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Local Side Group Dynamics of Poly(methylphenylsiloxane) (PMPS) As Studied by Quasielastic Neutron Scattering

G. Meier,*,[†] F. Fujara,[‡] and W. Petry[§]

Max Planck Institut für Polymerforschung, Postfach 3148, D-6500 Mainz, West Germany,
Institut für Physikalische Chemie, Postfach 3108, D-6500 Mainz, West Germany, and
Institut Laue Langevin, 156X, F-38042 Grenoble Cedex, France.
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ABSTRACT: Heterotactic PMPS has been used as a model system in order to study the occurrence of side group motion below and around the onset of the softening of the glassy structure. Incoherent quasielastic neutron scattering experiments and ^{2}H NMR spectra consistently identify this side group motion as a phenyl ring π-flip. The significance of this local motion process for the glass transition is discussed and put into the context of other available experimental results on the primary glass transition.

Introduction

The experimental and theoretical study of glass transitions is of high actual interest. Recent theoretical approaches[1] claim the occurrence of fast local dynamics (β-processes) as a precursor of the primary softening of the glassy structure (α-process) in *simple* liquids. The emphasis is on "simple"; i.e., β-processes are found in systems formed of Lennard-Jones particles without internal dynamics. So, a priori only interparticle dynamics is possible. Obviously the experimental verification of such β-processes depends on the availability of model systems resembling simple liquids as used in theory. However, *real* systems are much more complex. The more "simple" the liquid (metallic glasses etc.), the higher is its tendency to crystallize. In order not to leave the theoretical predictions only on the academic shelf, the experimentalist must allow for compromises and has to look for suitable real glass formers; but the search is not easy.

Networks (SiO_2, H-bridge types) certainly cannot be considered as good model systems because of the strong directional bondings, since it is expected that local dynamics is strongly coupled to structural degrees of freedom.

Molecular van der Waals liquids seem to be better model systems because of the individuality of their approximately spherical constituents. Intermolecular forces (van der Waals) are much weaker than intramolecular forces (bondings). Recently, it has been shown[2,3] that molecular liquids follow the predictions of mode coupling theory at least qualitatively. However, it is also true that in this case intramolecular motion cannot be fully excluded. The molecules are not necessarily stiff.

Polymers are also used to test theory. Although a chain represents an extended quasi one-dimensional bond structure, we again deal with intermolecular van der Waals bondings as in the case of molecular liquids. But of course, many more intramolecular modes may exist and interfere. Consequently polymers are by no means "simple". One way to avoid difficulties is to use main-chain polymers as is done in ref 4.

Let us adopt an opposite standpoint and look at a system where well-defined intramolecular motions, e.g., of side groups, are expected. Then we can ask again how such motions—to be called β-processes as well—are correlated with the glass transition. It was our goal to look for such a β-process. We chose a phenyl ring flip in a polymer. The system was chosen such that the phenyl ring flip is largely decoupled from other degrees of freedom and introduces a significant "dynamic" plasticizer effect; i.e., it triggers the glass transition.

We mainly performed incoherent quasielastic neutron scattering experiments because this method identifies the type of motion on a "microscopic" time scale which we believe to be the relevant time scale. The experiments are accompanied by some ^{2}H NMR spectra where the line shape is used for identifying the phenyl motion as a 180° rotational jump process.

[†] Max Planck Institut für Polymerforschung.
[‡] Institut für Physikalische Chemie.
[§] Institut Laue Langevin.

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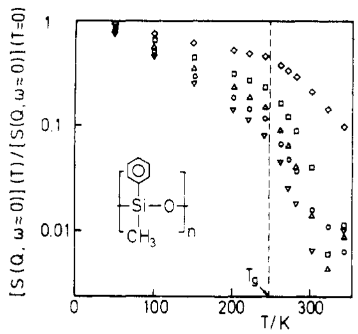

Figure 1. Neutron scattering elastic window measurements $S(Q,\omega = 0)$ normalized to its extrapolated value at $T = 0$ K vs temperature T, plotted for selected Q values: ◇, 1.6 Å^{-1}; □, 2.6 Å^{-1}; △, 3.4 Å^{-1}; ○, 4.2 Å^{-1}; ▽, 4.8 Å^{-1}. The data are averaged within an interval of about ±0.4 Å^{-1}. Whereas below T_g the elastic intensity obeys the Debye–Waller factor $\ln S(Q,\omega = 0) \sim -T$, an extra decrease due to motion is observed above T_g.

After presentation and discussion of the experimental results on the phenyl ring flip, this paper also reviews the existing spectroscopic results, mainly on the α-process of the chosen polymer.

Experimental Section

Material. For the incoherent quasielastic neutron scattering experiments we used fully protonated heterotactic PMPS. It was anionically polymerized by the ring-opening polymerization of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane. The full procedure and sample characterization are described elsewhere.[5] The weight- and number-average molecular weights were found by gel permeation chromatography (GPC) to be M_w = 28 500 D and M_n = 27 300 D (M_w/M_n = 1.04). For this measurement, a silica gel column with THF as eluent was used. Universal calibration with polystyrene standards was used.[6] The glass transition temperature T_g was determined from DSC at a heating rate of 20 K/min to be T_g = 247 K. For the NMR experiment we used PMPS that was selectively deuterated at the phenyl ring.[5] The physical properties were identical with those of the fully protonated sample.

Procedures. The experiments were performed on the thermal neutron backscattering spectrometer IN13 at the Institute Laue Langevin. The spectrometer combines the possibility of high Q measurements (0.3–5.0 Å^{-1}) with a high-energy resolution (8 μeV fwhm). The energy range covered was from −100 μeV to +200 μeV. These features allow one to look at local small amplitude (high Q) and slow (high energy resolution) motions. [Note the following conversion factor: 1 μeV (half-width at half-maximum) corresponds to 6.58×10^{-10} s correlation time.] The samples were hydrogenated heterotactic PMPS placed in flat Al containers (sample thickness 0.7 mm), yielding a transmission of about 89%. Since we use protonated PMPS, we essentially observe the incoherent scattering of the protons. Thus, quasielastic scattering measures the time Fourier transform of the single particle propagator

$$S_S(Q,\omega) \sim \int e^{-i\omega t} I_S(Q,t)\,\mathrm{d}t \sim \int e^{-i\omega t} \langle e^{-i\vec{\mathbf{Q}}\vec{\mathbf{R}}(0)} e^{i\vec{\mathbf{Q}}\vec{\mathbf{R}}(t)} \rangle\,\mathrm{d}t \qquad (1)$$

In a first approach we set the spectrometer to zero energy transfer in order to measure the temperature dependence of the elastic intensity, as shown in Figure 1. The elastic intensity is a measure of the long time limit of the intermediate scattering function $I_S(Q,t{\to}\infty)$. We find that up to 250 K the loss of elastic intensity is essentially caused by phonons (i.e., its decrease is well described by a Debye–Waller factor), whereas above 250 K an extra decrease is observed. This anomalous decrease is due to motion, as will be revealed in detail by the full spectra (see below). From a comparative elastic scan on isotactic PMPS (not shown here) we also find that there is no significant difference if we compare the measured elastic scans for isotactic and heterotactic PMPS.

In order to learn about the *type* and *time scale* of the extra motion, full spectra $S_S(Q,\omega)$ were measured at six different temperatures: 275, 289, 293, 300, 331, and 350 K. All spectra show a clear quasielastic broadening in addition to the strict elastic part and some significant background. A typical spectrum showing all these features is plotted in Figure 2.

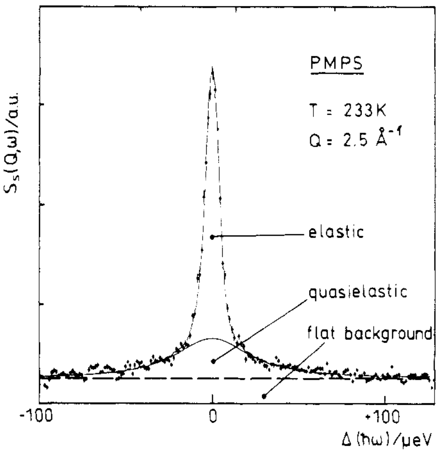

Figure 2. Typical quasielastic neutron scattering spectrum. The upper full curve represents the fit of a δ-function and a Lorentzian (convoluted with the spectrometer resolution function) on top of a flat background. The quasielastic past is indicated separately by the lower full curve and the background by the broken line.

From ^{2}H NMR spectra (see below), it can be presumed that the quasielastic broadening is caused by phenyl ring flips. The flip geometry must then result in a certain spectral line shape.[7] Four out of five phenyl ring protons perform 180° jumps on a circle with radius a = 2.28 Å = sin 60° ($r_{\mathrm{C-C}} + r_{\mathrm{C-H}}$) yielding[8]

$$S_S'(Q,\omega) = {}^1\!/_2\,\delta(\omega)\left(1 + \frac{\sin 2Qa}{2Qa}\right) + {}^1\!/_2\left(1 - \frac{\sin 2Qa}{2Qa}\right)\frac{1}{\pi}L\left(\frac{2}{\tau}\right) \qquad (2)$$

with

$$L\left(\frac{2}{\tau}\right) = \frac{2/\tau}{\omega^2 + (2/\tau)^2}[\mathrm{hwhm} = 2/\tau \text{ rad s}^{-1}]$$

with a Q-independent line width of Lorentzian shape. One phenyl ring proton does not move during the ring flip and yields

$$S_S''(Q,\omega) = \delta(\omega) \qquad (3)$$

The methyl group protons are expected to move much faster, leading to some constant background in the IN13 dynamic regime. The overall line shape is therefore expected to be given by

$$S_S(Q,\omega) = {}^4\!/_5\,S_S'(Q,\omega) + {}^1\!/_5\,S_S''(Q,\omega) + \text{const} \qquad (4)$$

The elastic part of $S_S(Q,\omega)$ is called "elastic incoherent structure factor" (EISF) and is given by

$$\mathrm{EISF} = {}^1\!/_5 + {}^2\!/_5\left(1 + \frac{\sin 2Qa}{2Qa}\right) \qquad (5)$$

for the phenyl π-flip.

In order to check the validity of the model, the measured spectra are fitted with a curve consisting of an elastic part, a Lorentzian, and a flat background. This fitting curve is convoluted with the spectrometer resolution function, which is independently measured by a vanadium run. Free fit parameters are (1) the background, (2) the quasielastic line width, and (3) the relative weight of the elastic line with respect to the sum of the elastic and the quasielastic part. As is illustrated by the full curve in Figure 2, the fits turn out to describe the measured spectra reasonably well. From this fitting procedure the EISF is obtained as the relative weight of the elastic line, more precisely

$$\mathrm{EISF} = \frac{\text{elastic area}}{\text{elastic area + quasielastic area}} \qquad (6)$$

which should coincide with the EISF as given by eq 5. In Figure 3 this EISF is compared to some experimentally determined ones. To avoid overloading the figure, EISFs from only three out of six temperatures are included. The overall tendency is a monotonic decrease of the EISF with increasing temperature. For $T \leq 300$ K, only a slight decrease in the EISFs occurs. Thus, in this temperature regime a reasonable agreement with the calculated curve from eq 5 can be stated. The systematic deviations

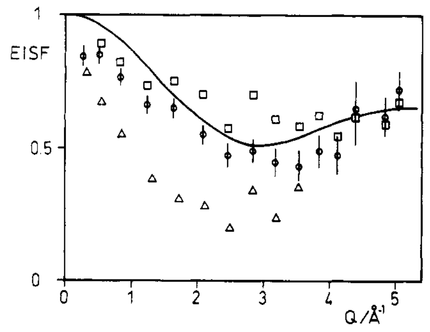

Figure 3. Experimental EISF data obtained from PMPS quasielastic neutron scattering spectra using a fitting procedure as described in the text: □, 275 K; ●, 293 K; △, 331 K. Typical error bars are shown for the 293 K data.

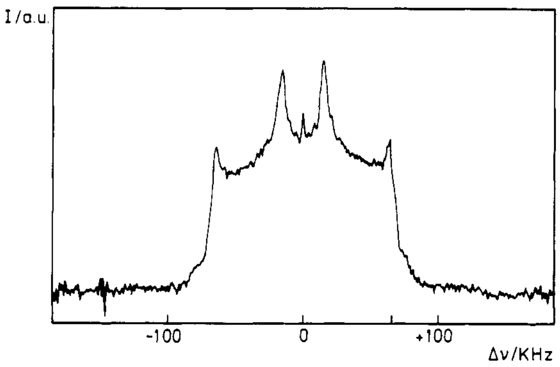

Figure 4. ^{2}H NMR solid echo spectrum of PMPS-d_5 at 250 K using the pulse sequence $(2\ \mu s)_x$–30 μs–$(2\ \mu s)_y$. The number of accumulations was 200 and the waiting time 20 s, yielding a fully relaxed spectrum. The spectral shape can be well described by 180° phenyl ring flips.

at small Q are due to multiple scattering, which is not corrected for. As the temperature is raised to 331 and 350 K, the experimental EISFs drop markedly below the curve describing the phenyl ring flip. This implies that another motional degree of freedom enters into the dynamic range. As will be discussed below, it is the α-relaxation of the glass transition that couples to the phenyl flip. So far for the geometry of motion. From the quasielastic line widths we can further learn about the correlation times of the process. It turns out that in the T range where the phenyl ring flip can be isolated (275–300 K) line widths are essentially Q independent in accordance with eq 2; the correlation times are $(3.0 \pm 0.3) \times 10^{-11}$ s. There is no significant apparent temperature dependence within the experimental accuracy.

Two subsidiary experiments were performed: (i) a neutron scattering run on a time of flight machine for identifying the background as due to methyl group dynamics; (ii) a ^{2}H NMR run for supplying an independent check for the phenyl ring flip. Experiment i was performed on the ILL time of flight spectrometer D7. The spectrometer energy resolution was set to about 100 μeV fwhm allowing to look at fast motions in the 10^{-12}–10^{-13} s time regime. Using a sample selectively deuterated on the phenyl rings, we essentially looked at the CH_3 group dynamics. The spectra, taken at $T = 300$ K in the Q range of 0.2–2.5 Å^{-1}, show a Q-independent quasielastic broadening on top of the phonon part. The quasielastic line can be reasonably well fitted by a Lorentzian with a line width corresponding to a CH_3 group correlation time of $(1.6 \pm 0.2) \times 10^{-12}$ s. The sample, selectively deuterated at the phenyl ring, was then used for the other auxiliary experiment ii. We performed a series of pulsed ^{2}H NMR echo experiments at a ^{2}H Larmor frequency of about 55 MHz in the temperature range from 210 K up to 265 K. The spectral line shape of flipping phenyl rings in the "fast-exchange limit" is well-known[9] and is reproduced by our spectra at all measured temperatures (see Figure 4).

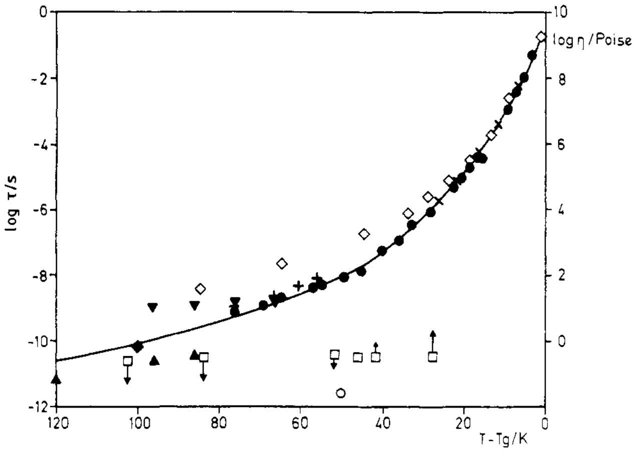

Figure 5. Plot summarizing all available experimental data on the PMPS dynamics in terms of correlation times τ vs reduced temperature $T - T_g$: ●, DK;[10] +, ultrasonic;[11] ▼, depolarized Rayleigh;[12] ▲, Brillouin;[13] ◇, from maximum phonon line width;[13] □, quasielastic neutron scattering on phenyl ring flip (this work), arrows indicating tendency of shift if distribution of correlation times are taken into account; ○, quasielastic neutron scattering on CH_3 group rotation (this work). The plot also includes viscosity data (◇, this work). The solid curve represents a fit[10] of the VFT law to the DK and PCS data. For a detailed discussion see text.

Discussion

In order to identify the nature of the relaxations as measured by quasielastic neutron scattering—i.e. whether they contribute to the secondary relaxation (β-process) or to the primary and structural relaxation (α-process)—we will first comment on the findings from several other methods. The purpose of Figure 5 is to show all relaxation times in PMPS known to the authors. Since in the various studies materials with different molecular weights have been used, we decided to use for all relevant relaxation times a temperature scale relative to the individual glass transition temperatures of the materials.

Reference 10 compares dielectric relaxation (DK) and quasielastic light scattering data. The measured dielectric loss curves $\epsilon''(\omega)$ were analytically described by the Havriliak–Negami model which allows us to fit the width of a distribution independent of its asymmetry. With this model the experimental data were transformed into the time domain representing the autocorrelation function of dipolar reorientations. A fit of a stretched exponential (Kohlrausch–Williams–Watts; KWW) to these data yields mean correlation times that are plotted as full dots in Figure 5. Further the results from quasielastic light scattering (photon correlation spectroscopy; PCS)—measured in the time domain directly—are analyzed by using a KWW representation of the density autocorrelation function. The corresponding mean correlation times are also plotted ("×") in Figure 5. It turns out[10] that the times from DK and PCS are identical, indicating that the collective dynamics measured by the $q \rightarrow 0$ method PCS goes along with the reorientation of the molecular dipoles. The full line in Figure 4 is a fit of the Vogel–Fulcher–Tamman (VFT) equation $\tau = \tau_0 \exp(B/(T - T_0))$ to the data. The parameters of the VFT equation, commonly known to describe the temperature dependence of the steady flow viscosity of viscoelastic materials, are $B = 1015$ K and $T_0 = 214$ K, being obtained from the DK and PCS data simultaneously.

Four data points ("+") from ultrasonic absorbance measurements by Onabajo et al.[11] are also included. They have found two distinct relaxation processes that they interpret as fast segmental relaxation and slow chain dynamics. The latter relaxation mode was adequately described within the Rouse model. Since the α-mode reviewed here is understood in terms of segmental relaxation, we include in Figure 5 their data points for the fast ultrasonic mode, which indeed follow nicely the VFT line of the α-relaxation.

We have measured the steady flow viscosity η_0 of our PMPS sample with a Rheometrix torsion pendulum. This is achieved by measuring $\lim_{\omega \to 0} G''(\omega)/\omega = \eta_0$. We have made sure that in any case the low-frequency plateau value of $G''(\omega)$ has been obtained. For temperatures just above T_g a lowest frequency of $\omega = 0.01$ rad s^{-1} was small enough to reach a constant value. At T_g the viscosity is usually 10^{12}–10^{13} P. The VFT line in Figure 5 becomes very sharp close to T_g but certainly reaches the given viscosity value although the figure suggests a $\eta \simeq 10^{10}$ P for $T = T_g$. As shown in Figure 4 ("◇") η_0 follows the VFT line only close to T_g. This finding is consistent with the fact that near T_g only segmental motion can affect the flow properties whereas at larger $T - T_g$ chain properties enter. In a regime below a critical molecular weight, M_c, the viscosity scales with M. So the η_0 values should correspond to the slow ultrasonic mode[11] (the different molecular weights have to be taken into account) which we have found to be correct.

For correlation times shorter than $\simeq 10^{-8}$ s results from light scattering are only achievable by interferometric methods (neglecting optical grating spectroscopy for very fast dynamics for the moment). Depolarized Rayleigh spectra ("∇") have been mesured by Lin et al.[12] and polarized Rayleigh–Brillouin spectra ("Δ") by Fytas et al.[13] From the latter work a data point ("◇") is included by using the condition $\omega_B \tau \simeq 1$ for a phonon velocity at the maximum of the phonon line width. This point is met by the α-line as extrapolated by using the VFT parameters[10] mentioned above. This behavior is similar to that we have found in the *o*-terphenyl case.[14] Clearly the Brillouin spectroscopy yields segmental dynamics at high frequencies. The most updated way to describe both the measured sound velocity and the damping is a theory by Lin and Wang:[15] the longitudinal modulus relaxes with a structural relaxation time τ_S; the spectra are of Lorentzian shape; the temperature dependence of τ_S is assumed to be of the Arrhenius type. A recent study by Börgesson, Stevens, and Torell[16] indicates that one can have confidence in combining low-frequency (DK and PCS) and ultrasonic results *and* in assuming a stretched exponential (KWW) for the Fourier transform of the measured spectra. However, the difference between the results[12] and the α-line[10] is roughly half a decade and certainly reflects the error of the method.

The τ_S values from the depolarized Rayleigh spectra[12] are larger by nearly 2 decades compared to those from Brillouin spectroscopy.[13] This is typical behavior found in all such systems where both methods have been applied.[17] The reason for this finding may be that the correlation function of the optical anisotropy, measured in the VH geometry, can only relax via reorientational processes, whereas in the VV (polarized) case additional translational paths are possible. Moreover we know from rotational dynamics that the viscosity entering the Debye–Stokes–Einstein equation is closely related to the macroscopic viscosity.[18] However, the viscosity that partly governs the sound propagation is measured at gigahertz frequencies and is therefore reduced. Consequently, the times from Brillouin spectroscopy are shorter than those from rotational dynamics.

So far we have exclusively commented on the primary relaxation. Experimental findings on secondary relaxations (β-processes) on PMPS do not exist in the literature to our knowledge. Figure 5 also contains correlation times as obtained from fits of our quasielastic neutron scattering spectra ("□") using the procedure as described in detail above. At high temperatures we find that the local dynamics found by neutron scattering is close to the dynamic range of the α-process. Primary and secondary relaxations cannot be distinguished. If only the α-process would dominate, the EISF would be zero; if only the phenyl ring flip occurs (within the dynamic range), the EISF is described by eq 4. At 331 and 350 K the experimental EISF is "intermediate" between the two cases showing that α- and β-processes are about to merge. Spectra at even higher temperatures could not be measured because of lack of beamtime. Note that the signal drastically drops at high temperatures because of the strongly decreasing Debye–Waller factor (Figure 1). Already at 331 K the single spectra are of rather poor quality resulting in a larger uncertainty of the EISF points in Figure 3. Further, a proper statement on the Q dependence of the quasielastic line width is not possible. (Some "admixture" of a Q^2 dependence in the hydrodynamic regime is expected.)

As T is lowered down to and below 300 K, the phenyl ring flip becomes uncoupled from the α-process, as already described in the Experimental Section. We again note that there has been a small but systematic drop of the EISF when T is raised from 275 K up to 300 K, the best agreement to the calculated EISF (eq 5) being obtained at 289 K. The decrease is caused either by a starting admixture of the α-process or by a distribution of correlation times. It is again because of the limited quality of the spectra that we have contented ourselves with single-Lorentz fits. Qualitatively, however, the slight T variation of the EISF and the T independence of the line width could have been invoked by the use of a single Lorentzian (i.e. an exponential correlation function) with the following argument: Suppose the correlation function is properly described by a stretched exponential (e.g. KWW) law. Then at any chosen temperature the spectrometer preferentially sees that part of the dynamics that falls into the dynamic window. Therefore the line width essentially seems to be T independent. The T independence goes along with an apparent vague T dependence of the EISF. This may be becuase at $T < 289$ K the slow edge of the quasielastic spectrum is hidden within the resolution function and is interpreted as an elastic line. At $T > 289$ K the effect is reversed, the elastic line being underestimated. This tendency is accounted for in Figure 5 by the arrows pointing up and down, respectively. We emphasize again that the data points at 331 and 350 K do not stem any more from a pure isolated phenyl ring flip but include strong contributions from the α-process. Hence the analysis assuming phenyl flip motion only leads to too slow dynamics as is seen from the corresponding data points in Figure 5.

Apart from these limitations the identification of the β-process is clear. Independent evidence for its physical nature as the phenyl ring flip is obtained from ^{2}H NMR spectra (Figure 4). ^{2}H NMR line shapes do not tell about correlation times faster than $\omega_Q^{-1} \simeq 10^{-6}$ s but quite sensitively identify the geometry of motion. (ω_Q is a measure for the spectral width determined by the ^{2}H quadrupolar coupling constant.) It is only in the "slow motion regime" $\tau_c \omega_Q \simeq 1$ where changes in the spectral shape tell about correlation times. This condition, however, has not been reached by our measurements down to 210 K.

Preliminary runs down to 150 K indicate only slightly line shape changes. Though quantitative line shape fittings can provide information upon correlation time distributions and/or a possible spread of jump angles around the "π-flip" of 180°,[19] we anticipate that the small spectral changes seen in PMPS will be difficult to attribute to one of both possibilities. A future analysis of spin–lattice relaxation times will provide an independent test on whether the average correlation time of the flip motion is temperature independent since the NMR "time window" differs from that of neutron scattering. The statement we like to make so far from ^{2}H NMR spectra is that even far ($\simeq$40 K) below T_g *all* phenyl rings are in the "fast-exchange limit", i.e., $\tau_c \ll 10^{-6}$ s.

It is reasonable to compare materials that are of similar microscopic chemical structure. Neglecting the different backbone compositions of PMPS and, e.g., polystyrene (PS), both polymers are characterized by phenyl ring side groups having a distinct separation of each other. Nevertheless a comparison of the phenyl ring flip dynamics between PMPS and PS shows significant differences:

For a given temperature (relative to T_g) the phenyl ring flip correlation times are much larger in PS.[20] Phenyl ring flips in PS are not seen on the neutron scattering time scale. Consequently the "bifurcation" of the α- and β-process is delayed by several decades. We conclude that phenyl ring flips in PMPS are hindered much less than in PS. This finding is also supported by a interferometric Raman study on the phenyl ring flip dynamics in PMPS and PS, respectively.[21] There the characteristic times differ by 1 order of magnitude in favor of the siloxane.

PMPS does not show a secondary dielectric relaxation peak.[22] Clearly, the isolated phenyl ring flip is not expected to be dielectrically active, but a coupling to the main chain would be. PS, however, does show a secondary dielectric relaxation peak[23] that might be coupled to the phenyl ring flip.

The same is true for the dynamic mechanical behavior at low temperatures. Whereas PS does show a β-process,[24] our PMPS sample does not (no maximum in $G''(\omega)$ down to $T = 90$ K as measured by a rheometry torsion pendulum with 0.1 rad s^{-1} in our laboratory).

^{1}H NMR experiments[25] of PS phenyl ring protons show relaxation phenomena that go along with corresponding observations on PS main-chain protons. It was argued that some coupling of the phenyl ring and the main chain exists.

From the chemical structure the above findings are quite plausible since a Si–O bond (1.63 Å) is longer than a C–C bond (1.53 Å), leaving more free volume to the PMPS phenyl rings.

Let us conclude the discussion by resuming the reflections of the introduction. We have clearly identified the phenyl ring flip as a β-process uncoupled from the α-relaxation at microscopic correlation times. What is the role of the β-process in the glass transition? The easy and trivial answer to this question is that phenyl rings represent "dynamic" plasticizers. What does it mean physically? One type of *speculation* seems to be attractive to us: As pointed out in the Introduction, mode–coupling theory[1] predicts the existence of a relevant β-process in simple liquids. It is our (speculative) proposal that in real systems this role can be taken over by any local degree of freedom ("dynamic" plasticizer) that uncouples on a microscopic time scale. It would be extremely interesting for the understanding of the physical nature of the β-process proposed by mode-coupling theory to introduce such degrees of freedom and calculate their influence on the glass transition.

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Registry No. 1,3,5-Trimethyl-1,3,5-triphenylcyclotrisiloxane (homopolymer), 25569-20-4; 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane (SRU), 9005-12-3; neutron, 12586-31-1.

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