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Methyl Rotation in Polydimethylsiloxane Studied by Neutron Transmission

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Synopsis

Neutron transmission of polydimethylsiloxane has been measured as a function of neutron wavelength in the range 4–10 Å, at room temperature. Scattering cross sections per hydrogen atom have been obtained and the slope (12.2 ± 0.2) barns/Å has been derived. Comparison with calibration curves relating the slope to the barrier hindering internal rotation as well as comparison with calculated neutron cross sections using the Krieger–Nelkin formalism for different dynamical situations indicates practically free rotation of CH_3 groups about their C_3 symmetry axes.

INTRODUCTION

The special physical properties of polydimethylsiloxane (PDMS), $CH_3[(CH_3)_2Si\ O]_{n-1}Si(CH_3)_3$, have been attributed to unusual freedom of molecular rotations, leading to high chain flexibility and to very low intermolecular cohesive forces.[1] The existence of relatively unhindered rotation of $(CH_3)_2Si$ groups about siloxy bonds has been suggested from diffraction studies.[1,2] However, NMR studies of several methyl silicones[3–7] evidenced that the only motion persisting at 77°K, far below the melting point at ca. 220°K and the second order transition at 150°K, is a practically free rotation of methyl side groups about their C_3 symmetry axis, which is independent of the degree of polymerization. Evidence has also been found[5,7] for chain rotation and some form of translational motion, resulting in an intramolecular spiral motion of the $(CH_3)_2Si$ groups at higher temperatures, which has been speculatively associated with self-diffusion.

The NMR results evidence reorientation of CH_3 about the C–Si bond and indicate almost free rotation. However, owing to the interaction time of the NMR experiment (ca. 10^{-9} sec), a hindered rotation with a small barrier may appear as free rotation. Slow neutrons have a much shorter interaction time (ca. 10^{-12} sec) and are especially valuable for studying CH_3 rotations, because of the high hydrogen scattering cross section and large amplitude of motion of the protons.[8–10] In the case of hindered rotation, the CH_3 fundamental

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torsional frequency is easily seen in inelastic neutron scattering spectroscopy, while it is very weak and difficult to detect in infrared and Raman spectra.

Two studies on neutron inelastic scattering by PDMS have been published. Henry and Safford[11] analyze results in terms of free C_3 methyl rotation and find evidence for the existence of further degrees of freedom for the CH_3 center of mass. Allen[8,12] arrives at a barrier of 1.9 kcal/mole hindering the C_3 methyl rotation and analyzes the broadening of the quasielastic line in terms of self-diffusion. The main difference is in the interpretation of the inelastic peak; Henry and Safford attribute it to an envelope of free rotational levels, with peak position given by the effective mass in the Krieger–Nelkin (KN) formalism,[13] while Allen attributes it to the first torsional level of a hindered rotational barrier.

To clear up these contradictory assignments the study of total scattering cross section as a function of neutron wavelength was undertaken. Although this is a more limited technique, it can provide valuable information on rotational freedom. Differential scattering measurements with very good resolution could clear up this controversy in a more definitive way, but such measurements would be possible only in very high flux reactors.

NEUTRON SCATTERING AND ROTATIONAL FREEDOM

Neutron scattering by hydrogen-containing compounds is mainly incoherent and due to scattering by the protons. For a monoenergetic neutron beam incident on a sample with N atoms the incoherent differential scattering cross section is given in terms of the time Fourier transform of an intermediate scattering function $I_s(\mathbf{Q},t)$ as[14]

$$\frac{\partial^2}{\partial\Omega}\frac{\sigma_{\text{inc}}}{\partial\omega} = \frac{k}{k_0}\frac{1}{2\pi}\sum_{j=1}^{N}(b_{\text{inc}})_j^2\int e^{-i\omega t}[I_s(\mathbf{Q},t)_j]dt$$

where $\mathbf{k}_0$, $\mathbf{k}$, and $\mathbf{Q}$ are the incident, scattered, and transferred wave vectors and b_{inc} is the bound nuclear incoherent scattering length.

One procedure for calculating neutron scattering cross sections by molecules consists in separating the $I_s(\mathbf{Q},t)$ function into translational, rotational and vibrational uncoupled components, following the formalism introduced by Zemach and Glauber.[15] Simplified theories, as the KN one,[13] are obtained from this approach, but they are of restricted validity.

In a more general approach, the intermediate scattering function is approximated by a Gaussian function of the time, and the differential incoherent cross section is given in terms of a generalized frequency spectrum $g(\omega)$ incorporating internal and external molecular modes, which may be coupled or well separated, according to[9,10]

$$\frac{\partial^2}{\partial\Omega}\frac{\sigma_{\text{inc}}}{\partial\omega} = \frac{k}{k_0}\sum_{j=1}^{N}(b_{\text{inc}})_j^2\,Q^2\frac{\langle U_j^2(\omega)\rangle}{4M_j}\frac{g(\omega)}{\omega}\exp[-W_j]\frac{\exp(h\omega/2kT)}{\sinh(h\omega/2kT)}$$

where W_j is a Debye–Waller factor and $\langle U_j^2(\omega)\rangle$ is the mean-square amplitude of displacement of the j-th atom (mass M_j) from the equilibrium position; this polarization factor is a linear combination of translatory, rotatory, and internal vibrational amplitudes. The exact calculation of $g(\omega)$ can be

made only in simple cases and usually information about this function is obtained experimentally.

Therefore it is not an easy task to interpret neutron inelastic spectra from complicated molecules. Only when the mode is flat and has no dispersion does it correspond to a delta function in $g(\omega)$. Besides, neutron resolution is in general very poor, resulting in a superposition of the several molecular modes.

The neutron scattering spectrum from a system undergoing free rotation consists of a broad inelastic distribution, since the free rotational levels are not resolved. With increasing hindrance the broad distribution evolves to a sharper maximum at the torsional frequency. Therefore, the main difference between a free rotational band and a torsional frequency is not the position of the energy peak, but its shape and breadth and it may be difficult to decide make this distinction for a particular molecule; this happened to be the case for PDMS.

In the case of freely rotating molecules or molecular groups, the simple KN formalism[13] has often been applied for calculating differential and total neutron-scattering cross sections; details of the KN theory are given in the Appendix. The shape and position of the maximum of KN spectra depend on temperature, scattering angle, an effective vibrational frequency $\bar{\omega}$, and an effective proton mass M_e for rotation and translation that depends on molecular structure and number of degrees of rotational freedom.

A good fit to the total scattering cross section σ_s is obtained in many cases;[14] results show clearly that σ_s for a variety of molecules in the gas phase can be described by the KN model. In the liquid and solid states, agreement of σ_s with KN calculations can sometimes be considered as verification of freedom of molecular rotations. For the detailed energy distribution, however, more exact descriptions of rotational motions are required and the KN model fails to describe neutron spectra even in the simplest case of freely rotating molecules in the gas phase.[14]

The approximations involved in the KN theory make even more questionable its application to the condensed state, and in general no agreement with differential scattering is obtained even in the case of freely rotating molecular groups.[16] All data appear to be shifted to higher energies than are calculated from theory, which means that a lower effective mass is always necessary to give agreement with data; experimental results lie between the calculated KN spectra and a Boltzmann distribution of a uniformly dense set of energy states of the scattering system, which would be expected to give an upper limit to the energy distribution of the scattered neutrons. Therefore, it can be misleading to rely on agreement of the KN theory with inelastic spectra as an indicator of the effective rotational mass in free rotation, and the interpretation of PDMS data by Henry and Safford[11] is questionable.

As shown by Janik,[16] it is more justified to compare spectra of the compound investigated with spectra of standard substances and analyze the broadening of the inelastic peak, which is inversely related to the hindrance. This was done for PDMS[11] in the analysis of the effect of crosslinking and fillers.

There is, however, no established empirical correlation between broadening and barrier height nor does a suitable theoretical framework exist for calcu-

lating this relation. Besides, the broadening can also be related to coupling between internal and external modes. In the case of PDMS, the two rival interpretations of data[11,12] do not follow this line of argument to support their assignments. The study of the total neutron scattering cross section, also sensitive to rotational barriers, can help in clearing up this doubt.

In hydrogen-containing compounds, neutron transmission measurements provide the total incoherent scattering cross section σ_H per proton. In the region of cold neutrons (energy $\ll 0.025$ eV) the curve of σ_H as a function of neutron wavelength λ can be approximated by a straight line, with slope determined by the inelastic scattering; at room temperature, the main contribution is due to de-excitation of energy levels corresponding to torsional or free rotational motions of the molecules or molecular groups containing hydrogen.[14]

The exact calculation of σ_H is also not easy, but all simplified models and approximate theories agree that the slope is related to the freedom of the rotational motion. If harmonic motion is assumed, it is possible to derive a very approximate dependence between the slope and the librational frequency,[17] showing that the more closely spaced the energy levels, the higher the slope. The same qualitative result is obtained considering the inelastic scattering as being due essentially to one torsional phonon, characterized by a Debye temperature that gives a measure of the barrier;[9] the larger the restriction, the smaller will be the slope.

In the KN formalism for free rotation, the slope of σ_H is given essentially by the effective proton mass and decreases with increasing M_e; the vibrational parameter has the effect of translating the curve, and σ_H increases with increasing ω. When rotation is not free the KN formalism is not applicable, but it has been shown by Ericksson[18] that, within the Zemach–Glauber formalism,[15] for a given moment of inertia for rotation, the slope increases with the freedom of motion of the H atoms; the effect of hindrance is equivalent to an increase of the effective mass in free rotation and lowers the slope.

The slope of σ_H versus λ, at room temperature, has been empirically correlated with the barrier hindering the internal rotation of the NH_4 and CH_3 groups in two calibration curves; one obtained by Rush for NH_4 from a study of ammonium salts,[19] which has also been used for CH_3, and another one obtained by Herdade[8,20] for CH_3 in unassociated liquids.

The slope does not depend directly on the barrier height, but does depend on the structure of energy levels available for energy gain by the neutron, which is determined by the height and functional form of the potential well and by the moment of inertia of the rotating group. The empirical correlation between slopes and barriers is reasonable only if the form of the barrier is the same for all compounds.

In the case of NH_4 and CH_3 groups, although the exact shape of the barrier may differ for the two groups, and depends also on the molecular frame, it is usual to assume that both groups experience a threefold cosine barrier in reorienting between equivalent potential minima. For CH_3, rotation is around the fixed C_3 axes, while for NH_4 rotation is about one of the C_3 axes, with one proton fixed, and there is an interchange in the orientation axes about which rotation occurs.[21] The moments of inertia differ by only 6% (ca. 4.8×10^{-40} g cm^2 for NH_4, ca. 5.1×10^{-40} g cm^2 for CH_3). Therefore, one would expect

calibration curves to be similar for the two groups, especially because the slope is the same for both groups freely rotating in the gas state.

The discrepancy between the two existing calibration curves for small barriers, close to the limit of free rotation (0.4 kcal/mole) is certainly due to the gas limit used by Rush. For barriers larger than 1 kcal/mole, Herdade's curve gives results larger than those of Rush by ca. 1 kcal/mole. The discrepancy is probably due to a contribution from molecular motion in the liquid state, since the barrier for hexamethylbenzene in the solid state agrees with Rush's curve.[22] This interpretation finds support in a recent analysis of the calibration method,[23] where contributions of other modes besides internal rotation (translation and whole-molecule librations) to the cross section slope is evaluated. These other contributions can be significant, but change rather slowly with the energy of the modes and with temperature; the contribution from hindered rotations of small groups are not only quite large (50–90%), but change quite rapidly with changes in the freedom of rotation of different compounds. This analysis shows that it is possible to predict average torsional frequencies within about 10–20% from the observed cross-section slopes. Barriers of the order of some tenths of a kcal/mole up to 10 kcal/mole may be detected through these calibration curves.

It is worthwhile observing[14] that in the study of ammonium salts broad inelastic distributions were obtained for compounds having total cross sections with large slopes. The effect was interpreted as arising from free rotation of the NH_4 groups.

Thus, freedom of rotational motions in PDMS can be discussed in terms of two independent procedures: comparison of σ_H with the existing calibration curves and with KN calculations.

EXPERIMENTAL

Neutron transmission of PDMS as a function of neutron wavelength λ in the range 4–10 Å (5–0.8 meV) has been measured using a slow-neutron chopper and time-of-flight spectrometer[24] at the IEA-R1 swimming-pool research reactor. To minimize the effect of possible drifts in the neutron beam, transmission and background measurements were taken in short cycles, besides being controlled by a beam monitor.

The sample used was Union Carbide silicone fluid L-45, with a viscosity of 100 centistokes and density 0.962 g/cm^3 at 25°C. The average molecular mass of PDMS calculated from the viscosity is ca. 6600, giving a degree of polymerization of 89. Data were taken at room temperature (23.5°C), with the sample in an aluminium holder with 0.256 cm internal spacing.

The total neutron cross section is given by $\sigma = \ln T^{-1}/Nt$, where T is the measured neutron transmission, t is the sample thickness, and N is the number of molecules/cm^3. To obtain the average scattering cross section per hydrogen atom, σ_H, the total cross section was corrected for total neutron absorption and for thermal scattering by Si, C, and O atoms.

RESULTS AND DISCUSSION

Figure 1 shows the values obtained of σ_H for PDMS as a function of neutron wavelength λ. The slope of the experimental curve determined by a

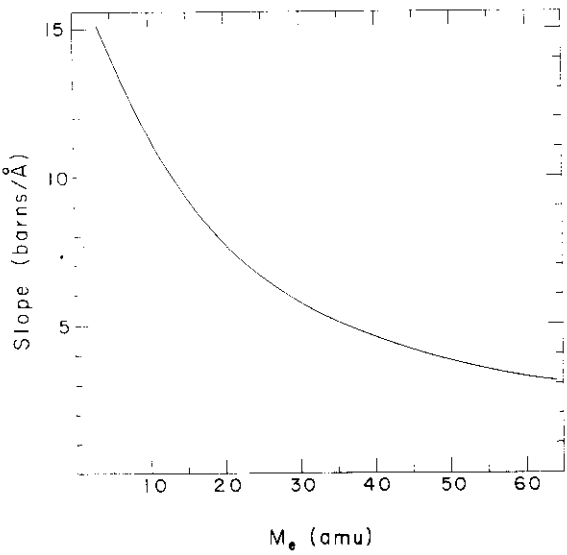

Fig. 1. Scattering cross sections per hydrogen atom, σ_H, as a function of neutron wavelength λ. Experimental points and calculated KN curves: (a), $\bar{\omega}$ = 0.1 eV, M_e = 9; (b)–(f), $\bar{\omega}$ = 0.3 eV, M_e = 9, 64, 8, 7, and 5, respectively.

weighted least-squares fit to the data in the wavelength range 5–10 Å is (12.2 ± 0.2) barns/Å; the linearity of the experimental results over this range is very good.

Inelastic spectra of PDMS[11,12] show that the methyl contribution is dominant and the experimental slope of σ_H can be used to estimate the freedom of methyl groups.

The experimental slope reported here is very close to the value 12.0 barns/Å previously obtained for liquid $CH_3C{\equiv}CCH_3$ and solid $(CH_3)_2SnF_2$ at room temperature, in which free rotation of CH_3 is assumed.[19]

Comparing this experimental result with the calibration curves,[8,19,20] it is possible to derive an upper limit of 0.4 kcal/mole for the barrier hindering methyl rotation in PDMS.

Following Allen's interpretation,[12] the inelastic peak would be due to the 1 → 0 torsional transition for a potential barrier of 1.9 kcal/mole. According to calibration curves for solid and liquid, this barrier would allow for a slope of 8–9 barns/Å, a result too low compared with the experimental slope. It is improbable that the rest of σ_H could be accounted for by other contributions due to low-frequency vibrations and further degrees of freedom involving larger rotational masses.

For comparing data with KN theory, effective proton masses have been calculated by the Sachs–Teller mass tensor concept,[13] ascribing the value 180° to the C-Si-C angle, instead of the tetrahedral value 110°, and using the structural atomic distances.[4,25] Calculations give: $M_e \approx 64$ for rotation of the $(CH_3)_2Si$ group about an axis passing through the Si atom and perpendicular to the Si–C bond, $M_e = 9$ for uncoupled rotation of CH_3 groups about their C_3 axes and $M_e \approx 8$ for the two simultaneous rotations. Further rotational degrees of freedom for the center of mass of each uncoupled methyl group could reduce M_e to 6 and translation could bring M_e down to 4.

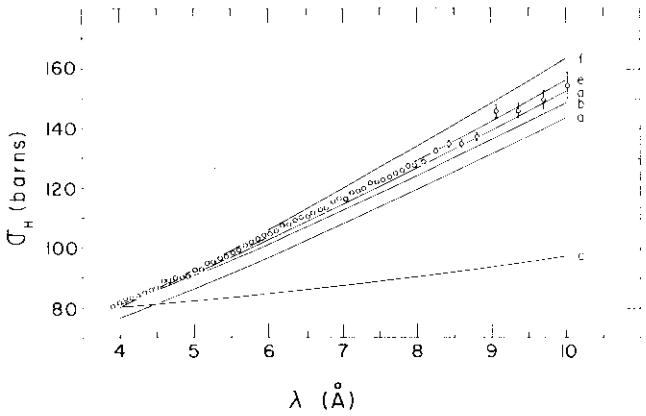

Fig. 2. Correlation between the effective proton mass M_e and the slope obtained from the KN curves in the wavelength range 6–10 Å.

KN calculations of σ_H have been performed for several values of M_e in the range 3–64 amu and for $\bar{\omega}$ in the range 0.1–0.4 eV. Figure 2 shows the correlation between M_e and the slope obtained from the KN curves in the range 6–10 Å.

Figure 1 shows the calculated KN curves for $M_e = 9$, $\bar{\omega} = 0.1$ eV and for $M_e = 64, 9, 8, 7, 5$ with $\bar{\omega} = 0.3$ eV. As the two parameters affect the KN curve in different ways, their determination is almost independent. The effective vibration that brings about agreement with calculations is $\bar{\omega} = 0.3$ eV (2400 cm^{-1}), a value between the methyl stretching vibration (2900 cm^{-1}) and deformations (1450 cm^{-1}).[26] The value of 7 or 8 for M_e gives the best agreement between experimental data and KN calculation, but considering only the slope of the curve 8 or 9 would be enough for a reasonable agreement.

According to Henry and Safford,[11] room temperature spectra cannot be accounted for, even approximately, by C_3 free methyl rotation alone, because agreement of the KN curve with data is obtained for M_e from 2 to 5. This has been taken as evidence of free rotation of the methyl center of mass in a plane and/or translation with large amplitudes. However, according to the previous discussion, it is not reliable to deduce dynamical situations from the effective mass that brings agreement between KN calculations and inelastic spectra, which is confirmed by our fit of KN theory to σ_H data, obtained for a higher effective mass.

Therefore, comparison with KN theory gives results compatible with the analysis of the slope using the calibration curves, indicating the existence of practically free rotation of CH_3 groups about their C_3 axes in PDMS. Free rotation of $(CH_3)_2Si$ about Si–O bond may also occur, but σ_H is not very sensitive to rotation of large masses. Further, KN theory is not so reliable that one can distinguish between $M_e = 8$ or $M_e = 9$.

CONCLUSIONS

Slow-neutron transmission measurements indicate the existence of practically free C_3 methyl rotation in polymethylsiloxane. These results favor Henry and Safford's interpretation of neutron inelastic spectra in terms of

free methyl rotation,[11] but show also that the very small effective mass necessary to bring agreement between KN calculations and inelastic spectra does not have a physical meaning and should not be considered as evidence of further degrees of freedom, either rotational and translational, of the CH_3 center of mass. Simultaneous rotation of entire $(CH_3)_2Si$ groups about the siloxy bond is, however, compatible with neutron transmission data.

The unusual freedom of methyl rotation about the C_3 axes may be ascribed to the greater radius of the silicon atom compared with that of carbon (which makes the Si–C bond longer than the C–C bond). Furthermore, the relatively wide separation of the methyl groups, due to the presence of oxygen atoms along the chain skeleton, tends to reduce the steric hindrance to this rotation.

APPENDIX

Krieger–Nelkin Cross-Section Calculation

In the KN theory[13] molecular rotational and vibrational effects are explicitly separated. The combined effects of rotation and translation are treated in terms of the Sachs–Teller mass tensor concept. Only elastic vibrational transitions from the ground vibrational state are considered. The applicable neutron energy range is restricted to values large compared to the rotational level separation but below the vibrational threshold. The method is applicable to the calculation of differential as well as total scattering cross sections and to molecules of arbitrary structure. Expressions in closed form for these cross sections are obtained through use of an approximate procedure for averaging over molecular orientations. The total scattering cross section per proton is given by[27]

$$\sigma_H(E_0) = \frac{\sigma_0}{2m\gamma E_0}\,(\mathrm{erf}\{c^{1/2}) - (1-P)^{1/2}\exp(-cP)\,\mathrm{erf}[c^{1/2}(1-P)^{1/2}|)$$

where symbols are defined as follows: E_0 is the incident neutron energy (eV); σ_0 is the free proton cross section (20.4 barns); m is proton mass; M is total molecular mass; T is sample temperature (eV); M_e is effective proton mass; $\bar{\omega}$ is effective vibrational frequency (eV); $\gamma = 1/(4m\bar{\omega})$ represents the mean-square vibrational amplitude of the proton; $c = M_eE_0/MT$; $P = 8\gamma\mu^2T/(M_e + 8\gamma\mu^2T)$ and $\mu = mM_e/(m + M_e)$; m_r is effective rotational mass; d_i is the distance from the bound H atom to I_i, the i-th principal axis of inertia of the molecule; and

$$m_r = \frac{3}{d_x^2/I_x + d_y^2/I_y + d_z^2/I_z}$$

$$\frac{1}{M_e} = \frac{1}{m_r} + \frac{1}{M}$$

It has been noted[27] that the KN approximation provides reasonable agreement with the experimental total cross section, even at very low energies, although the method is supposed to break down as the neutron energy approaches the rotational level spacing.

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