

Nanoscale mapping of composition and orientation in electrospun polymeric nanofibers loaded with carbon atomic wires

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Streszczenie

This study yields a comprehensive nanoscale investigation of the composition and molecular orientation of electrospun poly(methyl methacrylate) (PMMA) nanofibers containing halogen-terminated carbon atomic wires (CAWs), a finite-length analog of the carbyne construct. This is accomplished by conducting light-polarization-dependent experiments with advanced techniques such as atomic force microscopy-infrared spectroscopy (AFM-IR), optical photothermal infrared microscopy (O-PTIR), and hyperspectral photoluminescence (PL) microscopy. In PMMA nanofibers, AFM-IR reveals a remarkable, homogeneous uniaxial orientation of PMMA chains along the fiber axis, down to the ≈ 20 nm scale. Semi-quantitative analysis of IR dichroic ratios indicates a nearly orthogonal alignment ($\psi_{\text{avg}} \approx 79^\circ$) of the C = O dipole with respect to the nearly all-trans planar polymer backbone, consistent with expectations of the electrospinning process and in agreement with prior modeling of polymer chain dynamics. Congruous AFM-IR, O-PTIR, and hyperspectral PL data show that incorporation of CAWs into the PMMA nanofibers results in a peculiar compositional heterogeneity, with alternating 3 μm to 4 μm long PMMA-rich and CAW-rich regions across the fiber length. Notably, hyperspectral PL data reveal that CAWs preferentially align along the fiber axis, with sparse, 1.5 μm to 3 μm long domains displaying locally reduced or enhanced molecular orientation. We envision that the widely applicable approach used here will foster engineering of anisotropic nanostructures with advanced functionalities and complex compositions, laying the groundwork for future applications in nanoelectronics, photonics, and energy storage that demand anisotropic molecular orientation and composition.

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Carbyne, Electrospinning, Orientation, AFM-IR, O-PTIR, Hyperspectral Photoluminescence, Materials science, Nanoscience and technology, Optics and photonics

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