Experimental report

13/11/2021

Proposal:	**6-04-285**	**Council:**	10/2020
Title:	Low temperature methyl group tunneling in polynorbornenes		
Research area:	Soft condensed matter		

This proposal is a new proposal

Main proposer:	**Andreas SCHOENHALS**
Experimental team:	Markus APPEL
Local contacts:	Markus APPEL

Samples: PTCNSi1, $C_{12}H_{20}Si$
PTCNSi2g, $C_{15}H_{28}Si$

Instrument	Requested days	Allocated days	From	To
IN16B Si 111 BATS	3	3	05/03/2021	08/03/2021

Abstract:

The methyl group tunneling in amorphous materials is still not completely understood although some investigations are present in the literature. Especially no investigations at cryogenic temperatures are known. Therefore, it is suggested to carry out neutron backscattering on IN16B with the BATS option at cryogenic temperatures on a polynorbornene for which an anomalous broadening of the low temperature resolution measured at 4 K by time-of-flight spectroscopy in comparison to a corresponding polynorbornene was observed. The data will be analyzed by the rotational rate distribution model for methyl group rotation extended by the scattering function for quantum tunneling.

EXPERIMENTAL REPORT

EXPERIMENT N°6-04-284 INSTRUMENT IN16B-BATS

DATES OF EXPERIMENT 04/03/2021-08/03/2021

TITLE

Low temperature methyl group tunneling in polynorbornenes

EXPERIMENTAL TEAM

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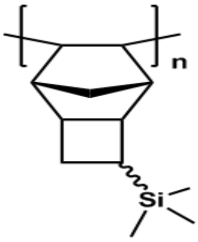
Date of report 13/11/2021

The rotational quantum tunneling of symmetric methyl groups (MG) is a well-known effect for crystalline systems. Inelastic neutron scattering is, besides NMR methods or specific heat capacity measurements, a tool to investigate the rotational tunneling of MGs directly. One must note that the size of the tunnel splitting is highly sensitive to both the strength and the shape of the rotational potential and therefore to structural disorder. Sharp tunneling lines are observed for crystals by inelastic neutron scattering at low temperatures (T<50 K). For amorphous systems a distribution of the tunnel splitting is expected due to the distribution of local environments.

Quantum molecular motions are discussed for amorphous materials like polymers since a long time. There is evidence from NMR measurements that the MGs in poly(vinyl acetate) (PVAC) can be active down to low temperatures [1]. Colmenero et al. reported a direct observation of MG tunneling for PVAC employing neutron backscattering [2]. Quantum motions of MGs are also reported for glassy toluene [3]. It is worth noting that the observation of quantum tunneling of MGs was observed by neutron scattering at relatively low energy resolutions. This is due to the activation energy for MG rotation usually leading to a ground state tunnel splitting of ca. 1.5 μeV. It is further worth noting that till now no neutron scattering investigations on amorphous materials at temperatures below 2 K are known.

PTCNSi1 and PTCNSi2g (see Figure 1 and 2) are high performance polynorbornenes bearing an intrinsic microporosity which can be employed in gas separation membranes. It was suggested to investigate the rotational quantum tunneling of the methyl groups of PTCNSi2g at cryogenic temperatures at IN16B in BATS configuration. A comparison of the spectra measured for PTCNSi2g is made with data measured for PTCNSi1 at ca. 2 K.

Figure 3 compares dynamic structure factor for PTCNSi2g measured at a programmed temperature of 40 mK for 110 min at a resolution of 5.6 μeV and an offset of 40 μeV. Compared to the spectra measured for PTCNSi1 the data for PTCNSi2g show a tremendous broadening which indicates quantum tunneling. The BATS measurements show this effect more unambiguously than in the experiments on NEAT and standard IN16B. All data are under further analysis by the rotational rate distribution model for methyl group rotation extended by the scattering function for quantum tunneling [3]. A distribution of tunneling frequencies will be considered.



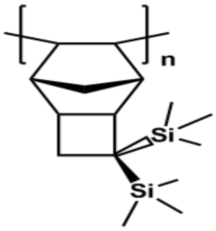


Fig. 1: Chemical structure of PTCNSi1.

Fig. 2: Chemical structure of PTCNSi2g.

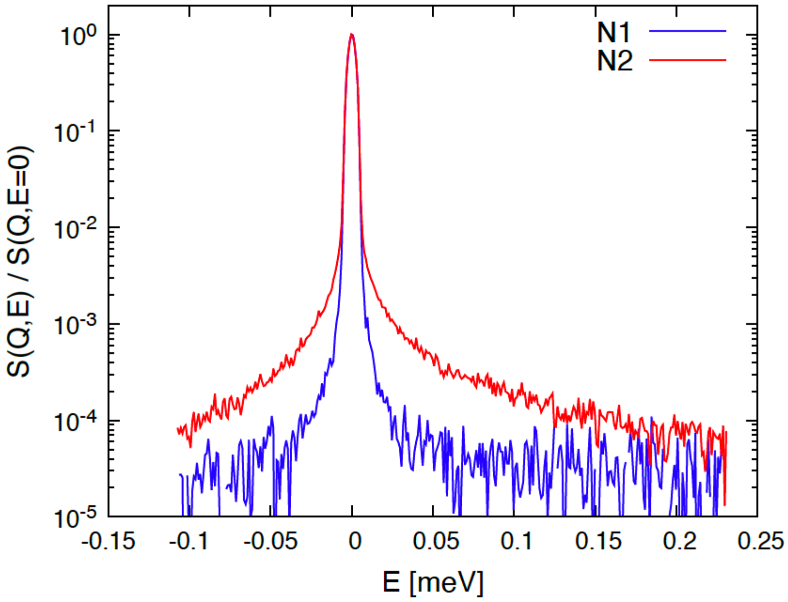


Fig. 3: Dynamic structure factor versus energy transfer measured for PTCNSi2g (red, programmed temperature 40 mK) and PTCNSi1 (blue, temperature 2 K). The data were averaged over all detectors.

[1] M. J. R. Hoch et al. Macromolecules 4 (1971) 712

[2] J. Colmenero et al. Phys. Rev. Letters 80 (1998) 2350

[3] A. J. Moreno et al. J. Chem. Phys. 115 (2001) 8958;