

Bottom Up Approaches to Improved Polyolefin Measurements

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Abstract

As a class of materials, polyolefins remain the largest production volume polymer in the world, as well as a highly desirable medium from which to engineer high performance and advanced properties for new applications. After decades of research, there are still major fundamental challenges to understanding the relationships between molecular structure, processing, morphology, and (ultimately) performance of these polymers. In two areas – surface adsorption for separation methods and melt crystallization – new tools and major advances in metrology are fueling a renewal of basic research into polyolefin characterization. Several approaches to these two problems, from theory and calculation to experimental models to elucidate each of these critical physical phenomena are undergoing current study at NIST.

Introduction

A major challenge in the measurement of polyolefins is being able to understand and quantify polyolefin behavior at the onset of a process. Very small changes in initial polymer orientation and interaction energy with the environment can shape the final state of the material. Accurate determination of the kinetics and thermodynamics of these changes is therefore critical to fully understanding polymer structure/property relationships. This knowledge gap is evident in the study of early polymer adsorption and crystallization processes. Polymer adsorption onto a surface is moderated by the equilibrium between polymer solvation near the surface and surface interaction energy. Crystallization of polyolefins is dictated by the nucleating structure in crystallization kinetics, which are often difficult to measure. Therein, our studies have approached the early polymer solvation and crystallization processes from two different angles – computational models that weigh included information for efficient simulation, and experimental models that use sensitive spectroscopic measurements to measure chain interactions. We will present current experimental and computational approaches at NIST to address polymer crystallization and

solvation from first principles and elucidate these processes from the bottom up.

Surface Adsorption for Polymer Separations

The onset of polyolefin adsorption at surfaces requires thorough knowledge of the thermodynamics of the polymer/solvent/surface interface and has important applications in composite compatibility and in optimizing methods for polymer separations, where the interacting surface is often a small particle. These are challenging measurements, as the particle surface is often rough and non-spherical, and the polymer near the surface is highly concentrated and not in its native random coil configuration. Difficulties in heterogeneous surfaces and concentrated polymers are each addressed through novel approaches to computational and experimental models, respectively.

Progress in understanding, quantifying and predicting properties of complex shaped particles, polymers, and composites at NIST has been achieved through a decade of combination of theoretical, computational and experimental efforts. In particular, the development of algorithms and computational programs such as ZENO and advances in the DiMarzio-Rubin transfer matrix formalismⁱ can provide precise calculations of polymeric-based material properties faster and in greater detail than prior computational tools. ZENO is a path-integral calculator that allows for precise computations of intrinsic and structural properties of polymer and particles having complex shapes.^{ii,iii} These calculations can then be used to determine classical polymer composite properties, which are influenced by the particle surface interaction, particle shape, and property contrasts between particle and polymer matrix. The transfer matrix formalism accounts for local structure and enumerates the possible states of the material represented within a discrete lattice-type model. Each lattice site is weighted within the fixed probability matrix to adjust interaction energy and calculate thermodynamic properties of a confined polymer. This method permits a more realistic representation of the polymer/surface interface as complexity in the surface and polymer can be added to the model; this is evident in recent expansions of matrix theory that include additional lattice dimensions and

heterogeneous boundary shapes and interaction energies.^{iv} Specifically, calculations of surface lattice sites with heterogeneous interaction energies show a decrease in the phase transition temperature (critical condition) of an adsorbing polymer chain. This finding signifies that chemical heterogeneity at the surface requires greater binding strength for a polymer chain to adsorb. Recent method developments at NIST have focused on including molecular subunits of each monomer to account for non-linear and rigid chemical structures.^v Models of individual monomers are built by forcing sequential steps in specific directions along lattice paths. A semi-flexible chain structure can also be studied by a “sub-matrix” approach that carries the history of the previous rigid monomer’s direction and employs energetic barriers for specific future directions. As a result, this enables the analysis of the impact of more realistic structure and composition on critical conditions. Ultimately, matrices that can incorporate the most realistic picture of the adsorption will produce the most accurate partition coefficient between adsorbed and free polymer chains, resulting in better prediction of chromatographic separation modes such as liquid-adsorption, size-exclusion, and critical-condition chromatography.

Solvent quality of polymer chains in proximity to a surface also mediates affinity of the polymer to adsorb to a surface or remain in solution. We have developed an experimental model to approximate the near surface condition of an adsorbing chain and measure differences in solvation thermodynamics at high polymer volume fractions. The model uses vapor phase swelling of end-tethered polymer chains, or brushes, swollen by different organic vapors at known concentrations. X-ray reflectivity measurements of swollen polymer film thicknesses and scattering length densities were used to calculate the polymer-solvent interaction parameter of the confined film. As a proof of concept, this system was first studied using poly(methyl methacrylate) (PMMA) with organic solvents to study confined solvation at ambient temperature. The x-ray reflectivity curves for the PMMA brushes vapor swollen with organic solvents are shown in Figure 1a; the increase in the number of fringes is indicative of the thickness increase of the film. An initial probe of the PMMA brush with different saturated solvent vapors revealed that solvation thermodynamics of the brush does not follow the Flory solution model (lines in Figure 1b), as solvents with a similar solution Flory-Huggins interaction parameter (χ) gave large changes in the thickness swelling ratio α , relative to the dry state (Figure 1b).^{vi} Consideration of the differences in molar volume of the organic solvents did not improve agreement with theory.

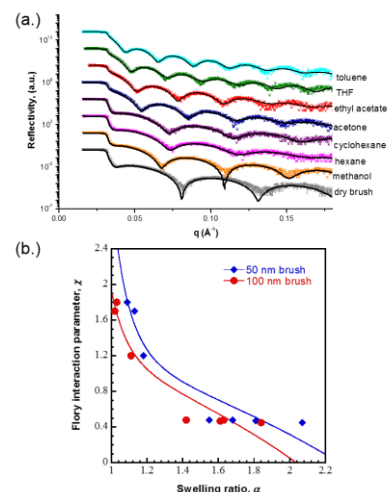


Figure 1. X-ray reflectivity curves of poly(methyl methacrylate) brush swollen with various organic solvents. (b.) Comparison of literature χ parameter with thickness swelling ratio α (swollen/dry) for a representative 50 nm and 100 nm brush trial, showing poor agreement of data with existing theory.^{vi}

The experiment was then repeated by using acetone and systematically varying the vapor concentration to probe χ over a range of activities from the dry state to saturation (activity of 1). The χ values of the brush are greater than solution value ($\chi_{\text{brush}} = 0.6 \pm 0.1$; $\chi_{\text{sol}} = 0.46$)[‡] and decrease with increasing activity, indicating that the solvent quality is concentration dependent and improves closer to brush saturation. We hypothesize the observed decrease in solvent quality (i.e. higher χ) of the concentrated polymer at the surface, relative to dilute solution, will help drive surface adsorption, especially at high volume fractions of polymer. Concentration dependence of χ is especially critical when considering separation processes for polyolefin copolymers such as CRYSTAF and TREF. We are currently adopting the experiment to accommodate high temperature dissolution of polyolefins and to study solvation of linear and branched chains near structured carbon surfaces.

Advances in Quantifying Melt Crystallization

Nucleation and early stage crystallization dictate the final structure, processability, and mechanical properties of a semi-crystalline polyolefin. Much is still unknown about how polymer crystals form for both super-cooled and isothermal crystallization processes. NIST is studying the onset of both crystallization types through simulations and experiments, respectively.

[‡] Represented uncertainty is one standard deviation of the data.

Early stage nucleation of crystals from supercooled quenching of the melt are on the scale of a few nanometers in size with induction periods on a nanosecond scale. This brief window makes analytical measurement of these phenomena impossible with current technology, making simulation an ideal tool to probe crystallization kinetics. On the nanometer scale, the united atom model (UA) can accommodate the details of both bonded and non-bonded interactions, but cannot be extended to the micron-scale or industrially relevant systems using a reasonable amount of computational resources. New work at NIST generates a novel coarse-grain (CG) model that incorporates two UA sites per one CG site. This approach allows for UA level detail to inform the CG model through parameterization of non-bonded interactions with multiscale CG and bond length and angle information through iterative Boltzmann inversion, respectively. This model can address longer hydrocarbons and larger chain sampling to model interactions more relevant to polyethylene than short chain aliphatic compounds, demonstrated here by using a system of 60 chains of *n*-pentacontane (C 150) melted at 580 K (306.85 °C) and quenched to 280 K (6.85 °C). Results of the CG system are highly quantitative with UA simulations at equilibrium conditions of crystallization for both nucleation size and for the elongated structure of individual chains (Figure 2). Due to the absence of an induction period in the CG model, which is usually present in UA, the melting temperature and crystallization rate of *n*-pentacontane is higher for CG than for UA model, although the trends of both models are qualitatively consistent.

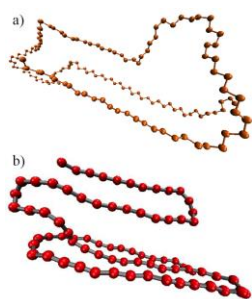


Figure 2. A single polyethylene chain after crystallization. Graph (a) corresponds to the united atom (UA) system and graph (b) corresponds to the coarse-grain (CG) system.^{vii}

Complementary experimental work on isothermal crystallization of polyolefins has used Raman spectroscopy to distinguish local conformational states from orthorhombic crystals at a concentration of a few weight percent. Raman can determine relative concentrations of alkyl stretching, twisting, and bending modes that can be utilized to determine interchain and intrachain structures of the material. The transition

mechanism of polyolefins from molten to semi-crystalline phase is highly debated and information about pre-crystalline structure can provide useful information about early polymer crystallization kinetics. Elongated chain conformations that are not part of the orthorhombic crystal, known as non-crystalline consecutive trans (NCCT) segments are of particular interest, as their concentration and distribution within the melt can enhance knowledge of chain dynamics during this induction period.

Crystallization of a linear polyethylene (NIST SRM 1475, nominal weight average molecular mass, (M_w) 53,000 g/mol) from the melt was measured by pressing a disk of the standard in a Linkam shear cell to a thickness 700 μm at 155 °C. Backscattered laser light from the sample is collected for Raman measurements, and transmitted light is collected to calculate turbidity and light depolarization. Measurements are performed during an isothermal crystallization wherein the sample is held at 130 °C after cooling from the melt temperature. Raman bands indicative of various modes of interaction for the melt and semi-crystalline state are shown in Figure 3a. Raman intensity for all spectra were scaled by the total integrated intensity in the CH_2 twisting region. The spectra were analyzed using the method described by Migler *et al.*, using normalized intensities of peaks representing the mass fractions of amorphous phase regions (1304 cm^{-1}), consecutive trans chain segments (1296 cm^{-1}), and crystalline phase segments (1415 cm^{-1}).^{viii} This measurement assumes a three state model; the polyethylene can only exist as amorphous, crystalline or NCCT chain segments. The resulting mass fractions of all segments determined from Raman data are shown as a function of time after quench in Figure 3b. Some NCCT segments are present at the start of quenching in the predominately amorphous PE. Additional NCCT clusters form in conjunction with orthorhombic crystals at the beginning of polyethylene crystallization.

Measurement of turbidity and depolarization transmission taken simultaneously with the Raman data suggest crystallization measurement sensitivity is greater than Raman as crystalline regions were detected at mass fractions of approximately 0.01. Turbidity measurements indicate clusters forming pre-crystallization that are not homogeneously distributed through the material. Localized alignment of chains is also observed simultaneously from depolarized transmission measurements. This observation is due to nucleating of NCCT pre-crystalline domains from the melt state. This phenomenon can potentially add value in ultimately determining the kinetic route of crystallization and determining the structure of nucleation crystals.

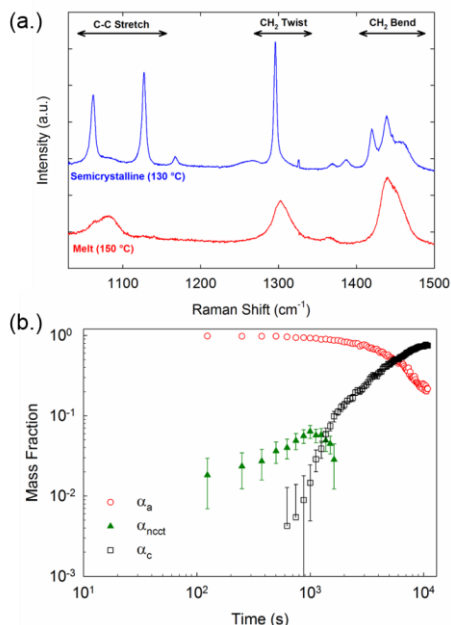


Figure 3. (a.) Typical Raman spectra of high-density polyethylene in the semi-crystalline state ($T = 130\text{ }^{\circ}\text{C}$) and melt phase ($T = 150\text{ }^{\circ}\text{C}$). The curves are scaled by the integrated intensity of the CH_2 twist region. (b) Evolution of the mass fraction of chain segments in the orthorhombic crystalline, the amorphous, and the non-crystalline consecutive trans (NCCT) states for HDPE following the 155°C to $128\text{ }^{\circ}\text{C}$ temperature quench.^{viii}

Conclusions

Sensitive scattering measurements such as Raman and x-ray reflectivity can be used to determine small compositional changes in polymer melts and thin films, as demonstrated in the measurements of low concentrations of pre-crystalline NCCTs in a polyolefin melt and organic solvent in a confined polymer thin film. Theoretical calculations can provide useful information about chain interactions on a finer scale than analytical instrumentation is capable of measuring. The use of theoretical and experimental models to measure subtle changes in polymer structure and composition will continue to be mutually beneficial to improve methodologies. This synergistic approach will be necessary in fundamental polyolefin research moving forward, as subtle changes in heterogeneous nucleation and complex branching architectures will affect multiple material properties. A systematic approach is required to improve materials design by understanding the intricacies of structure-property relationships and efficiently tailor new plastics for desired end-use properties. At NIST, it will be critical to inform design of the 21st century measurement technologies and reference materials necessary to support application of these materials.

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