Experimental report

16/10/2025

Proposal: **9-11-2230**

Council: 10/2024

Title: EFFECTS ON THE DYNAMICS IN CYANO-BASED POLYMERS AS HYGHLY POLAR MATERIALS: NEW INSIGHTS FOR ENERGY APPLICATIONS

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: Nitrile containing poly(tetrahydrofuran)-based copolymers

Instrument	Requested days	Allocated days	From	To
WASP	4	4	23/05/2025	27/05/2025
IN16B	4	0		

Abstract:

Lately, there has been a growing interest in the manipulation of individual polymer chains to produce macromolecular architectures, particularly in key areas such as organic electronics and energy-related applications. The focus has shifted towards single chain polymer nanoparticles (SCNPs), which have garnered significant attention due to their unique characteristics, including small size, softness, and internal segmentation. Polar polymers, in particular, are emerging as promising materials for various energy storage applications, exhibiting relatively high dielectric constants. This study aims to investigate the influence of the cyano group on the self-atomic (hydrogen) motions within a bulk system of P(THF-co- ECHCN). Additionally, we seek to explore how the presence of the cyano group impacts the copolymer composition and determine the effects of internal cross-links when preparing a bulk of SCNPs.

Effects on the Dynamics in Cyano-based Polymers as Highly Polar Materials: New Insights for Energy Applications

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In response to the growing demand for advanced polymer dielectrics in high-performance energy storage devices, particularly film capacitors, this study explores the influence of specific polar functional groups, nitrile (-CN), nitro ($-NO_2$), and trifluoromethyl ($-CF_3$), on the molecular dynamics of poly(tetrahydrofuran-*ran*-epichlorohydrin) (P(THF-*ran*-ECH)) copolymers. These functional groups were introduced through a post-functionalization strategy, enabling systematic tuning of the polymer's polarity and intermolecular interactions without altering the overall backbone structure. To elucidate how these chemical modifications affect segmental mobility and local relaxation processes, quasielastic neutron scattering (QENS) measurements were performed over a wide temperature range, providing insight into the time and length scales of molecular motion. Complementary thermal and dielectric characterizations were conducted to correlate dynamic parameters with macroscopic dielectric behavior.

Building upon our previous investigations derived from P(THF-*ran*-ECH), including single-chain nanoparticles (SCNPs) and all-polymer nanocomposites [1-3], the present work focuses on systematically tuning the polarity of this copolymer through controlled chemical modification. To this end, polar functional groups such as nitrile (-CN, 3.9 D) and nitro ($-NO_2$, 3.6 D) were covalently incorporated into the polymer backbone, enabling direct investigation of how specific dipolar substituents influence molecular dynamics and bulk dielectric performance. Functionalization was accomplished via a one-step nucleophilic substitution reaction using protonated linear copolymer precursors containing 27 mol% ECH units. The reaction employed thiophenol derivatives bearing the desired substituents and proceeded under the catalytic action of an organic base. This approach yielded a series of four copolymers, each differing only in the terminal group introduced: hydrogen (-H, reference), trifluoromethyl ($-CF_3$), nitrile (-CN), and nitro ($-NO_2$). All resulting polymers exhibited similar molecular weights (~30 kg mol^{-1}) and glass transition temperatures (T_g) within the range of 203-232 K, confirming that the backbone structure and overall chain flexibility remained largely preserved after modification.

QENS measurements were performed on the WASP high-intensity spin-echo spectrometer at the Institut Laue-Langevin (ILL, Grenoble, France) using an incident neutron wavelength of 6 Å. Experiments were conducted at four temperatures, 290 K, 320 K, 360 K, and 400 K, to probe the temperature dependence of the polymer chain dynamics across a broad dynamic range. The samples were carefully loaded into cylindrical aluminum holders, with sample thicknesses optimized to achieve approximately 90% neutron transmission, thereby minimizing multiple scattering effects.

Prior to measurement, the polymers were dried under vacuum to remove residual solvents and moisture.

Figure 1 presents a direct comparison of the QENS spectra recorded on the WASP spectrometer at a Q = 0.9 Å^{-1} for two representative temperatures. Figure 1a corresponds to data collected at 320 K, while Figure 1b shows the spectra obtained at 360 K. The solid lines in each panel represent fits to the experimental data using Kohlrausch-Williams-Watts (KWW) stretched exponential function, $S(Q,t) \propto \exp\left[-(t/\tau_s)^{\beta}\right]$, where the stretching exponent β was fixed at 0.5 as an initial approximation to account for the broad distribution of relaxation times typically observed in disordered polymeric systems.

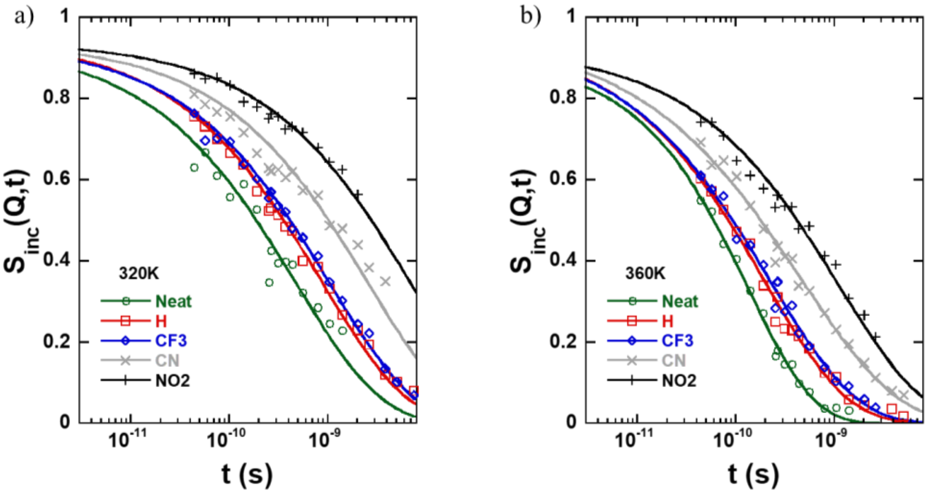

Figure 1. QENS spectra recorded on the WASP spectrometer at a Q = 0. 9 Å^{-1} at a) 320K and b) 360K. The solid lines represent fits to the data using the Kohlrausch-Williams-Watts (KWW) function, $S(Q,t) \propto \exp\left[-(t/\tau_s)^{\beta}\right]$, with the stretching exponent β fixed at 0.5 as an initial approximation.

The incorporation of highly polar functional groups leads to slower molecular dynamics, as clearly evidenced by the WASP experiments. In particular, the -CN and -NO_2 substituents induce a noticeable reduction in chain mobility, consistent with calorimetric analyses showing increased T_g values compared to both the reference polymer and samples bearing less polar groups such as -H or -CF_3. Additional dynamic measurements performed using the FOCUS time-of-flight spectrometer at SINQ further support these findings, and quantitative analysis of these results is currently in progress. Furthermore, dielectric spectroscopy data reveal a systematic slowdown of polymer dynamics with increasing dielectric constant of the functional groups, in full agreement with the trends observed by QENS.

References

[1] Maiz, J., Verde-Sesto, E., Asenjo-Sanz, I., Malo de Molina, P., Frick, B., Pomposo, J.A., Arbe, A. and Colmenero, J., 2021. Polymers, 13(14), 2316.

[2] Maiz, J., Verde-Sesto, E., Asenjo-Sanz, I., Mangin-Thro, L., Frick, B., Pomposo, J.A., Arbe, A. and Colmenero, J., 2022. Macromolecules, 55(6), 2320-2332.

[3] Verde-Sesto, E., Asenjo-Sanz, I., Juranyi, F., Pomposo, J.A., Maiz J., 2025. Journal of Colloid and Interface Science, 679, 785-797.