH}(\omega)$ spectrum. They show the molecular weight independent component to be due to the localized segmental motion. Fabry–Perot interferometry has also been used to study the motion of the phenyl group in poly(methylphenylsiloxane) by Lin et al.[6]

The main objective of this paper is to examine the applicability of depolarized Rayleigh scattering spectroscopy as a probe of the orientational dynamics of nonrigid molecules with low symmetry. We have studied the depolarized Rayleigh scattering spectra of four siloxane oligomers: (A) 1,3-diphenyl-1,1,3,3-tetramethyldisiloxane (B) 1,1,3,3-tetraphenyl-1,3-dimethyldisiloxane; (C) 1,1,5,5-tetraphenyl-1,3,3,5-tetramethyltrisiloxane; (D) 1,1,3,5,5-pentaphenyl-1,3,5-trimethyltrisiloxane. The depolarized Rayleigh scattering study of these four oligomers in the liquid state as a function of temperature has been carried out using a Fabry–Perot interferometer. In order to evaluate the molecular weight independent static properties such as the optical anisotropy and the

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(2) R. Recora, *J. Chem. Phys.*, **49**, 1036 (1968).

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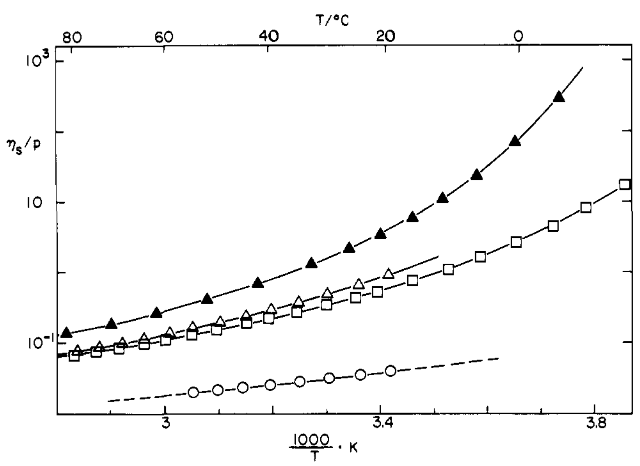

Figure 1. The temperature dependence of the viscosities of four siloxane oligomers (○, A; △, B; □, C; ▲, D). The curves are the fits to the data points in accordance with the VFT equation (eq 1). Parameters introduced in the fit are given in Table I.

pair-orientational correlation factor due to the presence of phenyl groups in these oligomers, we have also carried out the intensity measurement of oligomer A in CCl_4 at 295 K. The result is also compared with the corresponding concentration-dependent depolarized Rayleigh scattering study of poly(methylphenylsiloxane), published previously.[6]

Experimental Section

The depolarized Rayleigh spectra of the four oligomers and the solution of oligomer A were taken at a scattering angle of 90° using the light scattering apparatus similar to that described previously.[7] The radiation from an intracavity etalon selected single frequency argon ion laser operating at 0.4 W at a wavelength of 5145 Å was used as the excitation source. The incident beam was made polarized parallel (H) to the scattering plane. The frequency distribution of the scattered light with the polarization perpendicular (V) to the scattering plane selected with a Glan–Thomson polarizer was analyzed with a piezoelectrically scanned Fabry–Perot interferometer (Tropel). The spectra obtained for all samples were found to be well represented by the Lorentzian function, considering the overlap of neighboring orders. The spectra were corrected for the instrumental width corresponding to a typical finesse of 60. Two free spectral ranges at 30.9 and 9.77 GHz were used to analyze the spectral distribution of oligomer A and oligomers B, C, and D, respectively. The instrument corrected line widths were reproducible to better than 5%.

The depolarized (HV) spectra of the neat liquids were recorded at temperatures ranging from 276 to 392 K. The HV spectra for the solutions of oligomer A in CCl_4 at various concentrations at 295 K were also recorded to investigate the effect of pair-orientational correlation on the intensity and the relaxation time. The integrated intensities were obtained from the HV spectra recorded at 295 K using a free spectral range of 30.9 GHz.

Siloxane oligomer was purchased from Petrarch Systems, Levittown, PA. The dust-free samples used in the light scattering experiment were obtained by filtering through 0.22-μm millipore filters directly into dust-free rectangular light scattering cells. The temperature of the sample was kept to ±0.5 K with a circulating ethylene glycol–H_2O mixture and was monitored by a thermocouple. The viscosities of all samples at all temperatures were measured using a Hoepler falling-ball viscometer. The glass transition temperature T_g for each oligomer was determined from the DTA data (Mettler DTA 2000 B) at a scan rate of 10 °C/min.

Results

The temperature dependence of the viscosity of four oligomers is shown in Figure 1. The viscosity data are fit to the Vogel–Fulcher–Tamann (VFT) equation given by

$$\eta = \eta_0 \exp\left(\frac{B}{T - T_0}\right) \qquad (1)$$

where the values of the parameters η_0, B, and T_0 are given in Table I, together with T_g. One notes that, with the exception of D, T_0, lies below the value of T_g. For D, T_0 happens to be equal to T_g. The B values for all four oligomers are quite similar. The value of η_0 increases with increasing molecular weight of the oligomer.

Table I. Fitting Parameters for Viscosities and Measured Glass Transition Temperatures of Siloxane Oligomers

sample	T_g/K	η_0/cP	B/K	T_0/K
A	170	0.15	436	160
B	220	0.26	486	210
C	211	0.34	440	207
D	228	0.45	436	228

Table II. Values of the Fitting Parameters B and τ_0 Describing the Temperature Dependence of τ according to eq 3

sample	A	B	C	D
τ_0/ps	2.9	5.8	5.7	10.0
B/K	404	448	414	369

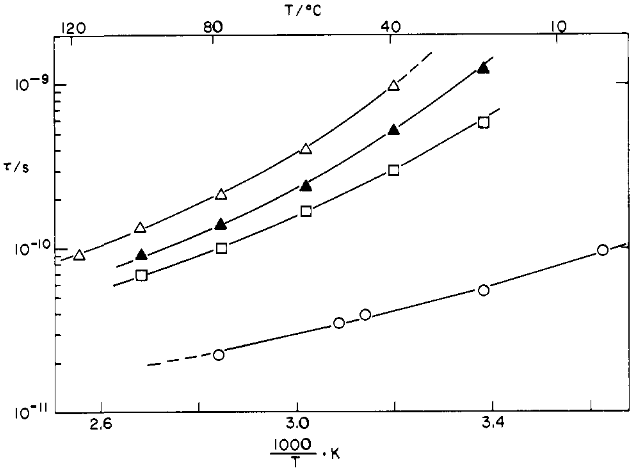

Figure 2. The temperature dependence of the Rayleigh relaxation times of four siloxane oligomers (○, A; ▲, B; □, C; △, D). The curves are the fits to the data points in accordance with eq 2. Parameters introduced in the fit are given in Table II.

Regardless of the asymmetric shape of four oligomers, experimentally it is found that the VH spectra of each sample can be fit to a single Lorentzian function with a half-width at the half-height Γ. The depolarized Rayleigh relaxation time τ is then calculated according to

$$\tau = (2\pi\Gamma)^{-1} \qquad (2)$$

The temperature dependence of τ for the four neat liquids are plotted with respect to $1/T$ in Figure 2, in which the experimental relaxation times are also fit to the VFT type of equation using the same T_0 values obtained from the viscosity fit:

$$\tau = \tau_0 \exp\left(\frac{B'}{T - T_0}\right) \qquad (3)$$

Analogous to the result of η_0, one notes that the τ_0 value also increases with increasing T_g.

Figure 3 shows the dependence of the integrated intensity I_{HV} ($=\int I_{HV}(\omega)\,d\omega$) on the oligomer A at 295 K. The unit for the oligomer concentration is g/cm^3. The integrated intensity I_{HV} does not include the high-frequency component of the collision-induced effect and is due to the permanent optical anisotropy of the scattering moiety. The quantity plotted in Figure 3 is $I_{VH}^* = I_{VH}/L$, corrected for the local field in accordance with the factor $L = (1/n^2)[(n^2 + 2)/3]^4$ based upon the Clausius–Mossotti relation. One notes that within the experimental uncertainty the intensity vs. concentration dependence is linear throughout the entire concentration range. For comparison, I_{VH}^* previously obtained for the corresponding polymer poly(phenylmethylsiloxane) (PPMS)[6] at the same temperature and solvent is also shown in Figure 3. In contrast, the dependence of I_{VH}^* on con-

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[7] Y. Y. Huang and C. H. Wang, *J. Chem. Phys.*, **61**, 1868 (1974).

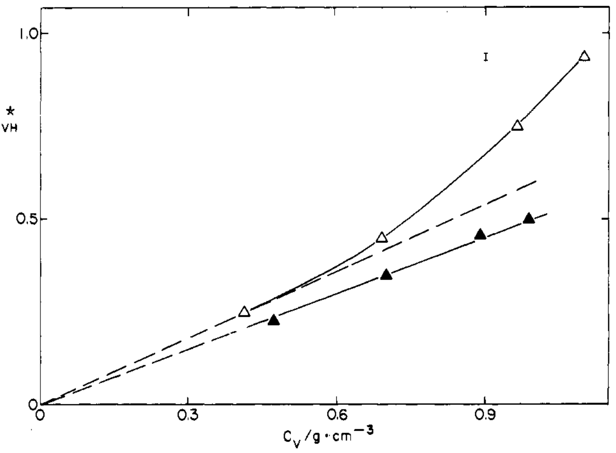

Figure 3. The concentration dependence of the integrated intensity oligomer A in CCl_4 (▲) and PPMS in CCl_4 (△). The integrated intensities have been corrected with the local field. The lines drawn through the data points are to show the trend.

centration in PPMS is nonlinear.

Discussion

The siloxane oligomers are asymmetric top molecules and, strictly speaking, the depolarized Rayleigh spectra of these molecules in the liquid state should consist of at least five Lorentzians, considering the possible contribution from the internal rotation of the phenyl groups. The fact that the spectrum fits well with one single Lorentzian indicates either that not all Lorentzians make equal contributions to the observed spectrum or that the line width reflects the average rate of reorientations about the various principal axes.

It is thus useful to analyze the depolarized spectrum in accordance with the expression:

$$I_{VH}(\omega) = NAL\beta^2 g_2 \frac{\Gamma}{\Gamma^2 + \omega^2} \tag{4}$$

where A is a constant, β is the optical anisotropy, N is the number density of scatterers, g_2 is the static orientational pair correlation factor which is equal to 1 if the orientation correlation is absent, and L is the local field correction factor, which is a function of the refractive index due to the polarization of medium surrounding the scattering molecule. There are several theoretical attempts to describe the local field factor,[8] but the theory is seriously limited by assumption of the size and shape of the cavity in which the scattering molecule is positioned. For practical purposes, we use the simple result of Clausius–Mossotti.

The Rayleigh relaxation time τ is obtained from Γ using eq 2. For small molecules τ is related to the single particle orientational relaxation time τ_s by[9]

$$\tau = g_2 \tau_s \tag{5}$$

where τ_s for an ellipsoidal molecule in a uniform fluid with shear viscosity η is given by the modified Stokes–Debye–Einstein (SDE) relation:

$$\tau_s = V_h \eta / kT + \tau_0 \tag{6}$$

where V_h is the effective hydrodynamic volume of the reorienting molecule and τ_0 is the empirical constant which is found necesssary for some molecular fluids in order to fit the data. In eq 5, the dynamic pair correlation factor is neglected. This is a good approximation because the dynamic pair correlation factor is known to be very small.[10]

As pointed out above, all of the VH spectra of siloxane oligomers fit well to a single Lorentzian function. If we assume that the line width is due to reorientation, then using eq 6 we can compute V_h and compare the experimental result obtained for V_h with the estimated one. This should help certify the specific type of molecular rotation which gives rise to the VH spectra that were observed for the siloxane oligomers.

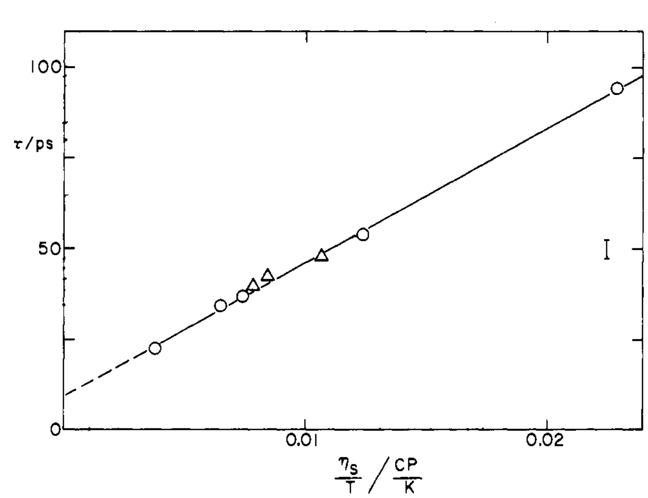

Figure 4. Plot of τ vs. η/T for oligomer A in CCl_4 (△) and for the neat liquid of oligomer A (○) at 22 °C.

If the orientational pair correlation factor is important, as is the case of the PPMS polymer, I_{VH}* should not vary linearly with the oligomer concentration. However, as one notes in Figure 3, I_{VH}* for oligomer A varies linearly with the oligomer concentration. Thus, from the intensity data (accurate to about 10%) one may assume that the effect of orientational pair correlation is negligible in oligomer A, and for this liquid, g_2 is equal to 1.

This result is supported by the dynamic measurement. Shown in Figure 4 is the plot of τ vs. η/T for oligomer A in CCl_4 at various concentrations. The τ vs. η/T data for the neat liquid are also included in the same plot. In the neat oligomer case, the viscosity is altered by changing the temperature, and in solution it is altered by changing the concentration; however, the data points for both the near liquid and the solution in the plot fit well to the equation

$$\tau = 9.3 + 3742\eta/T \tag{7}$$

in which τ is in ps (10^{-12} s) and η in cP. In the case that the orientational pair correlation is present, one would expect the data for the solution to behave differently from that of the near liquid. Since all of the τ data scale in accordance with eq 7, this indicates that the intermolecular orientational pair correlation, if present, is negligible in oligomer A. We have not studied the concentration dependence of other oligomers; however, since the structures of other oligomers are similar to that of oligomer A, it is reasonable to assume that the intermolecular orientational pair correlation is also negligible in these molecules.

Having established the insignificant effect of the pair orientational correlation, we now use eq 7 to calculate the effective hydrodynamic volume for oligomer A. In accordance with eq 6 and 7, we have found V_h to be equal to 52 Å^3. This value is in contrast to the molecular volume V_m = 284 Å^3 calculated by using the van der Waals radius data.[11] The result suggests that the origin of the VH spectrum is more likely to be due to the internal rotation of the $(CH_3)_2(C_6H_5)Si$ unit rather than from the overall rotation of the whole molecule.

The above conclusion is based upon the consideration of stick boundary conditions. However, it is still possible that the small V_h value may be due to slip boundary conditions.[12] To rule out this possibility, it is necessary to compare the V_h values obtained from the other oligomers.

If the depolarized Rayleigh spectrum of oligomer A is indeed due to the internal rotation of the $(CH_3)_2(C_6H_5)Si$ units rather than the overall molecular rotation, one would expect to obtain a more or less equal V_h value for these oligomers. In order to

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[8] See, for example, J. D. Ramshaw, *J. Chem. Phys.*, **73**, 5294 (1980).
[9] T. Keyes and D. Kivelson, *J. Chem. Phys.*, **56**, 1057 (1972).
[10] D. Kivelson and P. Madden, *Annu. Rev. Phys. Chem.*, **31**, 523 (1980).
[11] J. T. Edward, *J. Chem. Educ.*, **47**, 261 (1970).
[12] C. M. Hu and R. Zwanzig, *J. Chem. Phys.*, **60**, 4354 (1974).

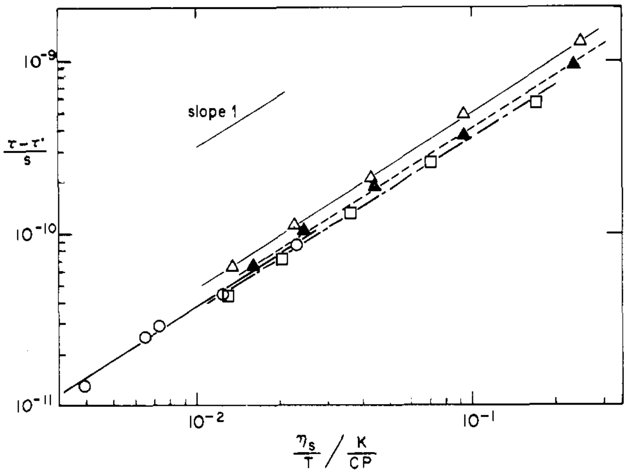

Figure 5. Plot of $(\tau - \tau_0)$ vs. η/T for neat liquids of oligomer A (○), B (△), C (□), and D (▲). The plot is given in the log–log scale. The results indicate that the modified Debye–Stokes–Einstein equation is valid over a wide η/T range for the siloxane oligomers.

investigate this possibility, we now calculate the V_h values from the relaxation time data obtained for the other three siloxane oligomers.

Shown in Figure 5 are the log–log plot of $(\tau - \tau_0)$ vs. η/T data for all of the four oligomers. The logarithmic plot is necessary because of the large range of the τ and η/T values covered. Analogous to the τ vs. η/T equation given in eq 7 for oligomer A, we have found

$$\begin{aligned} \tau &= 25 + 5020\eta/T \quad &\text{for B} \\ \tau &= 24 + 3696\eta/T \quad &\text{for C} \\ \tau &= 27 + 4046\eta/T \quad &\text{for D} \end{aligned} \tag{8}$$

Assuming that the pair orientation effect is also negligible for oligomers B, C, and D, we find from eq 8 the value of V_h to be equal to 69, 51, and 56 Å^3 for B, C, and D siloxane oligomers, respectively. These values should be contrasted with the V_m values for 386, 454, and 507 Å found respectively for B, C, and D.

Thus, despite the increase in the molecular volume, the fact that the hydrodynamic volume V_h is found nearly to be the same for all four oligomers suggests very strongly that the depolarized Rayleigh spectra from these molecules arise from the intramolecular rotation involving the $(CH_3)_2(C_6H_5)$–Si or $CH_3(C_6H_5)_2$–Si end unit. It should be noted that the V_h value is insensitive to the presence of a second phenyl group on the same Si atom. This is evident considering the fact that the volume swept out by rotating the $(CH_3)_2(C_6H_5)$–Si unit is expected to be similar to that by the $CH_3(C_6H_5)_2$–Si unit.

For oligomer A, the volume swept out by the rotation of the phenylmethyl unit about the Si–O bond is estimated to be 355 Å^3 if the phenyl ring is assumed to be perpendicular to the plane defined by the two adjoining Si–O bonds (α = 0 or 180°). Calculations based upon nonbonded interactions have shown that the most preferred orientation of the phenyl ring in substituted polystyrene is about $\alpha \simeq 60°$.[13] Using this α value, we have estimated the average swept volume of 500 Å^3 for the internal rotation in oligomer A. This value is considerably larger than V_h and hence suggests that the experimental value of V_h should be compared with the hydrodynamic model based upon slip rather than stick boundary conditions (i.e., $V_h = \sigma\cdot 500$ Å^3 where the coefficient α is less than one). The slip boundary conditions have proven to be more appropriate for describing the reorientation of noninteracting rigid molecular,[3,14] whereas stick boundary conditions became more appropriate for the reorienting molecule that strongly interacts with neighboring molecules through hydrogen bonding or when the reorienting molecule is much larger than the molecules which form the fluids; in this case τ displays a much stronger viscosity dependence because $\sigma \simeq 1$. In order to obtain σ, we followed ref 12 and estimated the ratio ρ by taking the ratio of the average of the transverse dimensions (x, y in the plane of the phenyl group) to the longitudinal dimension z using the Stuart–Briegleb space-filling model. From the obtained value of $\rho = 0.65$, we have found the corresponding ratio $\sigma = 0.106$.[12] The method of estimating the σ value in the present siloxane oligomers is similar to that presented previously.[15] With the σ value, we obtained V_h to be 51 ± 5 Å^3. Considering the large uncertainty which stems largely from the estimate of the rotation volume and from the approximation of the shape of the rotating unit by a ellipsoid of revolution, the computed value of V_h for the intramolecular orientation in oligomer A using the slip hydrodynamic model is in reasonable agreement with the experimental value of 52 Å^3.

For the other oligomers, the rotation volume of the diphenyl unit about the Si–O bond is expected to be very close to that of the phenylmethyl group (~500 Å^3), assuming that the second phenyl group is in the most preferred orientation. Since the planes of the two phenyl groups on the same Si atom are perpendicular to each other, one would expect only a slight difference in the V_h values among the four oligomers. However, considering the fact that the swept volume cannot be calculated with certainty, quantitative interpretation of the difference in V_h among the four oligomers is difficult.

Nevertheless, some small difference in V_h is found experimentally among the four oligomers. The V_h value for trimer C is 51 Å and is smaller than the value found for dimer B (V_h = 69 Å). The V_h value for the trimer D is 56 Å which is larger than that found for trimer C. The difference in the V_h values is outside of experimental uncertainty and may be interpreted as due to the presence of intramolecular orientational correlation between the neighboring phenyl groups. In the presence of the intramolecular orientational correlation, the hydrodynamic volume actually observed is equal to $V_h^0(1 + f_{\text{intra}})$, where V_h^0 is the hydrodynamic volume in the absence of intramolecular correlation and f_{intra} is the intramolecular orientational correlation factor. This picture is consistent with the result that trimer C has no phenyl group on the second silicon atom. On the other hand, in trimer D there is one phenyl group and pair orientational correlation is possible. hence a larger V_h, assuming that f_{intra} is positive.

Despite the fact that the B values associated with the η_s data (cf. eq 1) are quite similar among the four oligomers, there is a slight difference between the value for oligomer B and the other three oligomers. The activation energy E_a consistent with the VFT equation is related to the B value by $E_a = RB$ (or RB' if the τ data is used). We obtain the viscosity activation energy equal to 1.0 kcal/mol for oligomer B, in contrast to $E_a \simeq 0.9$ kcal/mol found for the other three. The slightly larger E_a for dimer B is probably due to the fact that the $CH_3(C_6H_5)_2Si$– unit is more hindered to rotate than the $(CH_3)_2(C_6H_5)Si$– because of its more bulky structure. It should be noted that the E_a value for the polymer PPMS (T_g = 227 K) is equal to 0.86 kcal/mol[16] which is quite close to the E_a value found in dimer A (E_a = 0.87 kcal/mol).

As mentioned before within the uncertainty of the present experimental result (about 10%), the intermolecular orientational pair correlation in siloxane oligomers is negligible. We obtain this conclusion from the analysis of the spectrum and the integrated intensity of the depolarized scattered light. The integrated intensity I_{VH} was obtained by integrating the experimental HV spectra taken at 20 °C using the same free spectral range of 30.9 GHz for all oligomers. In accordance with eq 4, the integrated intensity I_{VH} is equal to $\pi ALN\beta^2$, with g_2 taken to be 1. We have considered the effects of the local field and the number density of the scatterers N ($=(\rho/M)N_L$ where ρ is the density of the liquid and M and N_L are molecular weight and Avogadro's number,

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Table III. Values of Index of Refraction (η), Number Density (ρ), and Molecular Weight (M) of the Siloxane Oligomers

sample	η	ρ (g/cm^3)	M (g/mol)	I (arbitrary units)
A	1.518	0.99	286.5	1.0
B	1.587	1.08	410.7	1.9
C	1.558	1.07	484.8	1.6
D	1.580	1.10	546.9	3.3

respectively). Values of the index of refraction, density, and molecular weight of each oligomer have been determined and are given in Table III. Using these values, we calculated $I = I_{HV}/NL$ for each oligomer. The I values are also given in Table III. The intensity I for oligomer B is nearly twice the intensity of oligomer A, in accord with the number of phenyl rings on the molecule. The 5% discrepancy in the intensity per phenyl group between A and B is insignificant because it is within the experimental uncertainty.

In oligomer C, the two end $CH_3(C_6H_5)_2Si$ units are separated by an intermediate $Si(CH_3)_2$ group, and this results in a decrease in the total intensity in comparison with oligomer B in which the intermediate group is absent. This result suggests that the $Si(CH_3)_2$ group plays a role in affecting the scattering intensity. Consequently, substitution of the methyl group in $Si(CH_3)_2$ with a phenyl ring would result in a higher depolarized Rayleigh intensity in oligomer D. An intensity increase of about 38% more per phenyl group in comparison with dimer B is indeed observed in this oligomer. Thus, the depolarized Rayleigh intensity from the present siloxane oligomer liquids can be satisfactorily related to the intramolecular phenyl group configuration. The intermolecular pair orientational correlation does not directly affect the integrated intensity.

This situation is quite different in the polymer. As shown in Figure 3, as the polymer concentration increases beyond 0.5 g/cm^3, the change in the intensity with the polymer concentration is nonlinear. The intensity data in PPMS suggest the presence of a positive intermolecular pair orientational correlation factor. The positive pair correlation is apparently due to short-range orientational correlation between segments of neighboring chains. However, since the results of oligomers do not indicate the presence of intermolecular pair correlation, it should be of interest to locate the onset point of the intermolecular pair correlation by studying the molecular weight dependence of the Rayleigh scattering intensity of the PPMS oligomer. The result will be useful to correlate the second-order-like transition phenomena with the intermolecular pair orientational correlation function.[17] The effect of intermolecular pair correlation in PPMS on the depolarized Rayleigh spectrum has been discussed in ref 5.

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Registry No. A, 56-33-7; B, 807-28-3; C, 3982-82-9; D, 3390-61-2.

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^{29}Si Magic Angle Spinning NMR Study on Local Silicon Environments in Amorphous and Crystalline Lithium Silicates

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Abstract: ^{29}Si MAS NMR spectra of 12 glasses in the $Li_2O–SiO_2$ system ($15 < Li_2O < 40$ mol %) have been collected and interpreted in terms of Q_m distribution theory. This theory emphasizes the variation in local silicon environments in silicate glasses. The principal silica species found in the lithium silicate glasses are Q_2, Q_3, and Q_4. Rationalizations are given for the observed metastable liquid immiscibility, viscosity, thermal conductivity, and leaching behavior of amorphous lithium silicates in terms of observed Q_m distributions. Our devitrification experiments indicate that nucleation rates in the $Li_2O–SiO_2$ system depend on similarities between Q species in glasses and their crystalline analogues. As such the $Li_2O–SiO_2$ glasses are best described as Porai-Koshits type amorphous solids.

The polymeric structure of silica in amorphous silicates and the degree to which this structure determines the physical and chemical properties of silicate glasses have been a matter of considerable conjecture.[1] Primarily this has been due to the relatively uninformative experimental techniques with which amorphous solids can be probed. There are beyond this experimental barrier some theoretical questions regarding the meaning of structural concepts for amorphous solids.[2]

Recently we have argued on the basis of Si Kβ X-ray emission spectroscopic results on alkali and alkaline earth silicate glasses that the principal structural characteristic of silicate glasses, which is amenable to experimental verification, is the variation in the distribution of local silicon environments.[1] We have designated these distributions Q_m distributions, in analogy to the designation of Engelhardt et al. for silica species distributions in silica containing aqueous solutions.[1,3,4] This Q_m distribution concept, derived from interpretation of X-ray emission spectra, enabled

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(1) A synopsis of most of the salient literature is given in: de Jong, B. H. W. S.; Keefer, K. D.; Brown, G. E.; Taylor, Ch. M. *Geochim. Cosmochim. Acta* **1981**, *45*, 1291–1308.

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