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Processing Pathways Decide Polymer Properties at the Molecular Level

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ABSTRACT: Conditions of rapid processing often drive polymers to adopt nonequilibrium molecular conformations, which, in turn, can give rise to structural, dynamical, and mechanical properties that are significantly different from those in thermodynamic equilibrium. However, despite the possibility to control the desired nonequilibrium properties of polymers, a rigorous microscopic understanding of the processing-property relations is currently lacking. In an attempt to stimulate progress along this topical direction, we focus here on three prototypical and apparently different cases: spin-coated polymer films, rapidly drawn polymer fibers, and sheared polymer melts. Inspired by the presence of



common observations in the chosen cases, we search for order parameters as, for example, topological correlations and heterogeneities, which may allow characterizing the processing-induced behavior of polymers. We highlight that such approaches, necessitating concerted efforts from theory, simulations, and experiments, can provide a profound understanding leading to predictable and tunable properties of polymers.

INTRODUCTION

Polymers are an important class of materials with an ever-growing market.^{1,2} Their low cost, ease of processing, and broadly tunable properties are key reasons underlying their tremendous applicability, ranging from ordinary household items and packaging materials to high-tech fibers, medical devices, and wearable electronics. For most purposes, and most fabrication protocols, polymers are processed at rates much higher than the inverse of the equilibration time, i.e., the

reptation time.³⁻⁷ While the reptation time might be the longest relaxation time of individual entangled polymers, collective behavior and structure formation processes may involve time scales that are orders of magnitude longer. As a consequence, polymers (in melts and in solutions) often fail to

Received: June 11, 2019 Revised: August 7, 2019 equilibrate on the time scale of a typical processing experiment, causing the macromolecules to freeze into nonequilibrium conformations. For example, rapid quenching can effectively reduce the rotational degrees of freedom of polymer chains; this, in turn, can give rise to structural, dynamical, and mechanical material properties that differ strongly from those in thermodynamic equilibrium. Nonequilibrium processing, i.e., processing under conditions that do not allow for equilibration, can thus offer a practical means to extend the range of available properties for a given material composition, holding enormous application potential for the development of novel material functionalities. However, despite the exciting possibility to control the molecular configuration space and resultant material properties directly by the processing protocol, a rigorous understanding of the processing-property relations of polymers is still lacking.

Recent experiments,⁴⁻³⁶ reflecting conditions also relevant in industrial processing of polymers, provide intriguing observations, which add to the feasibility of designing macroscopic properties of polymers via nonequilibrium processing: (1) The extent of deviations from equilibrium conformations³⁷ increases with increasing processing rates, implying that the nonequilibrium nature of the material can be directly controlled by the processing time scale. (2) After processing, the system tends to attain a conformation that minimizes the free energy. However, this equilibration kinetics is often so slow that one can harness the desired nonequilibrium deviation over time scales longer than those of technological interest. Following such strategies, it is thus possible to tune properties such as mechanical strength,^{10–17} thermal expansion,^{23,27} thermal conductivity,³⁵ and viscosity^{10,13,15} by designing appropriate nonequilibrium processing protocols. (3) The above observations hold true for various geometries, ranging from bulk to nanoconfined systems. Importantly, such processing-induced nonequilibrium conformations have also resulted in novel applications. For example, polyethylene fibers composed of highly stretched molecules, whose conformations strongly deviate from those at equilibrium, show extremely high mechanical strength, enabling various uses ranging from bulletproof vests to cables for towing ships.^{4,34} Despite such enormous application potential, the current state-of-the-art relies on empirical relations for obtaining desired properties. In order to controllably target specific material structures and functionalities, new concepts must be developed that directly relate processing protocols to the molecular nonequilibrium conformations and resultant macroscopic polymer properties.

The purpose of this article is to guide and stimulate discussion on the design, synthesis, processing, and characterization of novel polymeric materials. In particular, our longterm goal is to generate a fundamental understanding providing answers to the following questions: (1) What are the relevant molecular parameters that describe the nonequilibrium state of a processed material? (2) How do processing conditions affect material properties; that is, how does the macromolecular structure affect the magnitude and lifetime of deviations in chain conformations? (3) How can we design materials with desired properties via nonequilibrium processing pathways? To address these questions, among the virtually endless number of nonequilibrium processing pathways, we focus here on three prototypical and apparently different cases: spin-coated polymer films, rapidly drawn polymer fibers, and sheared polymer melts. Our choice of these three cases allows us to discuss various phenomena, like the deformation of polymers, reduced entanglement density, structure formation, and crystallization at conditions far from equilibrium, which are essential to various industrial processing techniques like injection stretch blow molding of plastic bottles and gel electrospinning of polymer fibers. Inspired by the existence of common features in various nonequilibrium processing pathways, we search for order parameters characterizing the behavior of polymers induced through processing. We highlight how the concerted effort from theory, simulations, and experiments on polymers at controlled nonequilibrium processing conditions can provide a profound understanding leading to predictable and tunable properties.

KEY EXPERIMENTAL OBSERVATIONS

Spin-Coated Polymer Films. Spin coating is a widely employed method to fabricate smooth polymer films of precisely controllable thickness, even in the nanometer range. Briefly, the technique amounts to depositing a polymer solution onto a flat surface, which is then rotated at high speed to spread the solution by centrifugal force. At the same time the solvent is rapidly evaporated—a key process that induces a transition to a dry polymer film. Polymer conformations are subjected to significant changes while going from separated polymer coils dispersed in the solvent (prior to spin coating) to a condensed phase upon vitrification (a few seconds later) (Figure 1). In the course of solvent



Figure 1. From isolated polymer coils to glassy polymers: In the course of evaporation, the initially separated polymers in a dilute solution begin to overlap, at a concentration³⁷ $c^* \sim N/V_e$ (where V_e is the envelope volume of the polymer consisting of N monomers), then interpenetrate, and entangle with each other. Above a threshold concentration c_c , the relaxation time of polymers becomes so high that their dynamics is frozen.¹⁶ Continued evaporation induces a deformation of coils along the z-direction. Finally, at c = 1, we obtain dry glassy polymer films, with only partially interpenetrating polymers with $x < \sqrt{N}$, where x is the number of interpenetrating chains in a freshly spin-coated film and \overline{N} is the invariant degree of polymerization, characterizing the number of neighboring chains contained within the envelope volume of a reference chain.³⁸ Different colors were chosen to distinguish neighboring coils and emphasize overlapping regions. Reproduced with permission from ref 18.

evaporation, coils begin to overlap and to entangle. One might expect that at the end of this process the entanglement density would reach the equilibrium value typical of polymer melts. However, various experiments suggest that this is not the case. $^{8-17,19}$

As long as sufficiently many solvent molecules are present in the film, polymers will be able to relax and fully equilibrate. However, upon evaporation, the relaxation time of polymers progressively increases, inducing a "self-retardation" effect. Eventually, the structural relaxation time of the polymer chain will become longer than the time needed to evaporate the remaining solvent molecules, thus making equilibration effectively impossible. For some vitrifying polymers, this may occur even at polymer concentrations of the order of 50%. Evaporating the still remaining solvent molecules from this glassy polymer film will induce molecular deformations leading to stresses within the film. It is likely that such nonequilibrated coils interpenetrate only partially, in contrast to equilibrated polymers. In the latter case, one expects an average of \sqrt{N} interpenetrating chains (neglecting prefactors) within the envelope volume Ve of a polymer;37 a rapidly spin-coated film is expected to exhibit a far lower degree of interpenetration ($x \ll \sqrt{N}$, Figure 1). We anticipate that the ratio x/\sqrt{N} may serve as one order parameter characterizing some aspects of the nonequilibrium polymer conformations and concomitant correlations in freshly spin-coated polymer films. Importantly, the nonequilibrium molecular conformations achieved upon the rapid removal of solvent can give rise to in-plane tensile stresses, which are related to the experimentally measured preparation-induced residual stresses.^{8-12,15-17} Hence, by exploiting the competition between solvent evaporation and polymer relaxation-and thus the extent of deviations from equilibrium-it becomes possible to directly tune the mechanical properties of the film. Indeed, by using for example films obtained at different evaporation rates, 16,17 one can vary the residual stresses by several orders of magnitude. The degree of observed nonequilibrium dynamics, as encoded in the residual stresses and the corresponding (long) relaxation times, can also be associated with a dimensionless "processing parameter", which is defined by the ratio of the time scale of molecular relaxation to evaporation time.^{16–18} This parameter, analogous to the Deborah number or the Weissenberg number, thus offers a practical means to quantitatively control the degree of nonequilibrium, and the resulting mechanical properties of the material, directly via the processing protocol.

Future efforts from simulations and theory may help to understand the microscopic mechanisms underlying deviations from equilibrium caused by preparation-induced residual stresses. These studies should also take into account the vast number of experiments performed on spin-coated polymer films, which have revealed a large number of intriguing properties induced by preparation. For example, the glass transition temperature T_g of these films shows changes by 10-50 K_{1}^{39-41} which may translate to changes in the relaxation time by several orders of magnitude. In fact, experiments⁴²⁻ yield a broad distribution of relaxation times in spin-coated polymer films, suggesting temporal and spatial variations in polymer dynamics and, possibly, differences in local structures. Can we relate these intriguing observations with processinginduced changes in properties? A series of recent experiments demonstrate that the extent of deviations in $T_{\rm g}$ decreases upon annealing films at a temperature $T > T_g$ for times much longer than the time scales associated with the relaxation of equilibrated polymer melts,^{21,22,41,46} highlighting the metastable character of the observed deviations. Interestingly, variations in T_{g} with changes in annealing time are attributed to concomitant changes in the extent of polymer adsorption to the substrate. This, in turn, is related to the equilibration of the whole spin-coated film, which is facilitated via concerted rearrangements of a few segments.^{18,47} Such rearrangements increase the number of interpenetrating chains at the interface (and in the bulk) to approach the equilibrium value of \sqrt{N} (Figure 2), corresponding to an increase in the number of chains adsorbed per unit surface.⁴⁸ We argue that a better understanding of the link between this molecular picture and the emergent macroscopic mechanical properties will be key in



Figure 2. Equilibrating polymer conformations at an adsorbing interface: Schematic illustration of possible variations in polymer conformations at the substrate interface as a function of annealing time at temperatures $T > T_{gr}$ where T_{g} is the glass transition temperature. Immediately after spin coating, polymers at the interface are frozen with rather flat conformations and hence exhibit a reduced interpenetration with other chains at the interface $(x_i \ll \sqrt{N})$, where x_i is the number of interpenetrating chains at the substrate interface in a freshly spin-coated film). Upon annealing, changes in conformation and further adsorption are only possible by the reorganization of already adsorbed chains, which is a possible reason behind the observation that equilibrium $(x \sim \sqrt{N})$ is only possible for annealing times that are much longer than the time scale associated with the relaxation of equilibrated melts.³⁷ Reproduced with permission from ref 21. Copyright 2011 Nature Publishing Group.

designing and optimizing new processing pathways to harness nonequilibrium behavior for the development of novel functional materials.

Highly Stretched Polymer Fibers. Polymer fibers, consisting of stretched and aligned chains, and their enhanced mechanical properties represent a trademark example for "processing pathways deciding polymer properties".^{4,34,49–51} The essential step here is to stretch polymers to their full extension, such that the macroscopic material properties strongly differ from those in equilibrium. The chain extension can be characterized by the maximum draw ratio at a molecular level, $\lambda_{\text{max}} \sim \frac{N}{\sqrt{N}}$.⁵² In practice, the draw ratio λ is defined as the ratio of the final to the initial length of the macroscopic sample.⁴⁹ Various techniques including gel spinning, electrospinning, and melt spinning have been developed for achieving high draw ratios and high elongational stresses in order to increase the extent of polymer stretching.^{4,34,49,50,53} In addition, such strong stretching of polymers significantly affects structure formation of crystallizable polymers, which decides their macroscopic properties.^{4,29,34} Fibers of polyethylene obtained at a draw ratio of around 100 have yielded an elastic modulus of \approx 200 GPa, i.e., a factor of 300 higher than the Young's modulus of polyethylene in the bulk.^{4,34} Importantly, the specific strength, i.e., the tensile strength normalized by mass density, of such commercially available polyethylene fibers is a factor of around 10 higher than that of stainless steel.⁴ Currently, our understanding of these observations is largely empirical.^{4,34} Unfortunately, such empirical relations lack connections to the underlying processing-induced nonequilibrium conformations, hampering progress in the rational design of fully optimized processing pathways. For instance, if we were able to generalize and translate processing strategies, which have been successful in gel spinning/electrospinning of polymer fibers, to other polymeric products, we may anticipate advancements in various technologies, for example, through mechanically resilient yet lightweight materials. In analogy to the spincoated polymer films discussed above, in which the processing parameter is defined by the ratio of the evaporation time to the time characterizing the intrinsic dynamics, the fabrication of highly stretched fibers can also be characterized by dimensionless processing parameters.^{50,53} Such parameters

Macromolecules

validate our central hypothesis that quantitative experiments performed under controlled nonequilibrium conditions provide strategies to design properties of polymers at the molecular level.

Flow-Induced Crystallization of Polymers. During processing, the application of large shear or extensional flow rates will stretch and align polymers with respect to the flow direction (Figure 3). As these aligned polymers lack positional



Figure 3. Stretching polymer chains and its consequence on crystallization: (a) Schematic illustration of flow-induced stretching of polymers, where a transition from equilibrium interpenetration to no interpenetration of a test chain (shown in red) with neighboring chains (shown in black) is depicted. (b) Optical micrographs capturing the influence of the state of the initial melt on the resulting nucleation density of isotactic polystyrene crystals obtained at 180 °C. Prior to crystallization, the sample was sheared at 250 °C for 10 s at a shear rate of $\dot{\gamma} = 30 \text{ s}^{-1}$ followed by waiting for different times t_w at 250 °C, as indicated in the figure. The nominal melting point of isotactic polystyrene is $T_m = 230$ °C. Micrographs are adapted from ref 31.

long-range order, the local molecular structure resembles those of nematic liquid crystals.^{54–57} Even after the cessation of flow, it takes extraordinarily long waiting times for polymers to equilibrate, i.e., to change from processing-induced non-interpenetrating chains to the equilibrium entanglement density (Figure 3a). Such long-living memory effects are often dubbed as flow-induced memory. Interestingly, even at relatively high temperatures above the nominal melting temperature $T_{\rm m}$, experiments reveal the presence of flow-induced structures.^{29,31,32,58} After subsequent cooling to $T < T_{\rm m}$, these aligning chains are found to ease nucleation and, hence, accelerate the crystallization kinetics (Figure 3b).

Remarkably, crystals formed by cooling of flow-induced precursors exhibit morphologies otherwise not achievable from an equilibrated melt. Various continuum approaches⁵⁹⁻⁶²—based on Schneider rate equations—have been proposed to model such flow-induced changes in the crystallization kinetics. However, these macroscopic models cannot predict the nucleation rate for a given chain deformation but rather require this as an input for modeling (see the review by Graham for more details⁶²). In addition, the absence of molecular details severely limits their applicability to understand various intriguing processing-induced observations. For instance, complementary experiments³¹ show that the lifetime of flow-induced precursors increases rapidly upon decreasing temperature, yielding high activation energies. Such an increase in activation energy is commonly associated with a cooperative motion of segments-a condition expected for aligned segments of flow-induced precursors. A large degree of alignment among polymer chains might also be formed under other processing conditions. High flow rates can, for example, also be obtained when polymers slip rapidly on solid substrates, as in the case of dewetting.¹⁵ Thus, we expect the occurrence of flow-induced polymer alignment during dewetting of thin polymer films at $T > T_m$. Indeed, recent dewetting experiments on isotactic polystyrene¹⁵ show a temperature-dependent shear thickening behavior, accompanied by a relatively high activation energy. Both features hint at the presence of flow-induced structures. Importantly, in contrast to isotactic polystyrene, atactic polystyrene-polystyrene with irregularly arranged side groups-does not show high activation energies. Thus, it seems possible to harness the viscoelastic response of polymers by dialing in a certain regularity in the arrangement of side groups and by controlling the flow conditions during processing.

The experimental observations described above clearly demonstrate that rapid processing conditions, inducing significant changes in molecular conformations, play a key role in determining various macroscopic properties of polymers. Many of these so improved properties cannot be achieved from equilibrated polymer melts. Interestingly, nonequilibrated polymers obtained via different processing pathways exhibit dynamics of correlated polymers varying locally in space and time. The presence of common features in different experiments, such as the topological correlations between segments and the transition from \sqrt{N} interpenetrating chains in equilibrium to no interpenetration between the



Figure 4. Representative nonequilibrium conformations: Schematic illustration of a test chain (shown in red) adopting different representative nonequilibrium conformations: (a) polymers, with local stretching along the direction of pulling force, resembling stems and flowers, 63 (b) completely stretched chains in the shish of shish-kebab structures, 29,31,32,58 (c) knots, 64 and (d) polymer films with strong adsorption near the surface. 41

chains out of equilibrium, hints toward the possibility that general concepts may exist for predicting processing-induced nonequilibrium behavior of polymers.

PERSPECTIVES AND OUTLOOK

For a quantitative understanding of preparation-induced material properties, we need to consider the ever-changing structures and properties of nonequilibrated polymers on all relevant length and time scales. Such considerations could take advantage of the novel experiments⁶⁵⁻⁶⁸ and sophisticated simulation techniques that have recently been reviewed by Gartner and Jayaraman.⁶⁹ For instance, in Figure 4 we have shown different representative nonequilibrium conformations and key parameters that might help modeling the nonequilibrium structure developed. One goal may be to derive quantitative structure-processing relations that account for path- and time-dependent properties of polymers during processing. As demonstrated earlier, any processing-induced deviations in molecular conformations defined for example via deviations from a Gaussian distribution of chain conformations may induce transient order. Such order arises from temporal correlations between monomers or polymer segments, potentially reflected in variable static and dynamic heterogeneities. Therefore, a comprehensive understanding of such volatile molecular correlations and heterogeneities may shed light on the mechanisms underlying the processing induced deviations in polymer properties. As highlighted by the three chosen examples, we hypothesize that an appropriate metric of such correlations could serve as a possible order parameter characterizing the behavior of polymers induced through processing. The three examples focused on one-component polymer solutions and melts where nonequilibrium chain conformations and intermolecular packing immediately dictate system properties. These nonequilibrium molecular aspects, however, also impact collective structure formation in more complex polymer systems. For instance, (i) the as-cast structure of glassy copolymer films features frozen-in composition fluctuations that may impact microphase separation after heating above the glass transition temperature, (ii) the highly stretched chain conformations during roll casting⁷⁰⁻⁷³ dictate the final orientation of the copolymer morphology, and (iii) shear flow has been successfully employed to direct the orientation of self-assembled structures.⁷⁴⁻⁷⁶ Additionally, these multicomponent systems feature nonequilibrium structures, such as, for example, defects in directed self-assembly that arise from processing (i.e., the kinetics of structure formation) but that are not directly related to nonequilibrium chain conformations."

To explore and identify the presence of order parameters, we believe it is important to address the following fundamental questions: Under which conditions (for example, the extent of local vs global stretching, local order vs long-range orientation, and spatial and temporal fluctuations in the degree of entanglements) can we create the transient order? How can we bridge from such transient and variable molecular correlations to concepts based on entropic or enthalpic interactions established for equilibrium systems? Can we borrow ideas on heterogeneities and correlations from the complex dynamics⁷⁸⁻⁸³ experienced by various materials on approaching dynamical arrest? Can local correlations of monomers propagate through chain connectivity and induce long-ranged interactions between topological constraints? In

the following, we propose various simulations and experiments that may allow addressing these questions.

Experiments indicate that the time allowed for equilibration during sample preparation, such as the evaporation time in the fabrication of polymer films^{16,17} or the adsorption time in the case of further annealing,^{21,22} is an important control parameter characterizing the deviations in the resultant properties of polymer films. This time parameter may be a good starting point for simulations.^{84,85} Simulations that mimic experimental conditions (e.g., spinning rate and solvent evaporation rate) can provide unique molecular-level insight into the variations in chain conformations and entanglement density of systems such as freshly coated films or stretched polymer fibers. However, in comparison with experiments, simulated systems are often much smaller and the accessible time scales are typically much shorter. Therefore, it would already be a great success if one could obtain a qualitative agreement for some features, for example, changes of the thickness^{23,27} and different material properties as viscosity and glass transition temperature upon annealing.^{21,22,41} Apart from reproducing experimental results, simulations may also identify new experimentally testable regimes. Molecular conformations can be directly, and continuously, monitored in simulations, and their contribution to the (local) stress field (defined via a virial expression) can be determined. With such simulations, it might be possible to understand the origin of residual stresses and the length and time scales over which effects related to metastable states persist. Furthermore, simulations may shed light on the length scales and the extent of spatial heterogeneities in the mechanical properties of such non-equilibrated polymer films.⁸⁶⁻⁸⁸ On the other hand, recent advances⁶⁸ in the current state of the art of neutron scattering experiments (and data analysis) show promises to track the relaxation pathways as expressed through changes in polymer conformations on approaching equilibrium.

A powerful solving strategy to understand how nonequilibrium local structures affect macroscopic properties could come from experiments and simulations aiming at a rational understanding of nonequilibrium conformations resulting from polymer adsorption to a substrate. Equilibration of thin films prepared by spin coating seems to be driven by density fluctuations of monomers near the adsorbing interface.⁴⁷ As a starting point, we may utilize concepts developed through a simple analytical model⁸⁹ which highlights the importance of entropic (free energy) frustration and its thermodynamic consequences on the adsorption of a single chain. This model shows that if a polymer is adsorbed initially with a wrong sequence (e.g., a high-energy state), then any effort to minimize energy requires trajectories departing further away from the equilibrium state. Such topologically quenched states could kinetically freeze polymers almost indefinitely out of equilibrium. Using similar ideas for many interacting polymers in a crowded environment, as in the adsorption of polymer melts, we may anticipate a stronger topological frustration, a more complex free energy landscape, and much larger length scales of cooperative motion. Hence, minimizing the free energy at the adsorbing interface might require concerted rearrangements of several molecules. Furthermore, we could consider experiments where adsorption is driven over specific sites (e.g., on patterned surfaces), which would allow controlling nonequilibrium interfacial conformations. We would then explore how macroscopic quantities are affected by the adsorbed chains. In both cases, density variations of the

adsorbed chains (or segments)—a collective quantity characterizing the configuration of the system—could serve as an order parameter for the process of adsorption.

To understand the heterogeneous character of nonequilibrated polymers, experiments (e.g., nonlinear dielectric spectroscopy⁹⁰) and simulations could focus on higher-order nonlinear susceptibilities. These quantities, as already verified in the case of small molecules,^{91,92} provide signatures of the nature and the length scale of dynamic heterogeneities. Extending the investigation to star-shaped polymers or other nonlinear architectures of polymers is highly recommended as these systems are inherently heterogeneous in terms of both density and dynamics.^{93–96} Notably, recent experiments^{26,93,96} show that glassy star-shaped polymers age at a significantly lower rate than the corresponding linear chains, suggesting the importance of macromolecular architecture for tuning the lifetime of the processing-induced deviations in conformations. Finally, we might gain information on processing-induced nonequilibrium states by considering analogies with supercooled liquids, i.e., the precursors of glasses, which are arguably the most widely studied nonequilibrium materials. As is wellestablished from simulations of bulk glass formers, the rapid increase in the relaxation time of liquids approaching the glass transition temperature may be associated with the appearance of so-called locally preferred structures,78-83 quantifying a form of growing structural order within an amorphous material. Here, we may ask whether the experimentally observed long relaxation times of processing-induced nonequilibrium conformations of polymers are also accompanied by a growing degree of locally preferred structural motifs. Given a proper and unique definition, this "transient order" could serve as a reliable order parameter of nonequilibrium conformations.

To summarize, processing-induced nonequilibrium conformations, and the thereby created correlations between variable number of polymer segments, provide access to novel structural, dynamical, and mechanical properties. To design polymers or polymeric structures with desired and tunable properties requires a quantitative understanding of how properties of polymers depend on nonequilibrium conformations. Through the presented examples, we highlight common scientific challenges for apparently different scenarios, hinting at possibilities for developing quantitative concepts relating processing protocols to molecular conformations and to resultant properties. We have identified some possible future directions of research that will bring us toward realizing our goal of "molecular process design" by achieving quantitative processing-property relations based on a fundamental understanding of polymers in nonequilibrium conditions. Clearly, a concerted effort between theory, simulations, and experiments is required to identify suitable order parameters characterizing the preparation-induced nonequilibrium states in polymers. A better understanding of polymers in nonequilibrium conditions not only will introduce new research directions in fundamental materials science but also will establish how the choice of the processing protocol can act as an important and tunable control parameter in materials design. Ultimately, the ability to open up new processing-based pathways will enable a much broader spectrum of structural, dynamical, and mechanical properties that are unattainable in thermodynamic equilibrium, thus potentially creating a wealth of novel applications.

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Macromolecules

Perspective

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Koji Fukao was born in Osaka, Japan, and studied physics at Kyoto University. After receiving his Ph.D. in physics at Kyoto University and working at Kyushu University and Kyoto University as assistant Professor, he became associate Professor at Kyoto Institute of Technology in 2001. From 1992 to 1994, he stayed at Gert Strobls group at Freiburg University as an Alexander von Humboldt research fellow. Since 2007, he has been a full Professor of Physics at Ritsumeikan University in Shiga, Japan, to chair soft matter physics laboratory. Dr. Fukao has been an experimental physicist using scattering methods such as X-ray, light, neutron scattering, and dynamical methods such as dielectric relaxation spectroscopy and viscoelastic measurements. His primary research interest includes phase transition and dynamics in chain molecules, structure formation of polymers from the glassy state, the glass transition and dynamics in thin polymer films, and charge carrier motions in ionic liquid crystals.



Emmanouil Glynos studied physics at the University of Patras, and he received his PhD in 2007 in polymer physics at the University of Edinburgh. Until 2012, he was a postdoctoral research associate at the Department of Material Science and Engineering at the University of Michigan, working on the effect of macromolecular architecture on the physical properties of polymers at surfaces and interfaces. He was subsequently appointed as a Research Investigator at the University of Michigan at the Center for Solar and Thermal Energy Conversion where his research focused in addressing important scientific challenges associated with the structure-property relations and correlations of the morphology of the device active layer on the nanometer scale to the electrical and optical properties, the charge photogeneration, and overall performance of these systems. Since 2015 he is a Research Scientist at FORTH/IESL where the objective of his current research is to develop a fundamental understanding of, and controlling via macromolecular engineering, the structure and properties of nanostructured polymer materials that can be used as solid electrolytes in lithium-metal batteries and electrochromic devices and as active layers in organic photovoltaics.



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Macromolecules

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