Experimental report

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Proposal: **9-11-2121** **Council:** 4/2023

Title: Can the topological transition of vitrimers be observed in a neutron scattering scan?

Research area: Soft condensed matter

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Samples: Polyisoprene
vitrimer

Instrument	Requested days	Allocated days	From	To
IN16B	2	2	28/02/2024	01/03/2024

Abstract:

Vitrimers are 3D-networks that can change their topology through bond exchange reactions, which are thermally activated. Vitrimeric polymers are not only scientifically exciting but also constitute promising sustainable materials with thermoset-like properties and end-of-life reprocessability. As the glass-transition, the topological transition associated to the restructuration of the dynamic network in vitrimers is not an actual transition but a crossover range, and its characteristic temperature Tv depends on the cooling-heating rate. As far as we know, until now Tv has been mainly determined by mechanical or thermal expansion methods. On the other hand, microscopic finger-prints of the glass transition Tg in glass-forming polymers ¿usually determined by DSC-- can clearly be observed in a neutron elastic scan. With these experiments (elastic and inelastic scans on protonated samples), we want to discern whether the topological transition in vitrimers has, as the glass transition, a reflection in the atomic (H) displacements as directly monitored by neutrons.

Can the topological transition of vitrimers be observed in a neutron scattering scan?

Three model vitrimers based on well-defined polyisoprene chains (PI) with different molecular weights were investigated. The detailed synthesis and molecular characterization of precursors and final vitrimers is given in Ref. [1]. The samples were synthesized with the stoichiometry corresponding to a small excess (about 5%) of primary amines, to facilitate bond exchange reactions. The structural, dielectric and thermal characterization was reported in Refs. [2,3]. The more relevant characteristics are summarized in Table 1. Figure 1 shows SAXS results on the vitrimer samples investigated, which present prepeaks related with the self-assembled crosslikers. As reference, a 'regular' high-molecular weight PI sample was also investigated (Tg=205K).

Sample	Mn/kDa	PDI	Tg/K
PI-vit-2k	2.7	1.05	221.0
PI-vit-6k	6.3	1.04	216.5
PI-vit-11k	11.3	1.04	217.0

Flat Aluminum sampleholders were used, with thicknesses of the sample films of 0.15mm.

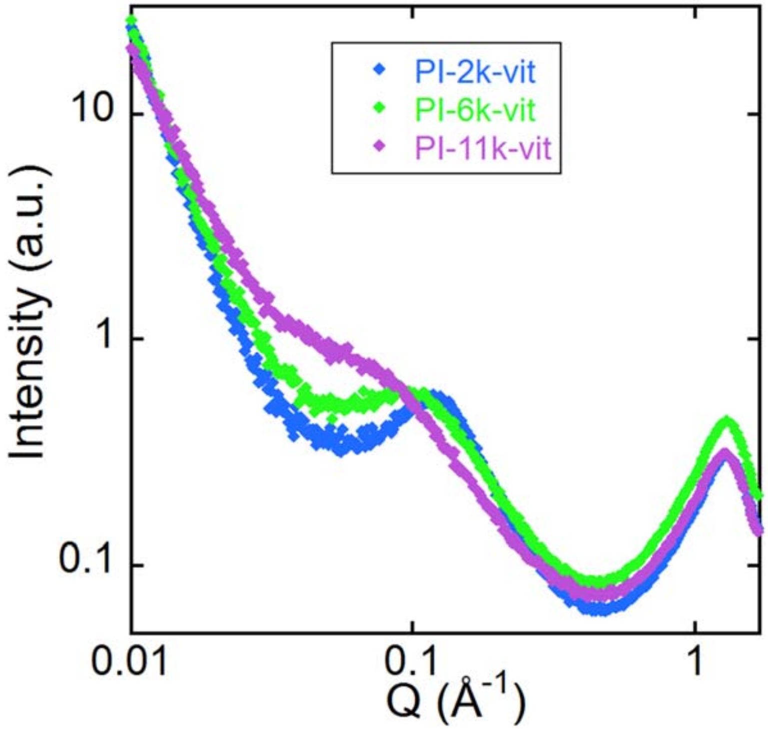

Figure 1: SAXS results at RT on the vitrimers investigated. The peak around 0.1 A-1 is due to correlations between clusters of cross-linkers

Samples were first heated up to 380K, kept at such temperature for 1 hour and then cooled down to 2K. Then, after stabilizing the sample temperature for 10 minutes, a controlled heating ramp with a rate of 0.8K/min was programmed. The scattered intensity was continuously recorded, alternating measurements of the elastic scattering (FWHM=0.75μeV) for 30 s, and of the inelastic intensity (ΔE=3μeV) for 90 s, during the ramps. Empty cell signal was also determined in the entire temperature range investigated. Vanadium was used for detector efficiency calibration.

Figure 2 shows the results obtained on the different samples investigated (sum over all detectors). At temperatures below approx. 200K all results are practically indistinguishable. They reflect the presence of vibrational contributions and methyl group dynamics, that are obviously not affected by the vitrimeric character of the samples. At higher temperatures, the intensities reveal the typical features of a glass transition. In fact, the shift of the bending point of the elastic intensity and the maximum of the inelastic intensity is correlated with that of the calorimetric grass transition (see table). The network induces constraints to the polymer motions that cause an increase in the glass-transition temperature. This effect is the more pronounced the higher the cross-linker concentration (i. e., the lower the molecular weight of the polymer chains). However, no evidence for a further transition occurring in the supercooled liquid state --the topological transition-- is found in the results. We recall that signatures of such a transition are present in the temperature dependence of the inter-cluster distance as monitored by SAXS, in the range 270K…310K [2]. The vitrimeric transition, involving the onset of rearrangements of the network due to the activation of dynamic bond exchange, might not be found at the relatively local length scales probed by IN16B.

REFERENCES

[1] S. Bhaumik, K. Ntetsikas, N. Patelis, K. Peponaki, Katerina, D. Vlassopoulos and N. Hadjichristidis, Macromolecules 57, 1751 (2024)

[2] A. Arbe, A. Alegría, J. Colmenero, S. Bhaumik, K. Ntetsikas and N. Hadjichristidis, ACS Macro Letters 12, 1595 (2023)

[3] A. Alegría, A. Arbe, J. Colmenero, S. Bhaumik, K. Ntetsikas and N. Hadjichristidis, Macromolecules 57, 5639 (2024)

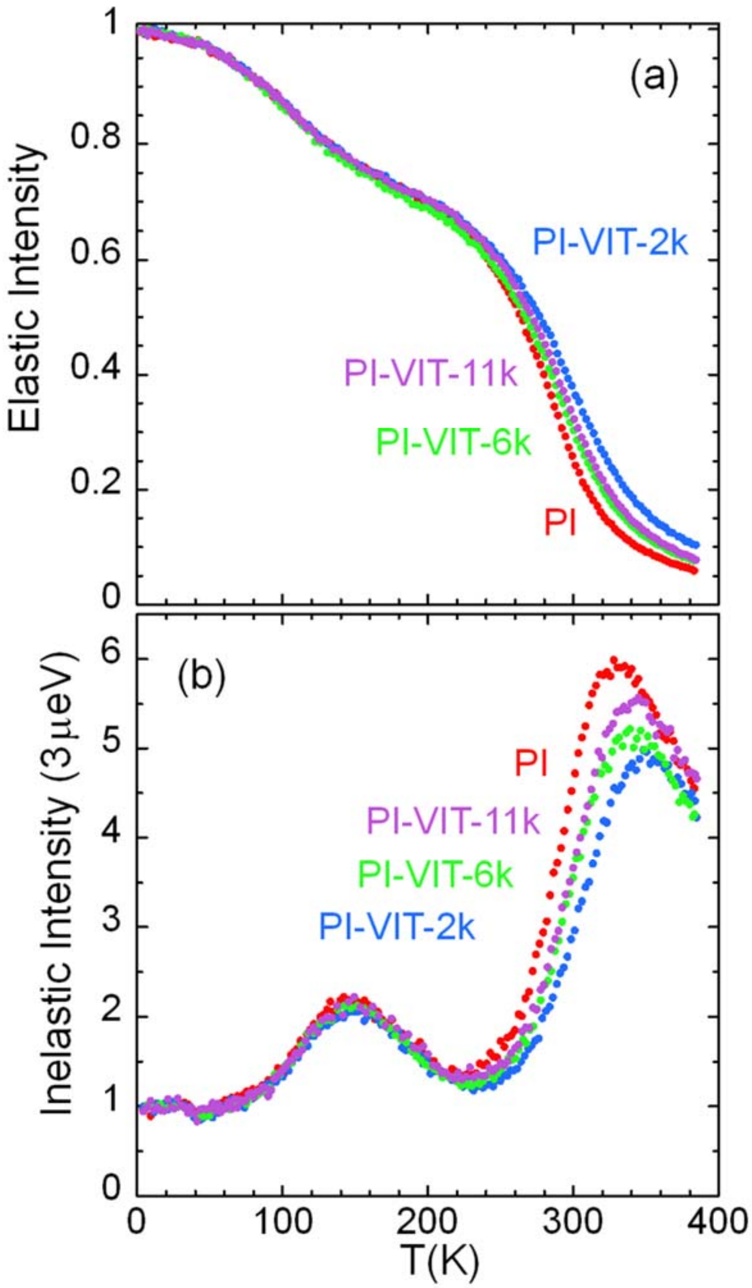

Figure 2: Temperature dependence of the elastic (a) and inelastic (b) intensities (summed over all detectors and normalized to the value at the minimum temperature) recorded during heating scans on the samples indicated.