

Advances in Next-Generation Polyolefin Standard Reference Materials

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ABSTRACT

NIST’s approach to modernizing its synthetic polymer reference materials is to target precise and robust synthetic methods, making homogeneous standards that can be easily tailored to include desired chemistry, molar mass, and topography. This strategy aims to meet the increasing demand for novel standards that are relevant to advanced materials and with minimal development time. Here, an alternative approach to synthetic linear and branched polyethylenes has been developed using a commercial metathesis catalyst to generate polyolefins with low dispersity and sequence control, where the degree of alkyl branching and alkyl branching distribution are known. This process is adaptable to many branch lengths and varied chemistries as it only requires replacement of the monomer feedstock with the desired chemical functionality. The resulting materials are characterized using size-exclusion chromatography with tetra detection to measure the molar mass, molar mass distribution, and degree of short chain branching. In addition to their role as potential standard reference materials (SRMs), these polymers are also being applied to study the effect of branching on polymer chain thermodynamics at surfaces, and comparing experimental results to established theoretical models.

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1 INTRODUCTION

The ability to accurately measure polymer molar mass, molar mass distribution, and chemical and topological heterogeneities is paramount to making appropriate structure-property relationships between a material and its desired end-use. All polymers contain some degree of dispersity regarding molar mass. Depending on the chemical and architectural complexity of the polymer, other types of distributions can exist as well, such as chemical composition and short- and long- chain branching. Identifying and quantifying all species of chains present in the material and

the resulting impact on material properties is one of the lasting challenges of materials science, despite the rapid progress in polymer science that has occurred over the last 70 years. Several examples of these structure-property relationships are listed in Table 1 [1].

Macromolecular Property	Representative End-use Properties Affected
Molar mass	Elongation, tensile strength
Long chain branching	Shear strength, tack, peel, crystallinity
Short chain branching	Haze, stress-crack resistance, crystallinity
Architecture/Topology	Flow modification, diffusion, encapsulation
Tacticity	Crystallinity, anisotropy, solubility
Chemical Composition	Morphology, miscibility, solubility
Chemical Heterogeneity	Toughness, brittleness, biodegradability
Chemical composition vs. molar mass	elongation, tensile strength, brittleness, toughness, blending, plasticization
Block Sequence	Dielectric properties, reactivity, miscibility

Table 1: Types of macromolecular distributions and their effect on end-use properties of polymers. Reproduced in part from reference [1]. Please see the reference for full list of macromolecular properties and measurement methods.

Measurement of polymers often involves separating samples by fractionation through a porous, packed column, using either enthalpic interaction with a stationary phase (liquid chromatography) or entropic diffusion through a column (size exclusion chromatography (SEC)). SEC fractionates a sample by hydrodynamic size, where the eluting fractions are fully characterized by sensitive physical and chemical in-line detectors to measure the molar mass and the molar mass distribution (MMD). SEC is considered a relative measurement method, since calibration standards of known molar mass are required to calculate number average

(M_n) and mass average (M_w) molar mass of the sample. Absolute measurements to determine molar mass exist, such as membrane osmometry to measure M_n and multi-angle static light scattering to measure M_w . These measurements, however, have the disadvantage of long measurement times and larger uncertainties due to manual sample preparation. SEC offers rapid analysis of polymer molar mass with enhanced measurement precision over absolute methods and can even provide more information than absolute methods about the full MMD. Coupling of multi-angle light scattering detection to SEC has also provided the ability to determine “absolute” M_w from a separation, with the assumption that all injected analyte elutes. SEC has therefore become one of most heavily utilized and revolutionary measurements for industrial polymer research and development in the last half-century. Standards development organizations have recognized the need for relative measurements of molar mass and have developed documentary standards for multi-detector SEC to describe best practices for separation and analysis of polymers [2].

Polyolefins, or hydrocarbon polymers generated from petrochemical feedstocks, are the largest volume of plastics produced yearly, at over 130 million tons. The revolution of synthetic processes and novel metal-based catalysts over the last few decades have drastically improved the ability to tailor molar mass, dispersity, and degree of long- and short-chain branching into polyolefins. These capabilities have resulted in polymers with more finely-tunable material properties. To characterize these materials, in-line infrared detectors for SEC have been developed in order to quantify average chemical and branching composition of a polymer across its molar mass distribution curve by measuring methyl and methylene content of the eluting polymer. Standards representative of these complex chemistries and architectures are ultimately required to properly quantify the relationships between molecular structure, processing, and performance of these materials.

NIST’s current inventory of polyolefin SRMs were developed beginning in the 1970s to quantify molar mass and melt properties of linear polyethylene and are founded from a common parent material, SRM 1475A, a broad distribution linear polyethylene ($M_w = 52,000$ g/mol). By fractionating and recrystallizing batches of 1475A, NIST was able to produce six additional narrow MMD standards ranging from 6.28 kg/mol to 196 kg/mol for standards certified to measure intrinsic viscosity, M_n and M_w . These linear standards continue to provide calibration and measurement traceability to stakeholders in academia and industry today, but in time have become less useful to calibrate advanced commercial materials. Specifically, linear polyethylene is not representative of the solution behavior of branched polyolefins and cannot alone be an adequate calibration standard for SEC.

Short chain branching reference materials are available commercially, though in limited supply, and are generally copolymers of ethylene and an α -olefin. These materials,

similar to NIST polyethylene SRMs, were isolated by large-scale fractionation to isolate polymers by the degree of short-chain branching. However, fractionating does not address localized dispersity, where different species of the same solubility and hydrodynamic size can co-elute from a column. This phenomenon can potentially lead to masking of small species of non-homogeneous material in the calibration curve and alter the molar mass and solution property measurements.

2 NEXT-GENERATION POLYMER MASS STANDARDS

2.1 Redesigning the Synthetic Approach to Polyethylene

NIST is developing a new approach to modernizing its polyolefin reference materials, which entails the development of new polymer standards essentially correlated to a parent polyethylene species using the same or comparable synthetic processes. These precision polymers, made by controlled polymerization, would minimize uncertainty due to material heterogeneity that is a concern for standards that are fractionated from a heterogeneous mixture (Figure 1).

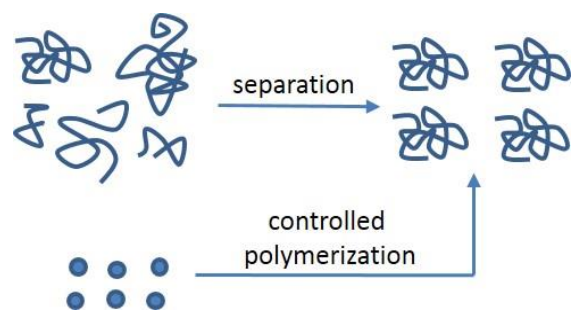


Figure 1: Depiction of homogeneous polymer standards achieved through fractionation (current methods) versus controlled polymerization (our studies).

NIST’s approach, shown in Figure 2A, is to use a highly strained cyclic alkene with a commercially available metathesis catalyst to prepare well-controlled polyalkenamers (I.) that can be hydrogenated post-polymerization to polyolefins (II.), a strategy first studied by the Hillmyer group [3]. This has the advantages of making the polymerization accessible to lower temperatures and pressures than commercialized polymerization of ethylene gas and making an initial polymer that is more easily processed and soluble in safer organic solvents. Control of the reaction is achieved by choosing catalyst and polymerization conditions amenable to a fast initiation rate so chain ends initiate simultaneously.

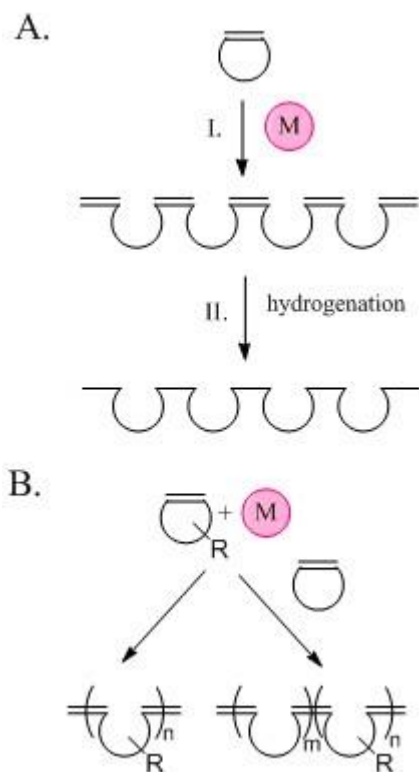


Figure 2: General reaction schemes of (A.) olefin metathesis to synthesize polyalkenamers (I.) with subsequent hydrogenation to polyethylene (II.) and (B.) polymerization of substituted cyclic olefins to generate idealized branched homo- and co-polymers.

2.2 Incorporating Branching and Functionality

The benefit of using a highly active alkylidene catalyst to make polyethylene is that similar polyolefins that incorporate branches and additional functional groups can be easily synthesized by changing the monomer feedstock without altering reaction conditions overall (Figure 2B). Current work at NIST has focused on the incorporation of alkyl branches by careful placement of the alkyl substitution on the ring to take advantage of steric interaction between monomer and the catalyst, and perfect regioregular control of the polyalkenamers was achieved [4]. This ideal head-to-tail addition of monomer places the branch point at a fixed interval along the backbone, yielding an absolute branch frequency and branch length. This material can then be tested as a prototype for a new standard reference material.

2.3 Testing of Linear and Branched Polyethylene Standards

This homogeneous material will undergo extensive testing to quantify molar mass and MMD using both absolute

(multi-angle static light scattering) and relative methods (SEC). These results will be directly compared to SRMs 1484A and 1475A, linear polyethylenes in the same molar mass range, but with varying degrees of dispersity. This comparison ensures that the candidate polyethylene provides equivalent molar mass calibration to these standards, so they may be discontinued once the new SRM is released.

Furthermore, the majority of NIST standards certify either M_n or M_w , which represent only the first and second moments of the molar mass distribution and are not fully descriptive of all molar masses and associated error throughout the entire distribution curve. Analysis of these new standards must address uncertainty across the entire MMD curve.

SEC testing of the linear and branched standards will utilize tetra-detection, including differential refractive index, infrared spectroscopy, viscometry, and multi-angle light scattering, to quantify molar mass distribution and degree of alkyl branching and compare to existing NIST polyethylene standards. The synergistic combination of physical detectors used will also permit measurement of polymer conformational constants, such as the contraction ratio (mean squared radius of a branched versus linear polymer) or the fractal dimension to provide valuable information to NIST customers in addition to certified molar mass values.

3 APPLICATIONS OF ADVANCED POLYOLEFIN MATERIALS

3.1 End-functionalized Polyolefins for Functional Surfaces

The controlled synthesis of polyalkenamers also is conducive to end-functionalization by reaction quenching with a modified alkene. This allows for reactions of the chain end with a reactive moiety immobilized on a surface. NIST is currently studying grafting of polyalkenamers to a surface before subsequent hydrogenation as a way to stealthily make polyethylene “brush” surfaces under mild solvent conditions, which has not been previously demonstrated. Recent theoretical studies [5] have used Scheutjens-Fleer self-consistent theory models to account for the impact of branching on the conformation entropy loss in polymer brushes in solvents of varying quality. Our studies on linear and branched polyethylenes grafted to the surface will permit experimental testing of that theory as well as permit study of solvent and surface interactions of branched polyolefins near an interface, similar to other work done previously on linear, glassy polymers [6,7].

3.2 Analysis of Asphaltenes

Asphaltenes are crude oil byproducts that can drastically modify crude viscosity and are largely responsible for the blockage of refinery pipes. The molar mass, MMD, and structure of asphaltenes has not been well-established due to the low critical nano-aggregation concentration (CNAC) observed in organic solvents at low temperatures [8]. Preliminary studies of an asphaltene sample collected indicates a high degree of branching at approximately 150 methyl groups per 1000 carbons, consistent across the molar mass distribution. Concentration studies are underway to determine the CNAC concentration of the asphaltene at 160 °C in 1,2,4-trichlorobenzene to determine accurate solubility conditions for quantifying the molar mass, MMD, and degree of long and short chain branching of the non-aggregated species.

4 CONCLUSIONS

NIST's development of next-generation polyolefin standards is aimed at bridging the gap between existing needs for polyethylene molar mass standards and the immediate industrial need for representative branched polyolefin standards. This approach establishes a systematic process to develop new polyolefin standards with control of monomer molar mass and structure. This infrastructure will ensure that NIST products continue to enable innovation at the forefront of materials science and technology, and provide a manufacturing route to quickly adapt new standards and provide traceable measurements to our stakeholders. This will ensure measurement accuracy remains as high for emerging polymers as the commodity materials that have been characterized for decades.

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