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Kinetics of isothermal crystallization in isotactic polypropylene monitored with rheology and Fourier-transform rheology

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Abstract

Linear and Fourier-transform rheology were used to study the influence of the oscillatory shear amplitude, γ_0 , on the isothermal crystallization at 140 °C of three commercial isotactic polypropylenes. The development of the crystallization was monitored through the time dependence of the dynamic storage modulus, $G'(t)$, and the normalized intensity of the third harmonic of the stress waveform, $I_3(t)$, a quantification of the degree of nonlinearity under oscillatory shear conditions. A change in the exponent, n , of the power law describing growth, according to $G'_{norm}(t) \sim t^n$, was observed at $t \sim 4$ h. For $t < 4$ h, n was between 3 and 4. This change in growth kinetics was also accompanied by a maximum in $I_3(t)$. Below $\gamma_0 = 0.05$, these results were independent of the applied strain amplitude. Above $\gamma_0 = 0.05$, failure of the polypropylene in the parallel plate geometry due to stress build-up was often observed in the late stages of crystallization. This was accompanied by a sharp decrease of $G'(t)$, and a simultaneous sharp increase of $I_3(t)$. Additionally, the presence of even harmonics in the spectrum was observed after failure. Notably, a plateau of $I_3(t)$ at least 1 h before actual failure indicating a greater sensitivity to its onset than that of $G'(t)$.

1. Introduction

Linear rheology via sinusoidal oscillation has become a well-established method for determining the mechanical properties of (e.g. polymeric) materials. The related theoretical aspects for the linear response regime are documented in several textbooks [1, 2]. Rheological characterization under nonlinear flow conditions is on the other hand of major interest but not as easy to accomplish, quantify, or interpret as in the linear case. One sensitive technique which attempts to gain specific information about the nonlinear regime is Fourier-transform (FT) rheology [3–6]. In this technique, an oscillatory strain is applied at a given

frequency, $\gamma(t) = \gamma_0 \sin(\omega_1 t)$, where γ_0 is the strain amplitude and $\omega_1 (=2\pi\nu_1)$ is the radial frequency. Sufficiently large strain amplitudes generate a stress response that is composed of the fundamental and progressively weaker higher-harmonic contributions at odd multiples, $\omega_1, 3\omega_1, 5\omega_1, \dots$ of the excitation frequency [7]. Each higher-harmonic stress component is characterized by an intensity and phase relative to the excitation frequency. I_n denotes the intensity (strictly, the amplitude in Fourier space) and ϕ_n denotes the phase of the n th harmonic.

In this work [8, 9] FT rheology was used to study the influence of oscillatory shear amplitude on the crystallization kinetics of isotactic polypropylene. The time dependence of the developing structure was monitored using both the dynamic elastic modulus, $G'(t)$, and the third-harmonic intensity, $I_3(t)$. The effects of molecular weight and polydispersity were investigated by comparing the results obtained for three commercial, unmodified polypropylenes. The sensitivity of the growth to the isothermal crystallization temperature was also briefly examined.

2. Theory

The explanation for the appearance of higher harmonics under oscillatory shear can be found in the literature [6–8] and therefore only a brief and simplistic explanation for a dominantly elastic material is given here. We start with the basic equation for elasticity:

$$\tau = G\gamma. \quad (1)$$

We assume subsequently a non-Hookian elasticity and expand the shear elasticity as a power series with respect to the shear amplitude in which only even exponents occur. This restriction is due to the symmetry of the underlying strain tensor or, in simple terms, the elasticity depends only on the absolute value of the strain and not on the direction of shear:

$$G = G_0 + a\gamma^2 + b\gamma^4 + \dots \quad (2)$$

Combining the applied oscillatory strain, in complex notation, with equations (1) and (2) gives the following result for the time dependence of the stress:

$$\begin{aligned} \gamma(t) &= \gamma_0 \sin(\omega t) \sim e^{i(\omega_1 t)} \\ \tau(t) &\sim G\gamma(t) \sim Ge^{i(\omega_1 t)} \\ \tau(t) &\sim [G_0 + a\gamma^2 + b\gamma^4 + \dots]e^{i(\omega_1 t)} \\ \tau(t) &\sim G_0 e^{i(\omega_1 t)} + ae^{i(3\omega_1 t)} + be^{i(5\omega_1 t)} \dots \end{aligned} \quad (3)$$

A FT [4, 10] of the time-dependent stress can then unravel the intensities and phases in the Fourier spectrum at $\omega_1, 3\omega_1, 5\omega_1, 7\omega_1, \dots$

3. Experimental results

Three isotactic polypropylenes, kindly provided by the BASF-AG, Ludwigshafen, Germany, were chosen for this study. Their molecular characteristics are displayed in table 1.

Table 1. Molecular and thermal characteristics of three industrial polypropylenes chosen for study. The melting temperatures were obtained via DSC at $+10^\circ\text{C min}^{-1}$. The samples were stable to $\sim 300^\circ\text{C}$, from thermogravimetric measurements.

	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	M_w/M_n	T_m (°C)
PP1	270 000	640 000	2.4	155
PP2	190 000	505 000	2.7	158
PP3	270 000	625 000	2.3	158

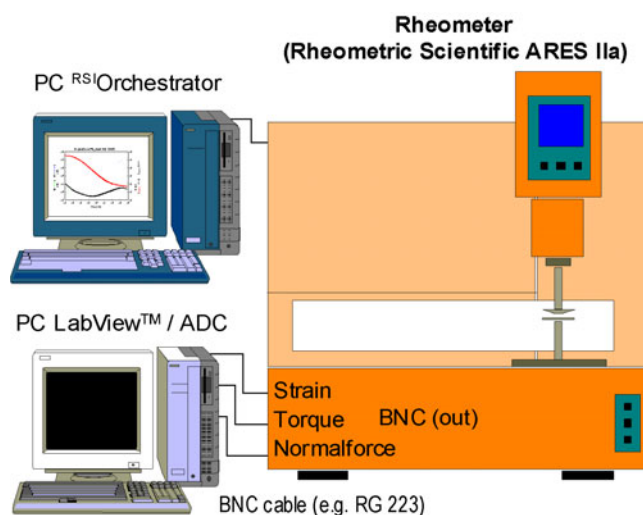


Figure 1. A schematic diagram of the set-up used in the linear and FT rheology isothermal crystallization experiments, comprising the ARES system and computers for equipment control and Fourier analysis via the stress waveform.

(This figure is in colour only in the electronic version)

The oscillatory shear measurements were carried out with a conventional strain-controlled rotational rheometer (ARES IIa, Rheometric Scientific). The 8 mm parallel-plate geometry was found to give access to the appropriate range of stresses encountered during crystallization, and was the only geometry used throughout the isothermal crystallization experiments. Samples were prepared by melt-pressing into 8 mm discs at 210 °C under vacuum for at least 1 h. The samples were first equilibrated in the rheometer at 200 °C under flowing N₂ to erase the thermal history, and then quenched *in situ* to the crystallization temperature, $T_c = 140$ °C. Following the quench, the ambient chamber air showed an undershoot of 3 °C; this was followed by equilibration at T_c accurate to within ± 0.1 °C after 4–5 min. The strain amplitude was then immediately applied following this equilibration. The crystallization isotherms were then monitored for 10–12 h, until the crystallization plateau was reached. The samples PP1, PP2, and PP3 were each measured at an excitation frequency, $\nu_1 (= \omega_1/2\pi)$, of 1 Hz and at a strain amplitude, γ_0 , of 0.005, 0.01, 0.02, 0.05, and 0.10. To examine the sensitivity of growth rates to temperature, additional measurements were made on PP1 at crystallization temperatures of 139 and 141 °C.

The parameters used to monitor the crystallization were the storage and loss moduli, $G'(t)$ and $G''(t)$, and the intensity of the third harmonic of the stress, $I_3(t)$, here normalized by the intensity of the first harmonic (i.e. bulk stress). Our current implementation of FT rheology, shown in figure 1, provides access to the full time-dependent stress function, and therefore the analysis of both the intensities and phases of all higher harmonics of the stress response; however, we chose for simplicity to monitor only the intensity of the third harmonic, a capability currently available directly in the commercial instrument software. The modulus data were reduced using the formula $G'_{norm} = (G'(t) - G'_i)/(G'_f - G'_i)$, where the initial modulus, G'_i , was defined as the lowest modulus observed at early times (typically at 0.5 h, reflecting the thermal relaxation time following the quench), and the final modulus, G'_f , was defined to be that at 10 h. Since the response at $\nu_1 = 1$ Hz was dominated throughout the crystallization by the storage modulus (G''/G' was ~ 0.7 at 1 h and ~ 0.15 after 10 h), we did not incorporate a

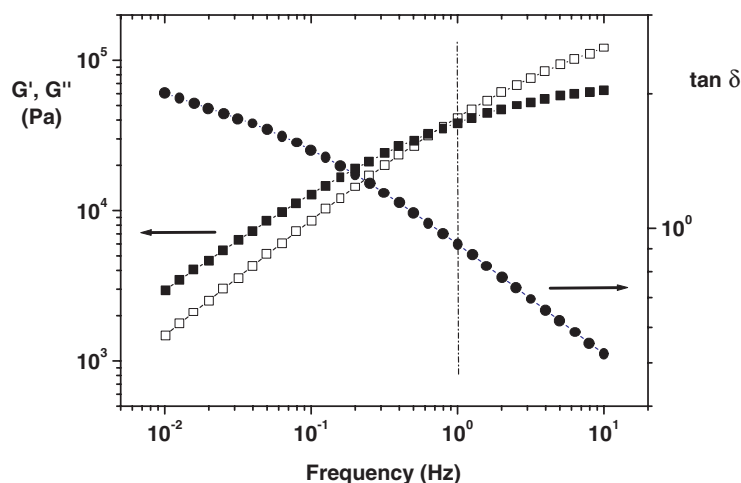


Figure 2. Linear flow properties of PP1 at 180 °C. The vertical line at 1.0 Hz indicates the frequency which was chosen for subsequent monitoring of the time-dependent crystallization after quenching to 140 °C. At 180 °C, $\tan \delta = 0.9$ at this excitation frequency, while at 140 °C (not shown) $\tan \delta = 0.7$ before crystallization; the response is therefore dominantly elastic.

full mechanical model of G' and G'' to describe bulk solidification. We assumed instead that $G'(t)$ was directly proportional to the extent of crystallization. This assumption is valid for early stages of crystallization, while for late stages the linear relation no longer holds [11].

4. Results

The linear rheological properties of PP1 in the melt at 180 °C, at least 20° above the nominal melting point, are shown in figure 2. Within the typical measurement window of the rheometer, from 0.01 to 10 Hz, the material response is dominated by the crossover between entanglement and flow dynamics. The crossover between G' and G'' at ~ 0.8 Hz indicates that the characteristic relaxation time is of the order 1 s for PP1 at 180 °C. Above ~ 0.8 Hz, the material response is largely elastic ($\tan \delta \equiv G''/G' < 1$) due to the restriction of the flow by chain entanglements on this timescale. Below ~ 0.8 Hz, the material response is viscous in character ($\tan \delta > 1$) and is dominated by the crossover from the entanglement plateau to flow dynamics. In the zero-frequency limit, the usual power laws for viscous flow apply: $G' \sim \omega^2$, $G'' \sim \omega^1$ [1]; however, this regime is not fully reached at the lowest measured frequency of 0.01 Hz.

No significant difference in linear flow properties was observed between PP1, PP2, and PP3 at 180 °C, suggesting that the bulk flow properties on this timescale are insensitive to the small changes in molecular weight and polydispersity of these polypropylenes. The characteristic times were all ~ 1 s at 180 °C. Subsequent isothermal crystallizations of the three polypropylenes were performed at $\nu_1 = 1$ Hz after the quench to 140 °C, as shown by the vertical line in figure 2. At the excitation frequency of 1 Hz, $\tan \delta$ was ~ 0.9 at 180 °C and ~ 0.7 at 140 °C (before crystallization), and therefore dominantly elastic, reflecting the weak (Arrhenius) temperature dependence of the flow properties. This is in accordance with the flow behaviour of other linear polymers well above the glass transition [1].

The isothermal crystallization rates showed a more sensitive dependence on the molecular parameters. The isotherms for PP1, PP2, and PP3 are compared in figure 3. The time at which the crystallinity has achieved half its ultimate value, $\tau_{1/2}$, is an estimate of the overall

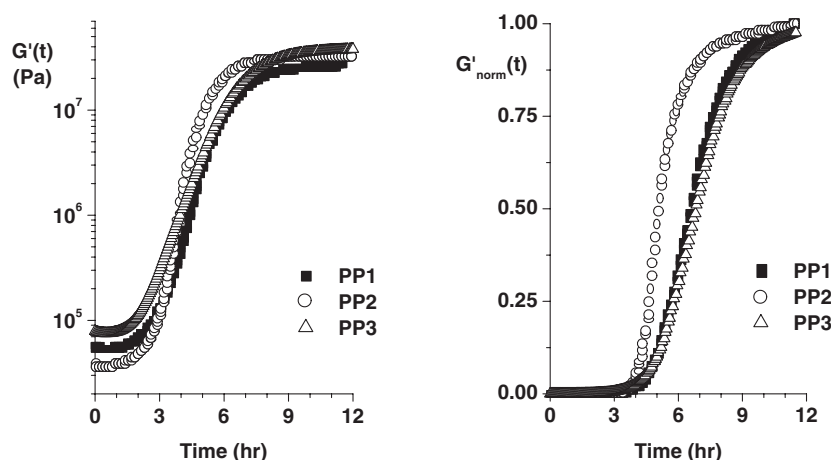


Figure 3. The time evolution of the dynamic elastic modulus for PP1, PP2, and PP3 at $T_c = 140\text{ }^\circ\text{C}$. The raw data are shown in (a) and normalized data in (b), as discussed in the text. The lower M_w of PP2 leads to faster crystallization, while the other two samples show roughly the same growth rates. The conditions of measurement were $\nu_1 = 1\text{ Hz}$ and $\gamma_0 = 0.02$.

crystallization rate. Using our definition, this is simply the time when $G'_{norm} = 0.5$. For both PP1 and PP3, $\tau_{1/2} = 7\text{ h}$, while for PP2, $\tau_{1/2} = 5\text{ h}$; with only minor differences in polydispersity between the samples, and no unexpected variations in backbone tacticity, this 2 h reduction of the crystallization time is most likely related to the lower M_w of this grade of polypropylene.

With these sample differences taken into account, we can proceed with the results from isothermal crystallizations, beginning first with the low-strain-amplitude measurements. In figure 4 the normalized elastic modulus, $G'_{norm}(t)$, is displayed along with the normalized intensity of the third harmonic of the stress, $I_3(t)$, observed during isothermal crystallization of PP1 at $140\text{ }^\circ\text{C}$. Data are shown for three strain amplitudes, $\gamma_0 = 0.005, 0.01, \text{ and } 0.02$, and are displayed on a log–log scale to clearly show the power-law dependence of the growth kinetics. Two features can be noted from the time dependence of the elastic modulus. First, at early times, until about 3 h, growth follows a power law with an exponent between three and four. Second, beyond about 4 h, more rapid growth occurs, as reflected in the steep increase in slope. Simple models of spherulitic growth are well known to capture the essentials of the early-stage growth [12, 13], and predict that the time dependence of the volume fraction of crystals (here assumed directly proportional to G'_{norm}) will follow a $\sim t^3$ power law for three-dimensional growth before crystal impingement, while the spontaneous appearance of additional nucleation sites alters the prediction to $\sim t^4$. The power-law behaviour shown by the time-dependent modulus at 1 Hz is therefore consistent with the presence of three-dimensional crystal growth before impingement. This is supported by independent crystallization experiments performed in an optical shear cell under the same conditions of oscillatory shear. It was observed at $T_c = 140\text{ }^\circ\text{C}$ that dilute crystallites were present at a size above optical resolution at times before 1 h.

The change in growth kinetics is reflected in the nonlinear response as well. Shown alongside the elastic modulus data in figure 4 is $I_3(t)$, displayed on a linear scale. It gives a general measure of the deviation from linear stress–strain response. As shown in the figure, $I_3(t)$ is dominated by noise at very early times, i.e. there is insufficient sensitivity of the torque

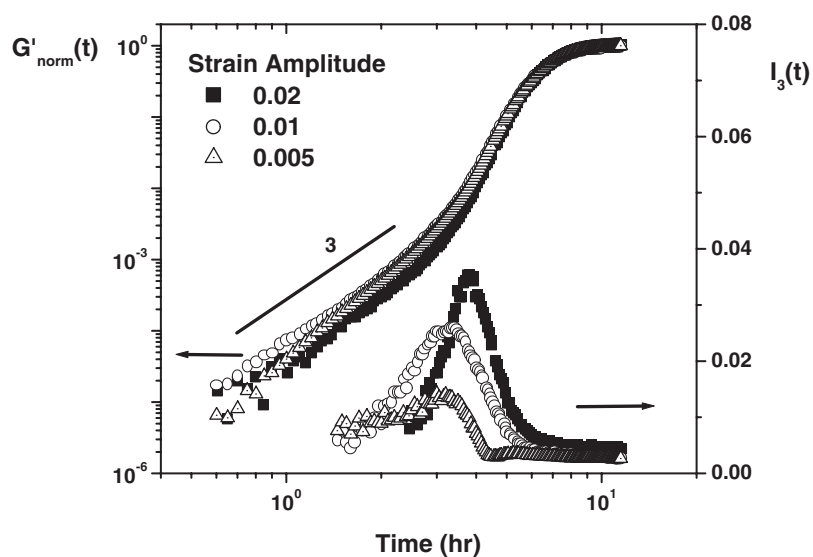


Figure 4. Comparison of $G'(t)$ and $I_3(t)$ during the course of crystallization of PP1 at low strain amplitudes. At early times, the growth kinetics shows a power-law dependence, $\sim t^{3-4}$, typical of growth in three dimensions before crystal impingement. A maximum in $I_3(t)$ is observed when the growth kinetics changes at about 4 h. The effect of the strain amplitude on the evolving structure can be clearly observed in $I_3(t)$ between 2 and 5 h, while $G'(t)$ appears to be independent of the strain amplitude. The conditions of the measurements were $\nu_1 = 1$ Hz and γ_0 as shown.

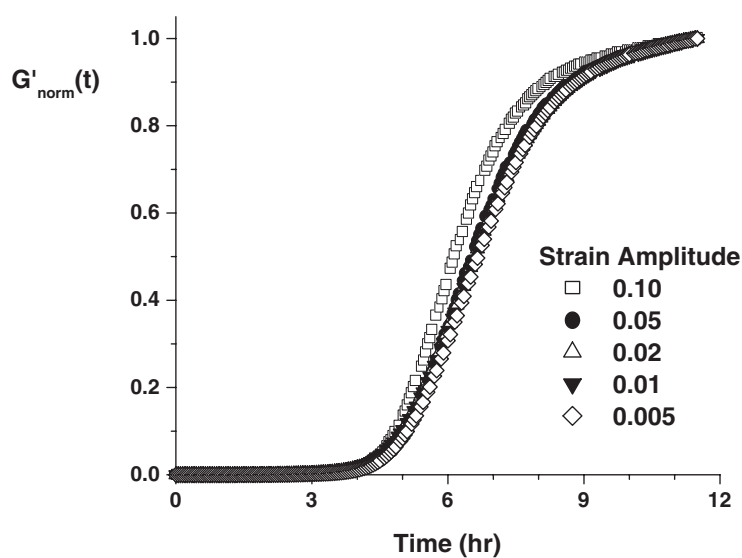


Figure 5. Comparison of crystallization isotherms of PP1 at $T_c = 140$ °C, showing a marginal effect of increasing strain amplitude on the bulk crystallization rate. Discernible effects are observed only for $\gamma_0 > 0.05$. The conditions of measurement were $\nu_1 = 1$ Hz and γ_0 as shown.

transducer, an effect which is somewhat compensated by employing higher strain amplitudes. At $t < 4$ h, $I_3(t)$ shows a continuous increase with time, while at $t > 4$ h, it shows a continuous decay with time until a terminal value is reached. Though not shown in the figure,

similar behaviour was noted for PP2 and PP3 at strains of 0.02 and lower. This maximum in $I_3(t)$, occurring simultaneously with the changes in $G'(t)$, indicates that there is a clear manifestation of a change in the type of nonlinear response at roughly 3–4 h. The evolving crystalline network appears to show the greatest nonlinearity, therefore, at times when the extent of crystallization is in the range of several per cent.

It is not clear, from either the microscopic observations or the evolution of the time-dependent elastic modulus, whether the distinct change in $G'(t)$ and the maximum of $I_3(t)$ evident at about 3 h are due to bulk crystal impingement or a mechanical effect arising from, for example, cooperativity of growing nuclei. It is well known that isotactic polypropylene displays a unique epitaxial growth process ('cross-hatching') when crystallized from the melt [14–16], in which splaying growth occurs tangentially from the primary radial lamellae. This process might be accompanied by significant changes in the mechanical properties evident at 1 Hz. Pogodina *et al* [17] have shown from frequency-dependent isothermal crystallization experiments that isotactic polypropylene undergoes a physical gelation transition at very low crystallinities, $\sim 2\%$, over a wide range of undercoolings, setting up a kind of structural network thought to guide the subsequent growth of crystallization in polypropylene. A similarity with our data might be suggested since these changes are also observed at very low crystallinities, $\sim 0.5\text{--}3\%$. Given the well-known risks of inferring details of the growing structures from bulk property measurements, especially in the more complicated case of polypropylene, these suggestions must remain speculative. Further structural analysis of these samples, for example by *ex situ* x-ray analysis or more extensive microscopic examination, might provide a better picture of the structural modifications suggested by the $G'(t)$ data to occur at about 4 h after the quench.

It can be further noted from figure 4 that the peak in $I_3(t)$ and its location along the time axis are correlated with the strain amplitude applied. In contrast, $G'(t)$ shows no significant dependence on the strain amplitude. This can be seen more clearly from figure 5, where there is no apparent deviation in the crystallization rates at strain amplitudes less than 0.05. This was in fact anticipated for $G'(t)$ at low strain amplitudes, since the dynamic modulus is an intensive quantity. Furthermore, drastic changes in the structure are not expected, because the shearing conditions are well below those reported to cause large-scale reorganization or shear-induced structures to appear [18], which would have readily observable effects on the moduli. It was unexpected that $I_3(t)$, also a normalized measure, proved sensitive to these low strain amplitudes. It would be interesting if these observations could be correlated with physical changes during crystallization, but, as discussed above, there is not yet a clear indication of the precise structural features to which $I_3(t)$ is sensitive during isothermal crystallization.

At the higher strain amplitudes investigated, $\gamma_0 = 0.05$ and 0.10 , failure occurred during many of the experiments. In figure 6, three typical isotherms are displayed, showing clear indications of sample failure either by sample delamination or, less likely, shear banding. As shown by the vertical lines, the failure can be observed from the rapid decay of $G'(t)$ and rapid increase of $I_3(t)$. Although the failures occurred at various times and values of the elastic moduli, they all occurred when the stresses were greater than 500 kPa, indicating that failure might be controlled by the bulk stress developed within the material. Notably, $I_3(t)$ has reached a plateau in all cases at least 1 h before failure occurs, while the continuous rise in $G'(t)$ indicates that the structure is still evolving. This result suggests that the nonlinear response displays a greater sensitivity to the onset of failure than the linear properties.

To examine this effect further, we undertook a full analysis of the stress waveform during high-strain-amplitude shearing, and observed the presence of even harmonics in the Fourier spectrum ($2\omega_1, 4\omega_1, 6\omega_1, 8\omega_1, \dots$) after failure, indicating that clockwise rotation was no longer equivalent to anticlockwise rotation under these conditions (see the theory section).

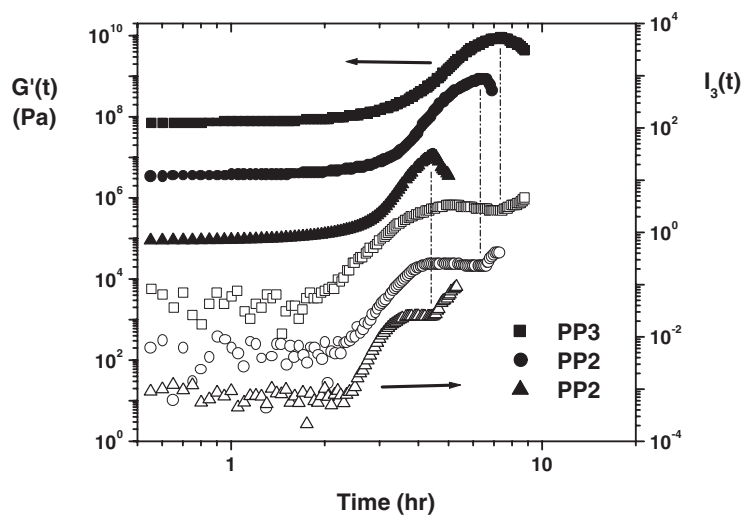


Figure 6. Representative isotherms for samples PP2 (2) and PP1 where failure occurred during the later stages of crystallization, all measured at $\gamma_0 = 0.10$. The vertical lines indicate when delamination/failure occurred. Notably, $I_3(t)$ reaches a plateau in all cases at least 1 h before the sharp increase at failure. The data are vertically shifted upward by zero, one, and two decades, respectively.

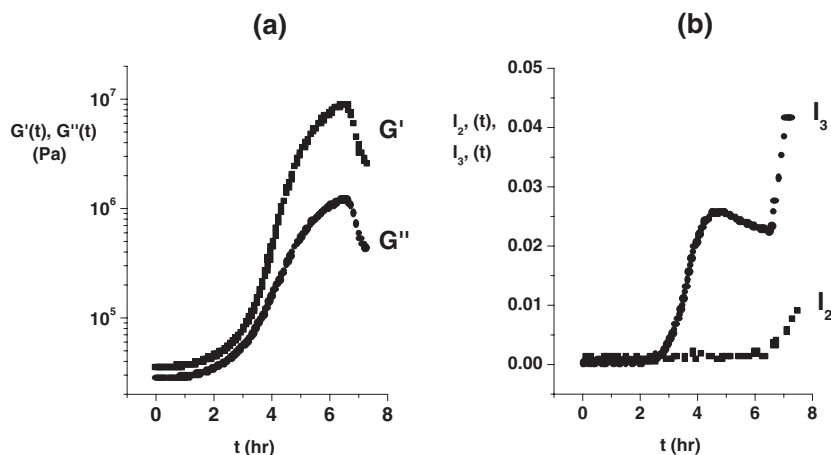


Figure 7. Comparison of the even- and odd-harmonic contributions appearing during crystallization to the elastic and loss moduli. Failure occurred at 6.5 h, where a significant even-harmonic contribution appears. As previously noted, $I_3(t)$ reaches a plateau well before failure—in this case 4 h before.

This effect is illustrated in figure 7, where both the even and odd harmonics are compared with the elastic and loss moduli. The same trend towards a plateau at $t = 4$ h is observed in $I_3(t)$, well before failure occurs at $t = 6.5$ h. After this point, a sharp rise in $I_2(t)$ is evident. It is possible that a stick–slip mechanism could generate this type of time-domain behaviour; further experiments and analysis should continue in this direction.

We finally note that the temperature sensitivity of the crystallization kinetics was checked by varying the crystallization temperature. For PP1, the crystallization half-time, $\tau_{1/2}$, was 2.7, 4.4, and 5.7 h at crystallization temperatures of 139, 140, and 141 °C, respectively. This

temperature dependence of the crystallization half-time was well described by the equation $\log(\tau_{1/2}) = 8.62 - 0.157(T_m - T_c)$, where the equilibrium melting point, T_m , was chosen to be 190 °C [19]. Although somewhat arbitrary, this representation of the crystallization rates as a function of temperature is nevertheless consistent with dynamic light scattering data in the literature [20].

5. Conclusions

Linear and FT rheology were used to study the influence of the oscillatory shear amplitude, γ_0 , on the isothermal crystallization at 140 °C of three commercial isotactic polypropylenes. The development of the crystallization was monitored through the time dependence of the storage modulus, $G'_{norm}(t)$, and the normalized amplitude of the third harmonic of the stress waveform, $I_3(t)$, a nonlinear parameter. Below $\gamma_0 = 0.05$, a change in growth kinetics was observed at $t \sim 4$ h, which was accompanied by a maximum in $I_3(t)$. Although $G'(t)$ was independent of the strain amplitude, $I_3(t)$ showed a sensitivity to strain amplitudes as low as 0.005. Above $\gamma_0 = 0.05$, failure of the polypropylene in the parallel plate geometry was often observed at the late stages of crystallization. Under these high-stress conditions, $I_3(t)$ was sensitive to the onset of sample failure well before the linear moduli indicated that sample failure had occurred. Additionally, even harmonics were observed in the spectrum to occur after failure.

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