

Percolation Implications in the Rheology of Polymer Crystallization

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Abstract

The rheology of polymer crystallization is an old problem that often defies explanation due to the complex interrelationships between crystallization and flow properties. Although separate measurements of rheology and crystallinity can give some information on their relationship, it is only through simultaneous measurements that ideas on the rheology of polymer crystallization can be tested and developed. This Perspective details recent experimental developments in simultaneous crystallinity and rheology measurements as well as continuum modeling efforts for the case of quiescent and isothermal crystallization. Experimental results reveal that the rheology is dominated initially by growth of individual spherulites that evolve into spherulitic superstructures that eventually span the measurement geometry. A generalized effective medium model based on this concept of percolation can explain both the growth of the viscoelastic modulus during crystallization and the changes in the relaxation spectrum of the crystallizing polymer, including a critical gel response at percolation. The success of the combined measurement techniques and percolation concepts motivate research to extend the semicrystalline polymer materials space where these methods are applied as well as further develop novel techniques to gain additional insight into the evolution of structure and relaxation dynamics during crystallization.

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I. Introduction

Melting, flow, and crystallization are critical steps in the industrial processing of semicrystalline polymers. All processing operations – such as extrusion, blow molding, or fiber spinning^[1, 2] – induce these steps by subjecting the polymer to dramatic changes in temperature and deformation fields. The solidification during the final crystallization step is critical to successful processing because it determines the final properties of the polymer, the thermal budget of the process, the achievable process parameters and the speed of manufacture. But despite its importance and despite much effort, our understanding of the interplay between the solidification and crystallization processes is limited.

The primary reason for the lack of understanding is the complexity of the non-linear feedback between process flow and crystallization. For example, process flow induces crystallization, which enhances the effective viscosity, which then affects the flow and stress fields, further affecting crystallization kinetics. Numerous aspects of this complexity have been described but fall short of a coherent description of the rheology-crystallization relationship.^[3, 4] To make progress in this multi-faceted problem, an alternate approach is to first solve simpler *ground state* problems.

A tractable approach is to eliminate the complex feedback loop by employing isothermal temperature jumps to induce crystallization, while employing small amplitude oscillatory shear (SAOS) as a probe of the evolving moduli (without altering crystallization kinetics). Indeed, this Perspective focuses on this simpler case with the goal of determining the underlying structural evolution that underpins the rheological properties of crystallizing polymers. This is a long-considered problem, and herein is described how recently developed experimental methods along with new modes of analysis allows construction of a coherent percolation-based framework.

It is well demonstrated that the SAOS modulus increases over multiple orders of magnitude during crystallization.^[5-7] Additionally, the relaxation dynamics of the polymer slow down, and there is a point during the crystallization process where the partially crystalline polymer exhibits power-law relaxation dynamics characteristic of a critical gel. Pogodina and Winter first identified this phenomena and used it to characterize the rheology of the crystallization process in isotactic polypropylenes.^[5] Oscillation frequency sweeps during crystallization indicate a change in the relaxation spectrum of the crystallizing polymer, but attempts to identify the gel point are often hindered by long relaxation times inherent in the polymer melts studied. Further progress along these lines has been stymied by lack of suitable methods to simultaneously measure crystallinity and rheology during the crystallization process.

Separate measurements of crystallinity and rheology are problematic, as they inevitably involve differences in temperature, thermal gradients, mechanical history, sample dimension and sample-surface interactions, which can all affect the kinetics of crystallization. A better approach is to incorporate the measurement of polymer crystallinity into the head of the rheometer and conduct simultaneous

measurements. These hybrid techniques are now reaching maturity and represent a powerful tool to relate crystallization kinetics to rheology; they are summarized in Section II.

These successful measurements drive the need for rheological models that explain the relaxation dynamics of the crystallizing polymer. Efforts to describe the rheology of partially crystalline polymers have been largely empirical apart from a few molecular-based models. A subset of empirical models is detailed in the work of Lamberti et al.^[7] where the viscosity is described as a function of the relative crystallinity. A more recent molecular-based model is the slip-link model of polymer crystallization, which describes the rheology of the crystallization process by an ensemble of single chains with a combination of free and fixed ends.^[8, 9] This molecular-scale model can reproduce small-amplitude rheology during crystallization. It does not consider the hierarchical length scales involved in the crystallization process, from lamellar organization up through spherulitic growth and impingement. A phenomenological approach based on a generalized effective medium (GEM) model was considered by Kotula and Migler,^[10] this was shown to describe the mechanical response of a crystallizing polymer. Though phenomenological, it has physical foundation based on concepts in particle suspensions and percolation theory. Described in Section III, the GEM model captures the relaxation dynamics of a crystallizing polymer through the percolation process, and at percolation the model reproduces the power law relaxation dynamics characteristic of a critical gel.^[11]

This Perspective describes the state-of-the-art in the techniques and models used to describe the rheology of crystallizing polymers. Experimental observations of the crystallization process during rheological measurements motivate the concept of a percolation-driven transition, where the characteristic structure and length scales are those of spherulites and impinged spherulite clusters. This percolation process implies that structure growth in the rheometer can be a function of both the polymer and the measurement geometry. This percolation process is well-characterized by the GEM model, which can be used to model the rheology of the crystallization process over two orders of magnitude in measurement frequency. Given this progress in the rheology of crystallizing polymers, the Perspective finishes with brief comments on unexplored materials and measurement techniques for further understanding of crystallization.

II. Experiments: Simultaneous Rheology and Crystallinity

The ideal method to relate crystallinity to rheology is via direct, *simultaneous* measurements of rheological parameters and crystallinity. Various crystallinity measurement techniques have been coupled to rotational rheometers for this purpose as summarized in Table 1. The measurement technique dictates how crystallinity is reported, which is crucial to understanding the relationship between the as-measured “crystallinity” and the structure modifying the rheology.

Each measurement technique in Table 1 quantifies crystallinity using different physical phenomena, and these differences must be considered when relating the as-measured crystalline property to rheology. Differential scanning calorimetry (DSC) measures the enthalpy of fusion during crystallization via heat flow and can be used to measure an absolute mass fraction α_{DSC} (if the enthalpy of fusion for the totally crystalline polymer at the equilibrium melt temperature is known) or a relative mass fraction $\tilde{\alpha}_{\text{DSC}}$. Nuclear magnetic resonance (NMR) relaxometry can quantify the absolute mass fraction crystallinity α_{NMR} , and Raman spectroscopy (RS) can be calibrated using DSC measurements to quantify the absolute mass fraction crystallinity α_{RS} . Optical imaging (OI) can be used for locating and sizing spherulites, and although the mass fraction crystallinity of each spherulite cannot be determined optically, the volume that the spherulites occupy at any given instant can be measured by analyzing multiple images at different focus distances through the sample thickness. This volume of spherulites relative to the total image volume is called the degree of space filling ξ_{OI} .

When space-filling semicrystalline domains are the dominant rheology modifier, the mass fractions described above must be converted into an equivalent degree of space filling. Kotula and Migler noted that α_{RS} measured during isothermal crystallization consists of a primary Avrami-like crystallization process followed by a much slower secondary crystallization process.^[10] The onset of the secondary crystallization process corresponds to the time where the spherulites have impinged ($\xi = 1$), which is based on the mass density and optical microscopy measurements of Zachmann and Stuart.^[12] By denoting the mass fraction crystallinity where the secondary crystallization process begins as $\alpha_{\text{RS},\infty}$, the mass fraction crystallinity can be converted to a degree of space filling via

$$\xi_{\text{RS}} = \frac{\alpha_{\text{RS}}}{\alpha_{\text{RS},\infty}} \left[\frac{\alpha_{\text{RS},\infty} + \frac{\nu_{\text{m}}}{\nu_{\text{c}}}(1 - \alpha_{\text{RS},\infty})}{\alpha_{\text{RS}} + \frac{\nu_{\text{m}}}{\nu_{\text{c}}}(1 - \alpha_{\text{RS}})} \right] \quad (1)$$

Where ν_{m} and ν_{c} are the specific volume of the amorphous and fully crystalline phases, respectively. The subscript denoting the measurement technique used to quantify crystallinity will be dropped for brevity for the remainder of this Perspective but can be determined from the references in Table 1.

One can classify the techniques in Table 1 into two types: “global” or “local”. Global techniques include DSC and time-domain NMR methods which measure the crystallinity of the entire sample volume; whereas local measurements probe crystallinity in a smaller region. For local measurements, the location of the region being probed relative to the rheometer geometry is important, since the shear rate varies with radial position for parallel plate geometries and the gap height varies for the cone-and-plate.

The orientation of crystalline domains is also important especially in cases where shear is applied during or prior to crystallization. Raman spectroscopy can be used to quantify the second and fourth moments of the orientation distribution of crystalline domains, but this requires multiple spectra recorded at various linear polarization states.^[13] Orientation of the sample relative to the polarization state of the

optical setup can also affect peaks used to evaluate crystallinity, however this effect can be reduced through the use of circularly polarized light.^[14] Structure growth at length scales above the diffraction limit can be made using brightfield optical imaging,^[15, 16] or polarized optical imaging can be used to assess molecular-scale orientation via birefringence.^[17]

Table 1. Crystallinity measurement techniques incorporated onto commercial shear rheometers

Technique	Reported crystallinity	Global / Local	Orientation sensitive?	Material studied*
DSC	Heat flow, ^[18-20] relative mass fraction ^[21, 22]	Global	No	sPP, ^[18] iPP, ^[21] PCL, ^[19, 21] HDPE, ^[22] PB ^[20]
NMR	Absolute mass fraction ^[23, 24]	Global	No	iPP, ^[23, 24] PI ^[24]
Raman spectroscopy	Absolute mass fraction, ^[9-11, 14, 25]	Local	Yes	HDPE, ^[14] LLDPE, ^[9] PCL, ^[10, 11, 25] PCL nanocomposites ^[25]
Optical imaging	Polarized light intensity, ^[10, 14, 25] birefringence, ^[17] degree of space filling ^[15, 16, 26, 27]	Global ^[17] or local ^[14-16, 26]	Yes	HDPE, ^[14, 17] iPP, ^[15, 16, 26, 27] PCL, ^[10, 25] PCL nanocomposites ^[25]

*Abbreviations: sPP – syndiotactic polypropylene, iPP – isotactic polypropylene, PCL – polycaprolactone, HDPE – high density polyethylene, LLDPE – linear low density polyethylene, PB – polybutylene, PI – polyisoprene

The measurements in Table 1 allow viscoelastic parameters to be analyzed as a function of crystallinity to determine the crystallization phenomena that dictate changes in rheology. SAOS measurements allow the elastic modulus G' and viscous modulus G'' to be determined as a function of angular frequency ω during the entire crystallization process. These measurements must be performed in the linear viscoelastic regime, however the maximum strain amplitude for a linear response is significantly lower for semicrystalline solids (maximum amplitudes less than 0.01)^[28] compared to polymer melts (maximum amplitude order 0.1).^[29] Nonlinearities in SAOS measurements during crystallization can therefore be reduced by limiting the maximum strain to that of the semicrystalline polymer.^[14] While this perspective focuses on SAOS, crystallinity measurements during steady shear have also been carried out.^[18, 19, 21, 27, 30]

SAOS measurements with simultaneous Raman spectroscopy,^[10, 11, 14, 25] optical imaging,^[15, 16, 26, 27] and NMR^[23, 24] over the crystallization process indicate a sigmoidal dependence of the log of the modulus with the degree of space filling ξ . The degree of space filling is the volume fraction crystallinity in the sample that is normalized such that the melt state corresponds to $\xi = 0$ and the semicrystalline state at the end of the primary crystallization process is $\xi = 1$. The inflection point in the log modulus-space filling curve tends to occur in the range of 0.2 to 0.4 space filling,^[10, 11, 16] however some groups have reported a steep rise in the modulus at lower crystallinities.^[24] The inflection in the modulus-crystallinity curve was found to shift to lower crystallinity when an anisotropic nucleating agent (cellulose nanocrystal)^[25] was dispersed in the melt.

Roy *et al.* noted that the turnover in the modulus-crystallinity curve had a strong gap dependence for isotactic polypropylene.^[16] Caution about small parallel plate gaps and cone-and-plate geometries (which have a small truncation gap at the cone center) was also noted by Pantani *et al.* for polypropylenes.^[15] Smaller gaps tended to shift the inflection point of the modulus-crystallinity curve as shown in Figure 1. The reason for this gap dependence was evident from Roy *et al.*'s optical microscopy measurements and deterministic reconstruction of the crystallization process via simulations – spherulites grown from the melt and plate surfaces would impinge and eventually form a spherulite superstructure that spanned the measurement gap of the rheometer. Crystallization measurements performed at smaller gaps require fewer spherulites to span the upper and lower plates, which results in an upturn in the modulus at lower degrees of space filling. These results highlight the role of the growth of semicrystalline spherulitic structures as the dominant effect in evolution of rheology during the crystallization process.

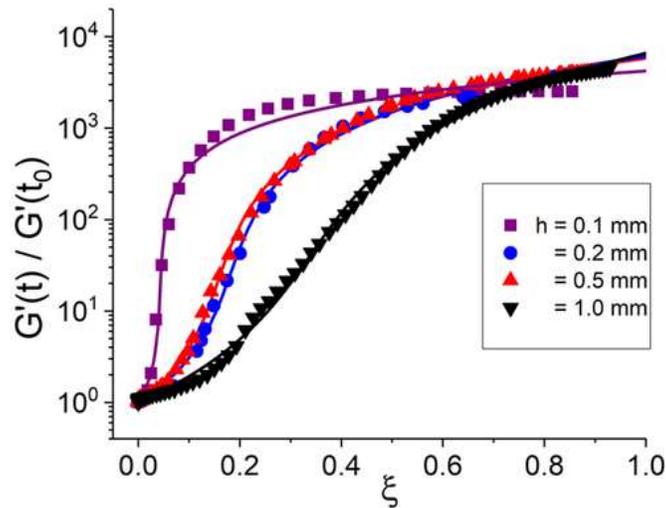


Figure 1. Normalized elastic modulus versus the degree of space filling ξ for the isothermal crystallization of isotactic polypropylene from the work of Roy *et al.*^[16] The data points indicate the storage moduli at four gap distances in the parallel plate rheometer. The solid lines indicate fits of the GEM model, eq (2).

The experimental results indicate that caution must be taken when measuring the rheology of crystallization processes such that geometry effects are mitigated. Figure 2 shows a few examples of possible conditions for a sample that is partway through crystallization. Figures 2a and 2b show a comparison between a cone-and-plate geometry and a parallel plate geometry with a similar degree of crystallinity. In Figure 2a, spherulites are distributed throughout the bulk of the sample, but within the truncation gap region at the center a few spherulites (either nucleated from the bulk or plate surfaces) span the geometry. This growth would significantly increase the torque required to rotate the upper tool, which

would result in a higher modulus and a viscoelastic solid relaxation spectrum reported at lower crystallinities. A similar degree of space filling in a parallel plate geometry (Fig 2b, with a gap much larger than the cone truncation in Fig 2a) would not have any percolating clusters yet, and the measured modulus at this degree of space filling would be lower. Such gap dependent effects are anticipated to disappear in cases when the average distance between spherulites is much less than the gap width.^[16]

Figure 2c shows a case where the degree of space filling is higher towards the outer edges of the sample, even though the total number of nuclei within the volume of the sample is similar to Fig 2b. A nonuniform distribution of spherulites can be generated when the sample is sheared by rotation of the upper plate at the start of the crystallization process. Both the shear rate and strain vary radially in a parallel-plate geometry from zero at the center to a maximum at the outer edge, and therefore flow-enhanced crystallization effects should be strongest towards the outer edge of the sample. Evidence of this is shown in the work of Iqbal *et al.* for poly(L-lactic acid) that was sheared in a parallel-plate geometry, then removed, sectioned, and imaged using polarized-light optical microscopy.^[30] Their images show few spherulites towards the center of the sample, but an increasing number of spherulites, including spherulite superstructures that span the upper and lower plate, at increasing distances from the sample center. In Fig 2c the measured rheological response will be due to this radially varying structure, but same “global” crystallinity as Fig 2b. Attempting to discern a viscoelastic model for the rheology of crystallizing polymers from a system that crystallized as in Fig 2c would be quite challenging without spatially-resolved *in situ* crystallinity measurements.

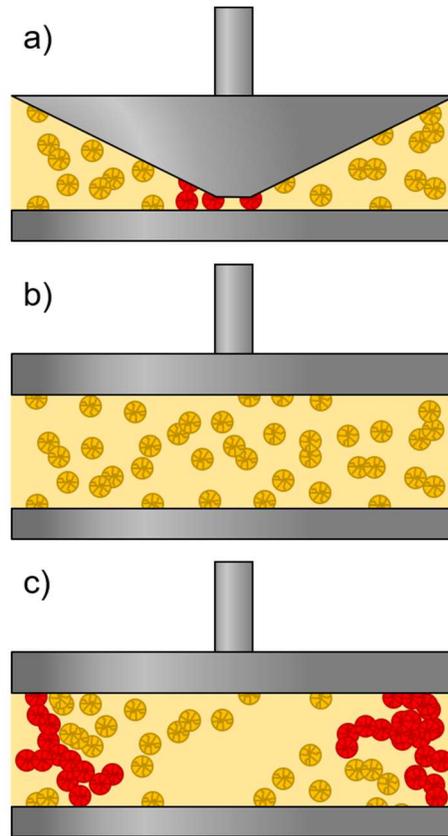


Figure 2. Implications of spherulite growth and spherulite superstructure percolation on the measured rheology (figures are not to scale). Spherulites and spherulite structures that connect the upper and lower geometries are colored red. a) Spherulites span the geometry near the truncation gap in a cone-and-plate system. b) A similar volume fraction crystallinity as (a) does not exhibit percolation in a parallel plate geometry when the crystallinity is evenly distributed throughout the sample. c) A nonuniform degree of space filling through the sample.

III. Modeling: A Generalized Effective Medium

The experimental evidence for a percolation-type process motivates the development and use of continuum models that can also describe the rheology of crystallization via percolation. Many of the proposed models for the rheology of crystallization are either empirical or based on phenomenological models for the rheology of solid particle suspensions. Collections of these models can be found elsewhere,^[7, 10, 22, 31-33] although it is important to note that many of the suspension-based models could only be applied at low crystallinities. At some critical crystallinity the suspension models predict an infinite viscosity when the suspension becomes “jammed” with crystalline material. These models also focus on the magnitude of the complex viscosity or the steady shear viscosity and are unable to explain changes in the relaxation spectrum during crystallization.

Recently, Kotula and Migler developed a generalized effective medium (GEM) model that provides an implicit relationship for the frequency-dependent complex modulus $G^*(\omega, \xi)$ of a partially crystalline polymer as a function of the degree of space filling of semicrystalline domains. The equation for the GEM model is

$$(1 - \xi) \frac{(G_0^*)^{1/s} - (G^*)^{1/s}}{\xi_c (G_0^*)^{1/s} + (1 - \xi_c) (G^*)^{1/s}} + \xi \frac{(G_\infty^*)^{1/t} - (G^*)^{1/t}}{\xi_c (G_\infty^*)^{1/t} + (1 - \xi_c) (G^*)^{1/t}} = 0. \quad (2)$$

As the degree of space filling increases, the rheology of the polymer increases from a melt state with complex modulus $G_0^*(\omega, \xi = 0)$ to a semicrystalline state with modulus $G_\infty^*(\omega, \xi = 1)$. Provided that G_0^* and G_∞^* are known, the three fitting parameters for the model are the critical degree of space filling for percolation ξ_c , the scaling exponent s for the modulus when $\xi < \xi_c$, and the scaling exponent t when $\xi > \xi_c$.

The meaning of the scaling exponents becomes clearer in special cases. As the semicrystalline modulus G_∞^* goes to infinity, eq (2) can be simplified to

$$G^* = G_0^* \left(1 - \frac{\xi}{\xi_c}\right)^{-s}. \quad (3)$$

Here, the exponent s indicates the sensitivity of the modulus to an increase in crystallinity below the critical percolation ξ_c . This equation has a similar dependence on crystallinity as the suspension-based models for viscosity discussed by Tanner.^[6] If the initial modulus is set to zero in eq (2), the GEM model becomes

$$G^* = G_\infty^* \left(\frac{\xi - \xi_c}{1 - \xi_c}\right)^t, \quad (4)$$

and t indicates sensitivity of the modulus to changes in crystallinity beyond the percolation threshold.

The shear modulus at the percolation threshold G_c^* can be approximated from eq (2) as

$$G_c^* \approx \left(\frac{\xi_c}{1 - \xi_c}\right)^{ns} (G_0^*)^n (G_\infty^*)^{1-n} \quad (5)$$

where $n = t/(s + t)$. This approximation holds when the modulus at percolation is much greater than the initial modulus and the critical degree of space filling is less than approximately 0.66.^[11] Eq (5) can reproduce Winter's gelation model for specific viscoelastic models for the melt and semicrystalline states; for example, a simple Maxwell material crystallizing into an elastic solid exhibits a relaxation modulus with power law dynamics at percolation,^[11] $G_c^* \sim \omega^n$, which can be directly observed in experiments only when the measurements frequencies are much less than the inverse relaxation timescale of the melt phase. However, the GEM model can be used to determine the critical percolation fraction and the power law exponent n without directly measuring the terminal response of the polymer melt, which is common in most industrial resins with a broad molecular weight distribution.

The values of the scaling exponents have been determined from fitting eq (2) to rheo-Raman microscopy measurements of polycaprolactones, where $1.5 < s < 2$ and $3.5 < t < 6$.^[11] These exponents

were applicable over two order of magnitude in the oscillation frequency (1 rad/s to 100 rad/s) over a narrow range of temperatures for isothermal crystallization (42 °C to 46 °C), as shown in Figure 3. The values of the scaling exponents indicate a simple conceptual picture for the rheology of the crystallization process. At early times, dispersed spherulites grow from the polymer melt and act as hard particles dispersed in a polymer melt matrix. The spherulites continue to grow and impinge until a critical degree of space filling occurs where spherulitic superstructures form a network within the sample. After this point the sample has the rheological signature of a solid material with dispersed regions of polymer melt, and the continued growth of semicrystalline fronts in the material increase the viscoelastic modulus towards the semicrystalline state at the end of the space filling process.

Other applications of the GEM model used simplifications where the exponents were assumed equal ($s = t = q$) and where different rheological parameters were used for fitting. Using equal exponents and fitting $G^*(\omega, \xi)$ at a single frequency, Kotula and Migler found reasonable success with the GEM model for $q = 2$.^[10] Roy *et al.* used the magnitude of the modulus $|G^*| = \sqrt{(G')^2 + (G'')^2}$ in place of the complex modulus in eq (2) and observed that q had values near 2 for as-received polycaprolactone, but the addition of cellulose nanocrystals to the matrix tended to drive values of the exponent to $q < 1$.^[25] A version of the GEM model where only the elastic modulus was used in eq (2) was successfully applied to polypropylenes, but q was found to be dependent on the gap used in the rheometer.^[16] The largest gap sizes yielded results that were well-fit using $q = 2$ and percolation around $\xi_c = 0.37$ as shown in Fig 1, but the fitting exponent and critical percolation fraction decreased to values $q \approx 1$ and $\xi_c = 0.06$ at the smallest gap height. At the smallest gap sizes the GEM model approaches a linear mixing rule^[16] which is a simple composite model where the strain is assumed equal in both phases. This makes conceptual sense within the percolation model for crystallizing polymers: at large gap heights, many spherulites are required to bridge the gap from one plate to another, and thus *bulk* percolation considerations are relevant. At small enough gap heights, single spherulites will nucleate, grow, and span the gap at very low degrees of space filling. Both the semicrystalline spherulites and the as-yet uncrystallized melt will then be subjected to the same strain from oscillatory deformation of the upper plate. The GEM model clearly shows promise in explaining the wide range of percolation processes that will affect the measured viscoelastic response of crystallizing polymers.

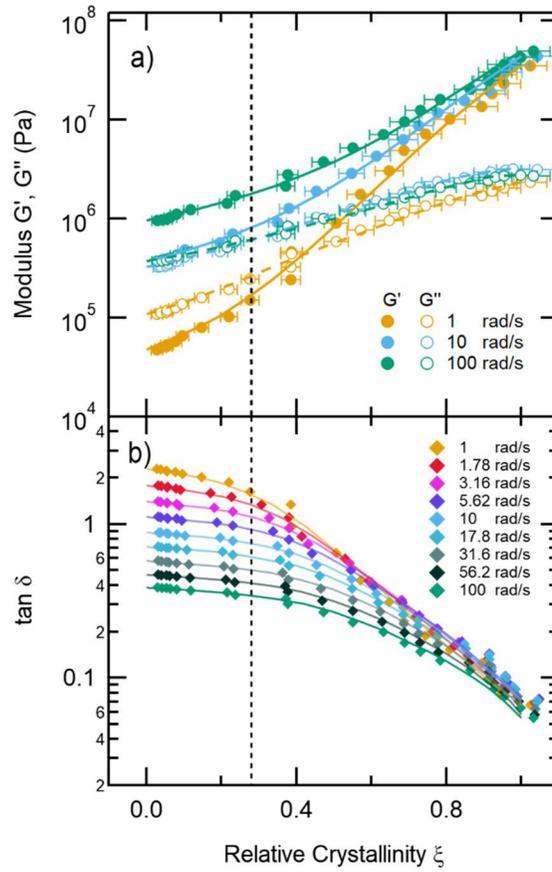


Figure 3. Application of the GEM model to the rheology of polycaprolactone crystallization from the melt at 42 °C from ref^[11]. a) Elastic and viscous moduli versus the degree of space filling. Points show the experimental results with the GEM model fit to the elastic modulus (solid lines) and the viscous modulus (dashed lines). b) Loss tangent versus the degree of space filling with lines showing the GEM model fit. The dashed vertical line indicates the critical degree of space filling for percolation.

IV. Future Directions

The progress made in recent years – correlating how the crystallization process drives the rheology transition from viscoelastic melt to solid – motivates work on two fronts. First, within the realm of the quiescent isothermal experiments, there is still much to do. In cases where the gap dependence cannot be ignored, the modulus-crystallinity relationship will depend on the nucleation rate, nucleation density, the shape of the crystallizing domains, and their growth rate. Simplifications should be possible in the regime where the gap dependence is negligible – under these conditions the size of an individual semicrystalline domain is small compared to the measurement geometry such that the nucleation density will not matter, and the parameters of the GEM model will depend primarily on the semicrystalline domain shape.

Additional experiments, simulations, and theory will be necessary to determine the extent to which these rheological measurements can characterize the structure of the crystallization process. The assumption of constant rheological properties for both the melt and semicrystalline phases is also worth exploring. For example, the current treatment of the spherulite as a spatially featureless entity is clearly an oversimplification. What is the effect of the complex hierarchical spatial structure within a spherulite on the rheological evolution? How are spherulites welded to each other and how is that manifest in the rheology of the superstructures? Further interest concerns moving beyond linear homopolymers; various polymer architectures, copolymers, and polymer blends are present in industrial polymer processing, and the relationship between these types of materials, the structure generated during crystallization, and the resulting rheological response is of key interest from both practical and theoretical viewpoints.

Second, the more complex problems of flow-induced crystallization and non-isothermal crystallization can be addressed using these new tools and analysis methods. Extensions of percolation concepts and the GEM model to flow-induced crystallization processes – where spherulites are not necessarily observed – are a critical need, since flows (both shear and extension) are inherent in polymer processing. If this percolation concept holds then the size of the characteristic semicrystalline domain relative to characteristic length scales in the process line will be of critical interest, as will methods to either promote or hinder percolation depending on the processing technique. Combinations of (shear and extensional) rheology with crystallinity measurements will be important to testing and developing models under controlled conditions that can subsequently be applied to process lines.

Lastly, more must be done in development of measurement techniques that combine rheology with crystallization. Combinations of small- and wide-angle X-ray scattering with shear rheology are underutilized despite the benefit of quantifying crystallinity, orientation, and structure over a wide range of length scales.^[34] Polarized small-angle light scattering probes both spherulite size and crystallinity^[35] but has not been applied to study crystallization processes simultaneously with rheological measurements. Complementary measurements of polymer dynamics during shear rheology should also answer critical questions regarding the effects of crystallization and structural percolation on chain relaxation processes over a wide frequency range. To this end, coupled dielectric spectroscopy and rheology measurements are available commercially; these techniques have also been combined with small-angle neutron scattering at the National Institute of Standards and Technology to provide an effective probe of structure and dynamics in selectively-deuterated soft matter.^[36] These powerful techniques are absent from polymer crystallization studies.

V. Conclusions

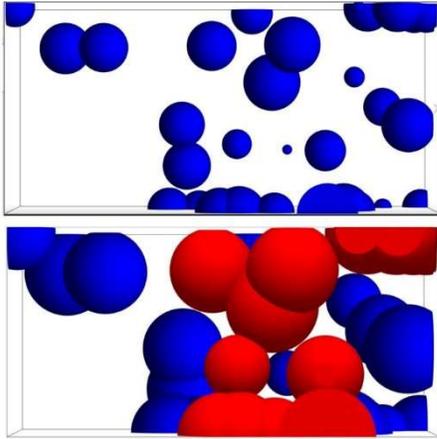
The rheology of polymer crystallization remains an active area of study, but efforts to probe the crystallization process by rheology alone cannot deliver sufficient insight. Simultaneous measurements of rheology and crystallization, however, provide a direct relationship between rheology and crystallinity that can be used to develop and probe models for the evolution of rheological properties during crystallization. It is from these measurements that semicrystalline domains (spherulites) and superstructures of impinged semicrystalline domains arise as the dominant rheology effect during crystallization, and the percolation of superstructures across the gap in the rheometer dictates the measured liquid-to-solid transition. A generalized effective medium model can describe the evolution of the viscoelastic shear modulus during crystallization, including finite size effects when single spherulites grow large enough to span the rheometer gap. These percolation concepts, as well as novel developments in the rheology of crystallization, can be readily studied by combined rheology-crystallinity measurement techniques that are as-yet unapplied to the problem.

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How does a polymer transition from a molten, flowable melt to a viscoelastic solid? This Perspective details efforts to answer that question via novel measurements and an effective medium model. Simultaneous crystallinity and rheology measurements indicate that spherulites are a dominant rheology modifier, which directly affects conceptual thinking regarding semicrystalline polymer processing and crystallizing polymer rheology.