

An investigation of micro-brownian motions in polydimethylsiloxane by complementary incoherent-neutron-scattering and nuclear-magnetic-resonance experiments below room temperature^{*})

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Abstract: Two different experimental methods, neutron scattering and nuclear magnetic resonance are used to investigate the random methyl group and segmental rotational jump motions in polydimethylsiloxane. It is shown that nuclear magnetic relaxation and line width experiments are complementary to incoherent neutron scattering “fixed-window” experiments, the principle of the “fixed-window” experiments being discussed in somewhat detail. Satisfactory agreement of these experimental techniques is achieved as to the determination of the two model parameters of the motional processes in question, i. e. the activation energy and the preexponential factor of the Arrhenius ansatz made for the correlation time or jump time, respectively.

Key words: Polydimethylsiloxane, micro-brownian motions, nuclear magnetic resonance, relaxation, incoherent neutron scattering, fixed-window experiments.

1. Introduction

The micro-brownian motions of polymeric systems, i. e. segmental and side group motions inside the macromolecules, have been the subject of extensive research activities. Polydimethylsiloxane (PDMS) exhibits five types of these intramolecular motions in the temperature range from room temperature down to liquid helium temperatures. With respect to segmental mobility these are random jumps of the chain segments about the Si-O skeletal bonds, and cooperative segmental motions. As to the side group mobility, we are faced here with a classical type of motion, the random jumps of methyl groups about their C₃-axis, and two quantum mechanical motional processes, the methyl group tunnelling rotation and librational transitions.

The experimental techniques applied to explore these motions, among others, comprise nuclear magnetic resonance (NMR) wide line and spin-lattice relaxation experiments [1–4], neutron scattering [5–8], X-ray scattering [9, 10] and dielectric measurements [3, 5]. Comparing the results obtained by different experimental methods, poor agreement is often found. So the values of the activation energy of the random methyl group hopping process differ considerably, as determined for example by inelastic neutron scattering, neutron transmission spectroscopy and NMR spin-lattice relaxation experiments [4–6].

As will be shown in this paper, a particular variety of incoherent quasi-elastic neutron scattering experiments, of the so-called fixed-window type, and NMR line width and relaxation time measurements furnish quite a good correspondence in view of a quantitative treatment of the random jump type motions, i. e. methyl group and segmental hopping. The main purpose of this publication will be to present the basic ideas underlying these two methodically different ex-

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perimental techniques, to point out their similarities and to compare the results obtained.

2. Experimental

2.1 Sample

The specimen is a high molecular weight linear polydimethylsiloxane ($M_w = 1.32 \cdot 10^5 \text{ g} \cdot \text{mol}^{-1}$), showing a glass transition at 148 K and first order phase transitions, i. e. crystallization at 185 K and melting at 226.5/232 K (double peak), in a differential scanning calorimetry (DSC) experiment (heating rate: $10 \text{ K} \cdot \text{min}^{-1}$) [11]. The material was kindly supplied by Wacker-Chemie, Burghausen, F.R.G. Prior to measurement the sample was purified according to a procedure described elsewhere [12].

2.2 Measurements

The NMR spin-lattice relaxation experiments were performed on a Bruker pulse spectrometer SXP 4-100, by applying a computer controlled $\pi/2 - t_e - \pi/2$ sequence. The measurements were done at 20, 40 and 60 MHz at temperatures ranging from room temperature down to liquid helium temperatures.

The neutron scattering experiments were performed on the back scattering spectrometer at the research reactor FRJ-2, DIDO, Kernforschungsanlage Jülich [13]. The spectrometer was adjusted to energy offsets of $E_{\text{off}} = -6 \mu\text{eV}$, corresponding to a frequency of $\nu_{\text{off}} = 1.45 \text{ GHz}$, and $E_{\text{off}} = 0 \mu\text{eV}$, respectively. The term "offset-energy" denotes the fact, that only those neutrons are registered, which in the scattering event suffer an energy change of magnitude $E_{\text{off}} \pm \Delta E$, ΔE making allowance for the finite instrumental resolution. Here we will point out that the offset frequency ν_{off} corresponds to the spectrometer frequency ν_o of the nuclear magnetic resonance experiment. The cryostat was operated from 15 K to 280 K.

3. Theoretical considerations

The frequency spectrum of a stationary stochastic process is represented by a single Lorentzian [14–16]

$$J(\omega) = K(O) \frac{\tau}{1 + \omega^2 \tau^2}; \quad (1)$$

the constant $K(O)$ and the characteristic time τ depending on the dynamical model parameters of the actual motional process. In case of thermally activated hindered motions, such as random methyl group and segmental hopping, the characteristic time τ is properly represented by an Arrhenius ansatz

$$\tau = \tau(\infty) e^{AE/RT} \quad (2)$$

R being the gas constant, ΔE the molar activation energy and $\tau(\infty)$ the limit of τ at high temperatures, $\tau(\infty) = \lim_{T \rightarrow \infty} \tau$. Equation (2) introduces the temperature dependence on the spectral density distribution function, $J(\omega)$, describing the molecular motional spectrum. This function is sketched by the solid lines in Figure 1 for three different temperatures ($T_l < T_e < T_u$). Measurable quantities that $J(\omega)$ is related to, are scattering intensities in the case of neutron scattering and relaxation times or line widths, respectively, in nuclear magnetic resonance experiments.

3.1 Nuclear magnetic resonance (NMR)

According to the theory of Bloembergen, Purcell and Pound (BPP), which has been improved by Kubo and Tomita, the frequency and temperature dependence of the spin-lattice relaxation rate $R_1 = R_1(\omega, T)$ and the spin-lattice relaxation time $T_1 = T_1(\omega, T)$ is given by the equation [17–19]

$$R_1(T) = \frac{1}{T_1(T)} = D \left[K^{(1)}(O) \frac{\tau_c}{1 + \omega_o^2 \tau_c^2} + K^{(2)}(O) \frac{\tau_c}{1 + (2\omega_o)^2 \tau_c^2} \right] \quad (3)$$

D is a constant comprising the spin operator matrix elements, whereas the interaction distance r_o enters into the constants $K^{(i)}(O)$. ω_o denotes the fixed spectrometer angular frequency. The notations $R_1(T)$ and $T_1(T)$ in Equation (3) are to emphasize the fact that the temperature is the experimental variable, whereas the frequency ν_o merely serves as a fixed parameter. A peculiarity of the NMR relaxation theory is the occurrence of two Lorentzians in Equation (3), the second of which allows for the double quantum transitions. The so-called correlation time τ_c , taking into account the fluctuating local magnetic fields, associated with the molecular motion, is given by an Arrhenius ansatz according to Equation (2).

Moreover this correlation time is accessible by nuclear magnetic resonance line width measurements. Assuming a molecular motional model as stated above, Powles and Gutowsky [20] derived a relation between the temperature dependent second moment

$\overline{\Delta B^2}$, resulting from line width measurements, and the correlation time τ_c :

$$\overline{\Delta B^2} = \overline{\Delta B_m^2} + \frac{2}{\pi} (\overline{\Delta B_r^2} - \overline{\Delta B_m^2}) \cdot \text{arc tg} (\Gamma' \cdot \tau_c) \quad (4)$$

$\overline{\Delta B_m^2}$ and $\overline{\Delta B_r^2}$ being the second moment contributions from the fully mobile and rigid "rotators", respectively. Γ' is the temperature dependent width of the NMR absorption line.

3.2 Incoherent neutron scattering (INS)

3.2.1 The scattering law

Starting from the theory of classical correlation functions van Hove [21] derived an expression for the double differential cross section of neutron scattering, being composed of two fundamental contributions to nuclear scattering, the coherent and incoherent scattering laws S_{coh} and S_{inc} , respectively. Both are functions of momentum transfer Q , frequency ω and temperature T . Scattering on hydrogen nuclei is almost exclusively governed by the incoherent part of the overall scattering law. In the case of random rotational motions being discussed in this paper, the incoherent scattering functions $S_{\text{inc}}(Q, \omega, T)$ and the scattering intensity $I(Q, \omega, T)$, which is the convolution product of the scattering law and the resolution function of the spectrometer, are essentially given by the subsequent expression [22]:

$$I \sim e^{-2W} \cdot S_{\text{inc}} = e^{-2W} \left\{ A(Qr_o) \cdot \delta(\omega) + \frac{1}{\pi} [1 - A(Qr_o)] \frac{\tau}{1 + \omega^2 \tau^2} \right\} \quad (5)$$

$A(Qr_o)$ is the Fourier transform of the proton distribution for long observation times $t \rightarrow \infty$, r_o being a characteristic length of the methyl group, as for instance the distance between the rotation axis and the protons. A unique feature of neutron scattering experiments is manifested by the Q -dependence of the incoherent structure factor $A(Q)$. Thus the scattering function simultaneously yields information on particle motions in space and time, the observable spatial dimensions being of the order of $1/Q$. The Debye-Waller factor e^{-2W} takes into account the reduction of the elastic and quasi-elastic intensity due to inelastic scattering. The average time τ between successive rotational jumps of the molecular unit under investigation, again

is assumed to show an Arrhenius behaviour according to Equation (2), thus introducing the temperature dependence into the scattering function.

It should be mentioned that the definition of the orientational correlation time τ of a molecule or a molecular group may depend on the method which is used to measure the time dependent reorientation. As an example we consider the reorientation, which is described by the rotational diffusion equation

$$D_r \cdot \Delta G(\Omega, t) = \frac{\partial}{\partial t} G(\Omega, t) \quad (6)$$

where Δ is the angular Laplacian and D_r the rotational diffusion constant [23]. The orientational correlation function can be expanded in spherical harmonics with the time dependence

$$F_l(t) = e^{l(l+1)D_r t} \quad (7)$$

In other words, the spherical harmonics Y_l decay with a time constant or correlation time

$$\tau_l = \frac{1}{l(l+1)D_r} \quad (8)$$

The Debye correlation time [24] is given by

$$\tau_1 = \frac{1}{2D_r} \quad (9)$$

For the NMR correlation time Bloembergen, Purcell and Pound [17] obtained

$$\tau_2 = \frac{1}{6D_r} \quad (10)$$

In the case of incoherent neutron scattering the correlation times of all spherical harmonics are measured [23]. For a more detailed treatment of this matter the reader be directed to a selection of papers quoted in the reference list [25–30].

The incoherent scattering law (Eq. (5)) consists of two parts, the purely elastic line at zero energy transfer, given by the distribution $\delta(\omega)$ and the quasi-elastic spectrum, represented by a single Lorentzian. Both the elastic line and quasi-elastic spectra for the three different temperatures ($T_l < T_e < T_u$) are indicated in Figure 1 by the dashed-dotted and solid lines, respectively.

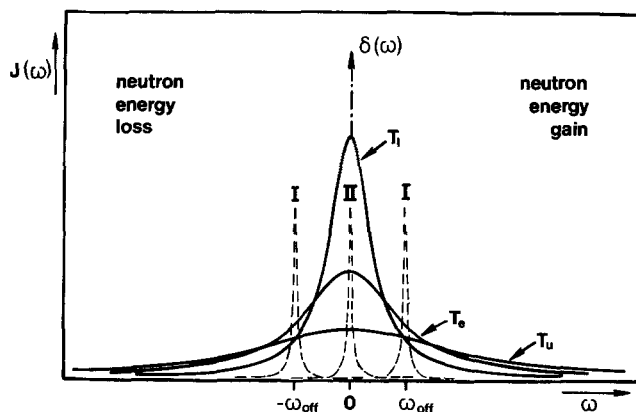


Fig. 1. Sketch illustrating the principle of neutron scattering fixed-window experiments: — quasi-elastic spectra, - - - purely elastic line, - - - spectrometer resolution function

3.2.2 The fixed-window experiments (FWE)

At constant Q the scattering intensity I is a function of ω and T only. In this case the quasi-elastic part of the scattering law resembles the expression for the nuclear magnetic relaxation rate R_1 , as defined by Equation (3). Beyond that, performing an experiment at a definite offset-frequency $\omega = \omega_{\text{off}}$ or an offset-energy $E_{\text{off}} = \hbar\omega_{\text{off}}$, respectively, we arrive at the so-called fixed-window experiments, two kinds of which can be established.

In the case of $\omega_{\text{off}} \neq 0$ (FWE I), the temperature dependent scattering intensity $I(T)$ is given by the quasi-elastic spectrum weighted by the resolution function centred at ω_{off} , thus leading to a weighted mean of the quasi-elastic spectrum at ω_{off} . The intensity gained by this procedure is given by Equation (11), which has been corrected for the contribution from the elastic line. For large offset-energies this correction can be neglected. The constant factor B occurring in Equation (11) is proportional to the width of the resolution function. The temperature dependence of the scattering intensity $\tilde{I}(T)$ enters into Equation (11) by τ according to Equation (2). $\tilde{I}(T)$ is the scattering intensity corrected for the Debye-Waller factor.

$$\tilde{I}(T) = \frac{B}{\pi} [1 - A(Qr_o)] \frac{\tau}{1 + \omega_{\text{off}}^2 \tau^2} \quad (11)$$

The notation $\tilde{I}(T)$ in Equation (11), and Equation (12) as well, indicates the fact, that in the fixed-window type experiments the temperature is the experimental variable, whereas the momentum transfer Q and the

frequency ω_{off} merely serve as fixed parameters. Equation (11) turns out to be the exact analogue to Equation (3), expressing the nuclear magnetic resonance spin-lattice relaxation rate R_1 .

The second type of fixed-window experiments is characterized by the condition $\omega_{\text{off}} = 0$ (FWE II). The scattering intensity $I(Q, O, T)$ follows from Equation (5) by weighting the scattering law with the spectrometer resolution function around $\omega_{\text{off}} = 0$. Denoting the width of the resolution function by Γ the temperature dependence of the scattering intensity $\tilde{I}(T)$ is given by the following Equation [22]:

$$\tilde{I}(T) = F_o(Q) + \frac{2}{\pi} [1 - F_o(Q)] \text{arc tg}(\Gamma \cdot \tau) \quad (12)$$

$\tilde{I}(Q, O, T)$ is the scattering intensity corrected for the Debye-Waller factor. $F_o(Q)$ is the Q dependent incoherent structure factor. The temperature dependence of the scattering intensity again enters by τ , defined by Equation (2). Equation (12) exhibits the same structure as Equation (4), meaning that the fixed-window experiment of type II is adequate to the nuclear magnetic resonance line width experiment.

Figure 1 may serve to elucidate the principle underlying the fixed-window experiments. Only those scattering events contribute to the intensity $I(Q, \omega, T)$ which fall energetically into the window placed at $\omega_{\text{off}} \neq 0$ or $\omega_{\text{off}} = 0$, respectively, and defined by the resolution function of the spectrometer, as indicated in Figure 1 by the dashed lines I and II. An example of a real spectrometer resolution function is represented by Figure 2. The shift of the reflection curve indicates the offset-frequency $\nu_{\text{off}} = E_{\text{off}}/\hbar = 1.45$ GHz used in the FWE I scattering experiment. The full width at half maximum of the resolution function is drawn from Figure 2 to be $\text{FWHM} = 2.4 \mu\text{eV}$, resulting in a spectrometer resolution of $\Delta\nu/\nu_{\text{off}} = 0.4$. For comparison, the resolution, which can be achieved by a high resolution NMR spectrometer, is of magnitude $\Delta\nu/\nu_o = 3 \cdot 10^{-10}$.

At low temperatures, as denoted by T_l in Figure 1, a narrow quasi-elastic line appears, resulting in a small scattering intensity in the FWE I case. As the temperature is raised the spectrum broadens, and a maximum spectral density will be reached in the resolution function regime at a characteristic temperature T_e , thus leading to a maximum scattering intensity. At even more elevated temperatures the spectral density distribution flattens out progressively, as visualized for example by the solid line T_u , i. e. the scattering intensity passes through a maximum and decreases with ris-

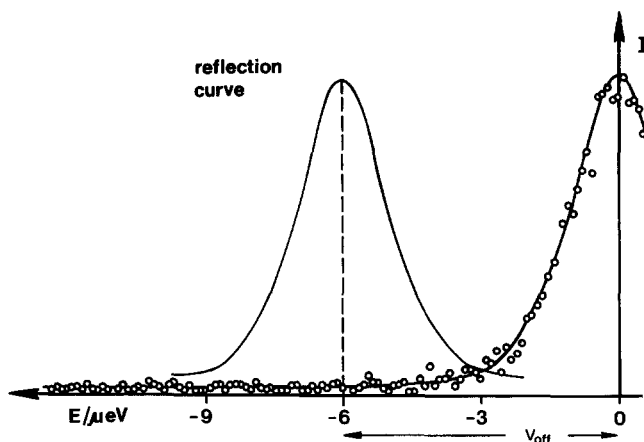


Fig. 2. Experimentally determined resolution function (neutron energy loss side) of the back scattering spectrometer [13] at the research reactor FRJ-2, DIDO, KFA Jülich; shift of the reflection curve illustrating the frequency-offset $\nu_{\text{off}} = E_{\text{off}}/h = 1.45$ GHz, used in one of the scattering experiments

ing temperatures. Following from Equation (3) the same behaviour is exhibited by the nuclear magnetic relaxation rate R_1 , as demonstrated by the Figures 3 and 4.

The fixed-window experiment of the second kind (FWE II), represented by the position II of the resolution function (dashed line) in Figure 1, can be understood as follows. At low temperatures the purely elastic line and the quasi-elastic spectrum lie entirely within the resolution function regime, confining the scattering intensity $\tilde{I}(Q, O, T)$ to a plateau. As the temperature rises the quasi-elastic spectrum broadens and increasingly migrates beyond the window defined by the resolution function. Consequently the scattering intensity decreases and reaches a plateau again, as soon as the quasi-elastic part of the spectrum is essentially outside the window, and only the elastic line remains within. The step in the intensity occurs in a temperature range where the characteristic time τ of the rotational jump motion and the inverse width Γ^{-1} of the resolution function are of the same order of magnitude. According to Equation (12) the step height is given by the difference $\Delta\tilde{I} = 1 - F_o(Q)$. Looking at Equation (4), this behaviour is equivalent to that of the second moment ΔB^2 , resulting from NMR line width measurements. Examples of these two complementary experiments are given in the Figures 6 and 7. T. Peterlin-Neumaier and T. Springer were the first to apply a neutron scattering fixed-window experiment of type II to a polymeric system [31]. A fixed-window

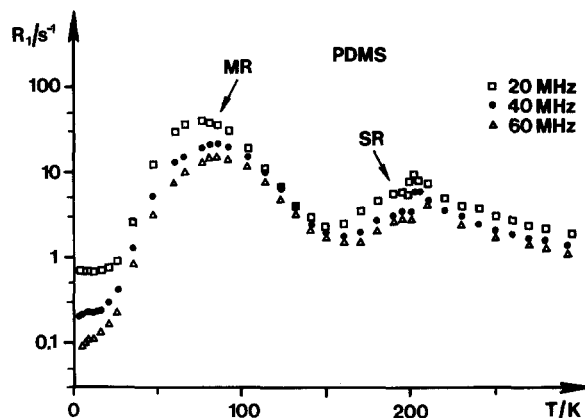


Fig. 3. Temperature dependence of the proton spin-lattice relaxation rate R_1 of polydimethylsiloxane (PDMS) at frequencies $\nu_o = 20, 40$ and 60 MHz

measurement of type I, to our knowledge has not been done prior to the experiment reported on in this paper.

4. Results and discussions

Figure 3 shows the temperature and frequency dependence of the nuclear magnetic spin-lattice relaxation rate R_1 . The classical random methyl group and segmental rotation, being exclusively discussed in this paper, create the two distinct maxima denoted by MR and SR, respectively. These maxima are also found in the fixed-window experiment FWE I, as demonstrated by Figure 4.

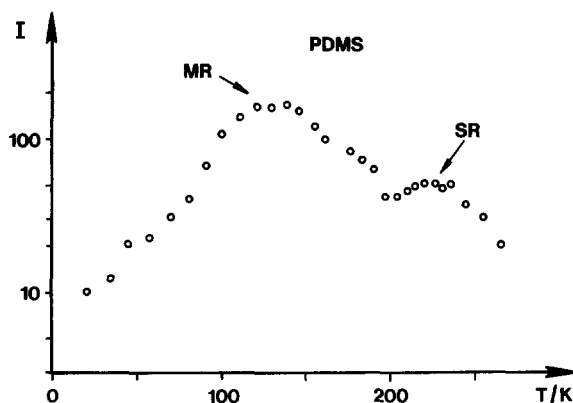


Fig. 4. Temperature dependence of the incoherent neutron scattering intensity I of polydimethylsiloxane (PDMS) as obtained by the fixed-window experiment FWE I: $\nu_{\text{off}} = 1.45$ GHz, $Q = 1.9 \text{ \AA}^{-1}$

Only for completeness the presence of other motional processes will be mentioned. The deviations of R_1 and I from theoretical predictions according to Equations (3) and (11), as occurring in the low temperature region, may be due to tunnelling rotation of the methyl group. Complications impeding the investigation of molecular motions in polymeric systems in the low temperature regime by NMR methods are discussed in Reference [32]. A further motional process, being associated with first order phase transitions, is evidenced by the discontinuity of the spin-lattice relaxation rate R_1 at about 200 K, leading to a disturbance of the maximum SR, generated by segmental rotational jumps. The corresponding discontinuity of the incoherent neutron scattering intensity at about 190 K, as shown by Figure 4, is somewhat doubtful, due to insufficient statistics.

In evaluating the thermally activated hindered motions, i. e. methyl group (MR) and segmental (SR) rotational jumps, advantage is taken of the frequency dependent shift of the maxima MR and SR, respectively. Applying the maximum condition to Equation (3)

$$\omega_0 \tau_c(T_e) = 0.616 \quad (13)$$

follows. T_e denotes that temperature at which the relaxation rate R_1 reaches a maximum. Inserting the correlation time τ_c , as defined by Equation (2), into Equation (13), we arrive at

$$\ln \omega_0 = -\frac{\Delta E}{R} \cdot \frac{1}{T_e} + \ln \frac{0.616}{\tau_c(\infty)} \quad (14)$$

Equation (14) yields a straight line in the Arrhenius plot $\ln \omega_0$ vs. $1/T_e$, which allows to determine ΔE and $\tau_c(\infty)$.

Applying the same arguments to Equation (11) we get

$$\omega_{\text{off}} \tau(T_e) = 1 \quad (15)$$

and finally

$$\ln \omega_{\text{off}} = -\frac{\Delta E}{R} \cdot \frac{1}{T_e} + \ln \frac{1}{\tau(\infty)} \quad (16)$$

thus demonstrating again the similarities between the neutron scattering fixed-window experiment FWE I and the nuclear magnetic resonance spin-lattice relaxation experiment.

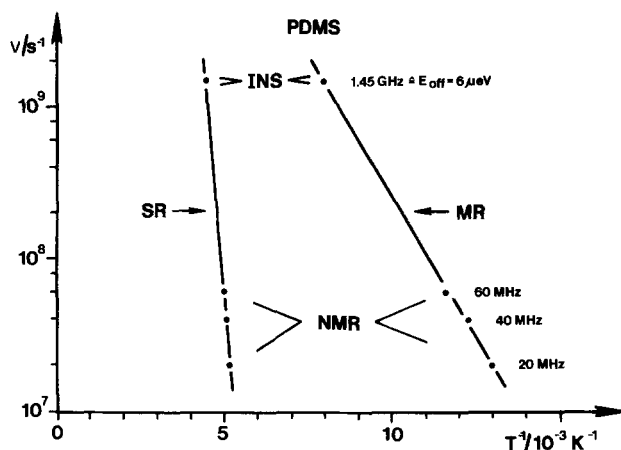


Fig. 5. Arrhenius diagram as obtained from the frequency dependent shift of the methyl group and segmental rotational maxima in Figures 3 and 4

The co-ordinate pairs (ω_0, T_e) and $(\omega_{\text{off}}, T_e)$, as obtained from Figures 3 and 4, are plotted in Figure 5, the Arrhenius diagram in its $\log \nu$ vs. $1/T$ representation. It proves that the nuclear magnetic resonance and neutron scattering data points fit well to two straight lines related to methyl group (MR) and segmental (SR) rotational jumping. From these lines the

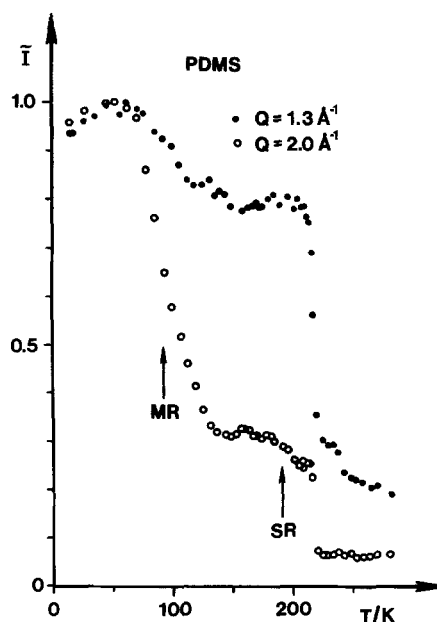


Fig. 6. Temperature dependence of the incoherent neutron scattering intensity I of polydimethylsiloxane (PDMS) as obtained by the fixed-window experiment FWE II: $\nu_{\text{off}} = 0$ Hz, $Q = 1.3, 2.0 \text{ \AA}^{-1}$

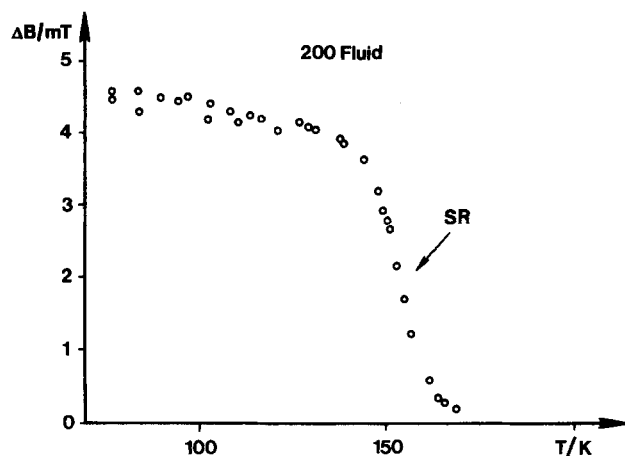


Fig. 7. Temperature dependence of the proton magnetic resonance line width ΔB of polydimethylsiloxane (200 Fluid, Dow Corning Corporation) as drawn from Reference [34]

model parameters follow to be $\Delta E^{\text{MR}} = 6.4 \text{ kJ} \cdot \text{mol}^{-1}$, $\tau^{\text{MR}}(\infty) = 1.7 \cdot 10^{-13} \text{ s}$, $\Delta E^{\text{SR}} = 50.2 \text{ kJ} \cdot \text{mol}^{-1}$ and $\tau^{\text{SR}}(\infty) = 1.4 \cdot 10^{-22} \text{ s}$, the latter being a fictitious value of no physical meaning.

Figure 6 shows the result of fixed-window experiments of the second type (FWE II) for two different values of momentum transfer, displaying intensity step functions according to Equation (12). The step steps in the scattering intensity labeled by MR arise from classical methyl group rotational hopping. An effect of segmental rotation may be realized in the moderate intensity step marked by SR. This step occurs only with the data belonging to the momentum transfer of $Q = 2.0 \text{ \AA}^{-1}$. The sudden jump in the scattering intensity at about 220 K is produced by a motional process associated with first order phase transitions. Below 50 K the scattering intensity drops beneath the plateau which is expected to appear according to Equation (12). This surprising feature seems to indicate the effect of methyl group tunnelling rotation. Stronger evidence of this quantum mechanical type of motion has been found in a supplementary neutron scattering experiment [8, 33].

To demonstrate the similarity between the neutron scattering fixed-window experiment of type II and nuclear magnetic resonance line width measurements, an example is taken from literature. Figure 7 shows the temperature dependent line width ΔB of a polysiloxane, 200 Fluid, as studied by proton magnetic resonance [34]. The step in the line width is produced by segmental rotational jumps.

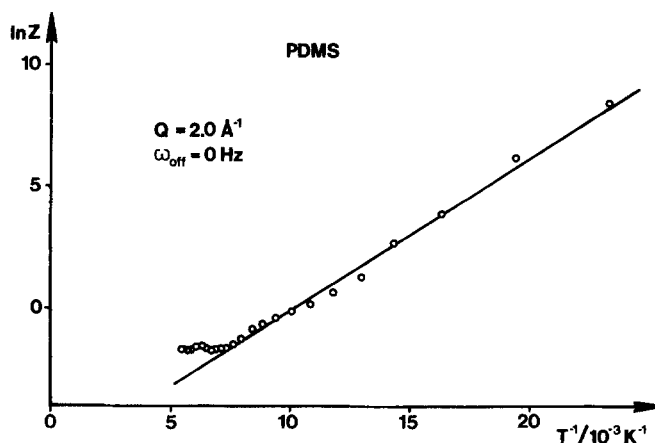


Fig. 8. Arrhenius diagram according to Equation (13) as obtained from the neutron scattering intensity step labelled by MR (methyl group rotational jumping) in Figure 6 (case $Q = 2.0 \text{ \AA}^{-1}$)

The fixed-window experiment FWE II provides an additional way to determine activation energies by means of Equation (12). By rearranging Equation (12) and proceeding to the inverse function of arc tg , we arrive at

$$\text{tg} \left(\frac{\pi}{2} \frac{\tilde{I} - F_o}{1 + F_o} \right) = \Gamma \cdot \tau = Z(\tilde{I}). \quad (17)$$

Again inserting the characteristic time τ , as given by Equation (2), we get

$$\ln Z = \frac{\Delta E}{R} \cdot \frac{1}{T} + \ln [\Gamma \cdot \tau(\infty)] \quad (18)$$

Equation (18) defines a straight line in an Arrhenius diagram $\ln Z$ vs. $1/T$. Plotting the co-ordinate pairs (Z, T) for methyl group rotation, as derived from Figure 6 for the case $Q = 2.0 \text{ \AA}^{-1}$, according to Equation (18) we get the representation displayed in Figure 8. The incoherent quasi-elastic structure factor $F_o(Q)$ was taken from Reference [35]. From the slope of the straight line in Figure 8 an activation energy $\Delta E^{\text{MR}} = 5.2 \text{ kJ} \cdot \text{mol}^{-1}$ follows, being somewhat smaller as compared with the value obtained from the FWE I and nuclear magnetic spin-lattice relaxation experiments. This may be explained to some extent by the reduction in the slope of the intensity step in Figure 6 due to the effect of methyl group tunnelling.

5. Conclusion

The micro-brownian motions in a polymeric system can equally well be investigated by incoherent

neutron scattering experiments of the fixed-window type and nuclear magnetic resonance relaxation and line width experiments. The resulting dynamical model parameters of the motional processes under investigation are in good agreement as to the nuclear magnetic spin-lattice relaxation and neutron scattering fixed-window experiment of type I ($\omega_{\text{off}} \neq 0$). Furthermore these experiments show the validity of an Arrhenius behaviour for random methyl group and segmental rotational hopping from the MHz up to the GHz region. A fairly good correspondence is still given to the fixed-window experiment of type II ($\omega_{\text{off}} = 0$).

Quite different values of activation energies for random methyl group rotation, however, were found by applying other neutron scattering techniques. By inelastic neutron scattering [7] a value of $8 \text{ kJ} \cdot \text{mol}^{-1}$ was obtained for the height of the hindering barrier which, neglecting the ground state torsional level, can be regarded as the activation energy. On the other hand the neutron transmission measurements [6] resulted in an upper limit of $1.7 \text{ kJ} \cdot \text{mol}^{-1}$ for the barrier hindering methyl group rotation.

These differences are probably due to the different model assumptions made to interpret the experimental data. In the nuclear magnetic resonance T_1 - and the neutron scattering FWE I-experiment the activation energy was determined from an Arrhenius ansatz for the correlation time or jump time respectively, without referring to a special potential form. The inelastic neutron scattering data were interpreted by adoption of a pure $\cos(3\Phi)$ -potential whereas in the neutron transmission case the limiting value was deduced from the slope of the wavelength dependent hydrogen scattering cross section, assuming, as to the terminology of the authors, a "practically free" methyl group rotation in polydimethylsiloxane. From this contradictory situation it has to be concluded that a merely threefold cosine potential is not adequate to describe methyl group reorientation in this system.

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