Supporting Information

Low frequency vibrational density of state of highly permeable super glassy polynorbornenes – The Boson peak

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Calculation of the scattering cross sections

PTCNSi1:

Number	Atom	coh. ind.	coh. total	inc. ind.	inc. total	abs. ind.	abs. total
12	С	5.551	66.6	0.001	0.012	0.0035	0.12
20	Н	1.7568	35.1	80.26	1605.2	0.3326	18.48
1	Si	2.163	2.2	0.004	0.004	0.171	0.48
Total / monomeric unit:			103.9		1605.2		19.07

PTCNSi2g:

Number	Atom	coh. ind.	coh. total	inc. ind.	inc. total	abs. ind.	abs. total
15	C	5.551	83.3	0.001	0.015	0.0035	0.15
28	Н	1.7568	49.2	80.26	2247.3	0.3326	25.87
2	Si	2.163	4.3	0.004	0.008	0.171	0.95
Total / monomeric unit:			136.8		2247.3		26.96

Exo-PNBSi:

Number	Atom	coh. ind.	coh. total	inc. ind.	inc. total	abs. ind.	abs. total
10	C	5.551	55.5	0.001	0.01	0.0035	0.10
18	Н	1.7568	31.6	80.26	1444.7	0.3326	16.63
1	Si	2.163	2.2	0.004	0.004	0.171	0.48
Total / monomeric unit:			89.3		1444.7		17.20

Calculation of the neutron cross sections for the materials used. The total cross sections were obtained by multiplication of the individual nuclear cross sections with the number of respective nuclei in the monomeric units. This procedure is correct for incoherent scattering and absorption; for coherent scattering it represents the high-Q limit. The absorption cross sections were corrected to the actual wavelength of the experiments, and therefore the tabulated values are multiplied a factor 5 Å / 1.8 Å in addition.

Calculation and correction of the vibrational density of states (VDOS)

In one-phonon approximation the result of an inelastic neutron scattering experiment can be expressed as [1]

$$S(q,\omega) = e^{-2W(q)} \left(\delta(\omega) + \frac{hq^2}{2\overline{m}} \frac{g(\omega)}{-\omega} \times \left(1 - \exp\left(\frac{h\omega}{k_B T}\right) \right)^{-1} \right)$$
(S1)

Here $e^{-2W(q)}$ denote the Debye-Waller factor and k_B is the Boltzmann constant. The average mass of an atom is represented by \overline{m} . What is measured during a scattering experiment is general a convolution of the dynamic structure factor of the material with the resolution of the instrument $R(q,\omega)$. In comparison with the resolution the boson peak is broad feature. Therefore, the convolution can be replaced by a sum and it holds

$$S_{obs}(q,\omega) = R(q,\omega) \otimes S(q,\omega) \approx e^{-2W(q)} \left(R(q,\omega) + \frac{hq^2}{2\overline{m}} \frac{g(\omega)}{-\omega} \times \left(1 - \exp\left(\frac{h\omega}{k_BT}\right) \right)^{-1} \right).$$
(S2)

If two measurements at different temperatures are done, preferentially one at very low temperature and one at a sufficiently low temperature that other dynamical processes are absent, a system of two linear equations can be established from which the vibrational density of states $g(\omega)$ and the resolution of the instrument $R(q,\omega)$ can be obtained.

A problem often observed in complex organic materials [2,3] is that this results in a $g(\omega)/\omega^2$ which is not flat for small energy transfers as expected from the Debye model of sound waves. Rather it increases strongly towards the elastic line. Although in principle this could be a strange feature of $g(\omega)$ we think that this is rather the consequence of residual quasielastic scattering (QENS) even at low temperatures. At the first glance this seems unlikely at a temperature as the 50 K used here because the activation energies involved would cause all dynamics but vibrations to be frozen on the time scale of neutron TOF spectroscopy. Nevertheless, to test this hypothesis, we used the rotation rate distribution model (RRDM) for the methyl group dynamics [4] because methyl groups are present in all materials studied here and their dynamics seems to be the most likely candidate for such an effect.

The total of elastic and quasielastic scattering from methyl group rotation can be written down as

$$S_{RRDM}(q,\omega) = exp^{[in]}(-2W(q))((1-f_{mob})\delta(\omega) + f_{mob}(A_0(q)\delta(\omega) + (1-A_0(q)\phi(\omega)))$$
(S3)

in the temperature range where the motion is hopping between three equivalent sites. f_{mob} is the fraction of hydrogen atoms located in methyl groups and $A_0(q)$ is the elastic incoherent structure factor (EISF) of the motion

$$A_0(q) = \frac{1}{3} \left(1 + 2 \frac{\sin(\sqrt{3} qr)}{\sqrt{3} qr} \right)$$
(S4)

where $\sqrt{3} r = 1.779$ Å is the jump distance fixed by the bond lengths and angles in a methyl group.

In the RRDM, the line shape $\phi(\omega)$ is obtained as an integral over a distribution of Lorentzians resulting from different activation energies of the methyl groups:

$$\phi(\omega) = \int_{0}^{\infty} \frac{1}{\pi \omega^{2} + \Gamma^{2}} \rho(\Gamma) d\Gamma$$
(S5)

In the RRDM, the line shape $\phi(\omega)$ is obtained as an integral over a distribution of Lorentzians resulting from different activation energies of the methyl groups:

$$\Gamma = \Gamma_0 exp\left(-\frac{E_A}{k_B T}\right) \tag{S6}$$

from the distribution of activation energies. The latter is usually assumed as Gaussian:

$$\rho(E_A) = \frac{1}{\sqrt{2\pi}\Delta E_A} exp\left(-\frac{\left(E_A - \bar{E}_A\right)^2}{2\Delta E_A^2}\right)$$
(S7)

Note that the resulting distribution $p(\Gamma)$ is 'log-normal'. This is a very broad distribution being the explanation for the surprising presence of QENS at low temperatures: Although the rate resulting from the average activation energy is much too high to be observed, there is enough intensity in the wings of the distribution to cause a discernible effect.

The complete fit function used for the test of RRDM is

$$S_{\text{obs}}(q,\omega) = R(q,\omega) \otimes \left(C_1 \exp\left(-C_2 q^2\right) \left(\exp\left(-\frac{\hbar\omega}{2k_{\text{B}}T}\right) S_{\text{RRDM}}(q,\omega) + \frac{\hbar\omega}{k_{B}T} \left(\exp\left(\frac{\hbar\omega}{k_{B}T}\right) - 1 \right)^{-1} \left(C_3 q^2 + C_4\right) \right) \right)$$
(S8)

The factor $\exp(-\hbar\omega/2k_{\rm B}T)$ is introduced to ensure detailed-balance also at low temperatures. The second term in the second-level parentheses is the vibrational contribution where constant $g(\omega)/\omega^2$ is assumed. C_4 takes care of a possible multiple scattering contribution to the vibrational scattering. The prefactor is the Debye-Waller factor for isotropic materials, C_2 being $\langle u^2 \rangle/3$ In the absence of multiple scattering and for correctly normalised spectra $C_1 = 1$. Indeed, the values found here are very close to one.

In addition, the mean activation energy E_A and its variance ΔE_A were fitted. Because of the 'compensation law' [5] the prefactor Γ_0 is strongly correlated with E_A and cannot be fitted independently; it was set to a typical value of $1 / 0.1 \text{ ps}^1$. So, the fit function contains six free parameters. Because of the assumption of Debye-like vibrational scattering the fit is restricted to $-0.4 \dots +0.4 \text{ meV}$. This is a compromise between staying away from the boson peak but still keeping enough data points outside the resolution. In q, the fit was restricted to the range 1.4 $\dots 2.2 \text{ Å}^{-1}$ to avoid too strong effects from multiple scattering. Under these restrictions about 750 data points are fitted simultaneously by the six parameters. As Figure 1 shows, the fit is surprisingly good. This is a strong argument for QENS being indeed the reason for the anomaly

¹ This is the more true here because S6 is only evaluated at one temperature leading to a complete correlation of E_A and Γ_0 . Therefore, the correction established here does not depend on the choice of Γ_0 at all. Nevertheless, the values of E_A in Table S1 depend (logarithmically) on the choice of Γ_0 .

usually found in the VDOS at low frequencies. At least it shows that QENS from methyl groups is a plausible explanation.



Figure S1: Time-of-flight inelastic neutron scattering data of exo-PNBSi fitted by the QENS-Debye model described in the text (red lines). The data are shown as measured at constant scattering angles $2\theta = 67.75^{\circ}$, 73.04° , 78.99° , 84.99° , 91.33° , 98.03° , 105.44° , 113.47° , and 122.32° (bottom to top). This corresponds to $q = 1.4 \dots 2.2 \text{ Å}^{-1}$ at the elastic position. The green vertical lines denote the energy transfer range in which the function was fitted.

The resulting activation energies and their variances are shown in Table 1. The values for exo-PNBSi are similar to those in other polymers (e.g. polyisoprene: $E/k_B=1170$ K, $\Delta E_A/k_B=353$ K [6]). For PTCNSi2g the variance is about a factor of two higher, and for PTCNSi1 both the average and the variance are a factor of two higher. But none of these values is completely unphysical. With regard to the comparison with literature values one also has to take into account that the latter are usually derived for the peak region of the E_A distribution while here only the low energy wing is relevant. Therefore, a strict agreement can only be expected if the Gaussian distribution for E_A is taken for granted.

	$E_{A/k_{\rm B}}$ [K]	$\Delta E_A/k_B [K]$
exo-PNBSi	851 ± 24	253 ± 13
PTCNSi1	1957 ± 79	1283 ± 76
PTCNSi2g	973 ± 22	686 ± 90

Table S1: Parameters of the activation energy distribution of the methyl group dynamics obtained from the QENS-Debye fits.

The QENS part of the fit function (8) was now used to remove this contribution from the data. The subsequent evaluation of $g(\omega)$ was done in the same way as for the raw data. Figure 2 shows the result for the three polymers studied here. In all cases the correction leads to a significant improvement of the quality of the VDOS obtained. For PTCMSi2g even the boson peak becomes visible as a maximum that was buried in the quasielastic wing before. Nevertheless, it is visible that the correction is not perfect and a faint increase towards the elastic line remains. This might be due to the fact that the actual distribution of activation energies is non-Gaussian. Indeed, other distributions have been proposed [7] But it is clear that just from the present data it would be difficult to fit further details as the skewness of the distribution.



Figure S2: VDOS correction for the three polynorbornenes studied here. The green curve shows the result of the one-phonon VDOS calculation if applied to the uncorrected data. The red curve shows the same after (partial) removal of the QENS contribution. The black curve is the final result after multiple scattering correction in addition. The central parts of the plots $(-0.15...+0.15 \text{ ps}^{-1} \text{ for exo-PNBSi and PTCNSi1}, -0.2...+0.2 \text{ ps}^{-1})$ are removed because the scatter of the corrected data is larger than the remaining values themselves in that region.

In comparison to the other polymers, PTCNSi2g is the most 'problematic' concerning this correction. From the raw data it clearly shows the largest QENS contribution. This is reflected in a 64% variance of the activation energies combined with a comparatively low value of the average. But there is also an apparent violation of detailed balance (which should lead to g(- ω)=g(ω)) visible close to the elastic line.

A second correction, applied to the VDOS data *after* their calculation, concerns multiple scattering. The presence of multiple scattering effects can be detected from the q dependence of the $g(\omega)$ values calculated using equation (2). Because it is a material property, $g(\omega)$ should be q-independent. In practice, the calculation always results in an apparently q-dependent

VDOS. The reason for this is that multiple scattering is more isotropic and the division by q^2 during the evaluation results in a contribution proportional to q^{-2} . Because most of the multiple scattering is elastic-inelastic and not inelastic-inelastic the spectral shape is roughly the same leading to an ansatz for the multiple-scattering-affected VDOS:

$$g_q(\omega) = g(\omega) \left(1 + \left(\frac{q^*}{q}\right)^2 \right)$$
(S9)

Here, q^* is the *q* value at which single and multiple scattering have the same weight. In order to determine it, the apparent VDOS was integrated in the range 0.5...5 meV for all *q* values considered (1.4 ... 2.2 Å⁻¹). The expected expression a(1+(q*/q)²) was fitted and subsequently, the g_q(ω) were corrected it dividing by 1+(q*/q)². The corrected spectra do not show a *q* dependence anymore and were averaged over all nine *q* values to give the final result shown as black curves in Figure S2.

Microporosity – The Boson Peak of PIM-1", Phys. Chem. Chem. Phys. 20 1355 (2018)

⁴ A. Chahid, A. Alegría, J. Colmenero: "Methyl Group Dynamics in Poly(viny1 methyl ether). A Rotation Rate Distribution Model", Macromolecules **27** 3282 (1994)

¹ S. W. Lovesey, Theory of Neutron Scattering from Condensed Matter, Oxford University, New York, 1987, vol. 1, p. 121.

² C. Krause, R. Zorn, F. Emmerling, J. Falkenhagen, B. Frick, P. Huber, A. Schönhals: "Vibrational Density of States of Triphenylene Based Discotic Liquid Crystals: Dependence on the Length of the Alkyl Chain", Phys. Chem. Chem. Phys., **16** 7324–7333 (2014)

³ R. Zorn, H. Yin, W. Lohstroh, W. Harrison, P. M. Budd, B. R. Pauw, M. Böhning, A. Schönhals:

[&]quot;Anomalies in the Low Frequency Vibrational Density of States for a Polymer with Intrinsic

⁵ P. Rüetschi "The Relation between Frequency Factor and Activation Energy (Compensation Law)", Z. Phys. Chem. **14** 277 (1958)

⁶ R. Zorn, B. Frick, L. J. Fetters: "Quasielastic neutron scattering study of the methyl group dynamics in polyisoprene", J. Chem. Phys. **116** 845–853 (2002)

⁷ A. J. Moreno, A. Alegría, J. Colmenero, M. Prager, H. Grimm, B. Frick: "Methyl group dynamics in glassy toluene: A neutron scattering study", J. Chem. Phys. **115** 8958 (2001)