Low-Field RheoNMR: Newly Developed Combination of Rheology and ¹H TD-NMR to Correlate Mechanical Properties with Molecular Dynamics in Soft Matter

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ABSTRACT

The newly developed low-field RheoNMR enables simultaneous measurement of the full rheological shear behavior (G', G'', LAOS, $I_{3/1}$, FT-rheology¹) and development of crystallinity⁷. To demonstrate the capabilities of this new technique, study on the crystallization of polyethylene as a function of crystallization temperature and applied shear are presented.

INTRODUCTION

Polyethylene (PE) and its copolymers constitute around 30% of the worldwide plastics production of 300 million tons per year². PE is used in a wide variety of consumer products². During thermoplastic processing, orientation of PE chains due to flow under supercooling causes shearinduced crystallization, which affects the final crystallinity³ and has a strong impact on the mechanical properties of the product. From the perspective of polymer processing, parameters such as molecular weight (M_w) and its distribution, branching properties and processing conditions, e.g cooling and deformation rate, play crucial roles in the resulting polymer crystallization³.

Low-field time domain (TD) NMR is a useful tool to quantitatively investigate and monitor the molecular dynamics in a crystallizing polymer⁴. Shear-induced crystallization experiments can be performed in a laboratory rheometer⁵. In order to gain a

deeper understanding of the material properties, one promising idea was to combine rheology with NMR. The newly developed, low-field RheoNMR set-up is a beneficial tool combining the full rheological shear characterization with measurement on the development of crystallinity in one experiment, without any possibility of different thermal histories. This technique allows the correlation of macroscopic properties and material microscopic molecular dynamics.

To demonstrate the capabilities of this new technique, this study examines the role of the temperature and applied shear on the crystallization kinetics of high density polyethylene (HDPE).

MATERIAL AND METHODS

HDPE with M_w =155 kg/mol and a polydispersity (PDI= M_w/M_n) of 15 was used in this work, provided by LyondellBasell, Frankfurt, Germany.

Differential scanning calorimetry (DSC)

A DSC 30 from METTLER was used to study the non-isothermal crystallization behaviour and the final crystallinity of the PE sample. To prevent oxidation, a nitrogen purge was used. Melting and crystallization peaks were obtained by multiple heating and cooling ramps applied to 10-20 mg of sample. To eliminate the thermal history, samples were heated at a rate of 10 K/min from room temperature to 190 °C and were kept at 190 °C for 10 min. The temperature was decreased to 20 °C and the sample was reheated to 190 °C using always the same rate (10 K/min). The same protocol was also used for the third cycle where the melting peak was measured to be 138 °C. Then, the melting peak was integrated and divided by the value of the heat of fusion of 100% crystalline PE (293.6 J/g)⁶ to obtain the percent crystallinity of the sample, which was found to be 67%.

RheoNMR

Our newly developed Rheo-NMR set-up is a combination of a custom-built low-field permanent 0.7 T magnet (30 MHz proton resonance) installed in a commercial highend strain-controlled rheometer (Rheometrics / TA ARES) using a Bruker minispec as the console/amplifier for the NMR probe (see Fig. 1). Machinable ceramic was used to make proton-free and nonconducting rheometric tools. The temperature range for the sample analysis can be controlled between -15 and 210 °C. A Halbach design allows the building of small magnets with field homogeneity $(\Delta B/B_0) \approx 1$ ‰ and a low stray field. NMR relaxation experiments determine the crystallinity via the remaining intensity of a Carr-Purcell-Meiboom-Gill echo (CPMG)^{4, 7}. The CPMG echo sequence provides information about the mobile (amorphous) part of polymer during crystallization. The CPMG decay curve was fitted using a biexponential function with amplitudes A_i and relaxation rates $1/T_{2,i}$ and back extrapolated:

$$I_{\rm CPMG} = A_a \exp(-t/T_{2,a}) + A_b \exp(-t/T_{2,b}) \quad (1)$$

Then, the backextrapolated I_{CPMG} was compared with the I_{CPMG} from a supercooled melt to obtain the crystallinity,

$$X_{\rm c} = 1 - \left[I_{\rm CPMG}(t) / I_{\rm CPMG}(t_{start}) \right], \tag{2}$$

where X_c is the crystallinity, and t_{start} is the time when the temperature reached the desired crystallization temperature (T_c).

The samples were press-molded under vacuum at 190 °C and 5 kN pressure for 15 min in a laboratory press to make 1 mm thick disks that were 13 mm in diameter. During the experiments, to ensure a homogeneous shear rate in the sample, a cone-plate geometry was used with a cone angle of 12° and a diameter of 13 mm. The large cone angle is necessary to have an enough sample to obtain a sufficient NMR signal.



Figure 1. Illustration of the new developed low-field RheoNMR set-up.

To evaluate the kinetic parameters of PE crystallization and correlate these parameters with rheological data, an Avrami model approach was used to fit all crystallinity curves up to 50 % of the final crystallinity. Up to this point, the Avrami theory provides a good fit because this is assumed to be the period of primary crystallization^{3, 8}:

$$X_{\rm c} = X_{\rm c}^{\infty} \left(1 - \exp[-(K.(t - t_0))^n] \right)$$
(3)

where X_c^{∞} is the final crystallinity and t_0 is the induction time needed for the creation of the nuclei at T_c; *K* and *n* are the Avrami rate constant and exponent, respectively. The exponent n reflects the dimensionality of the growth and the nucleation mode (heterogeneous and homogeneous).

The influence of several parameters such as temperature and the shear deformation rate on the resulting crystallization kinetics of PE was studied.

RESULTS AND DISCUSSION

In Fig. 2a typical crystallization experiment is illustrated. The sample was heated up to 177 °C (30 K above the equilibrium melting point, 141.5 °C^3) and held at this temperature for at least twenty minutes to erase the thermal history. Then, a rheological experiment at low strain amplitude, which does not influence the crystallization kinetics, (1% strain amplitude (γ_0) and 1 rad/s frequency (ω)) and an NMR experiment were started at the same time. The sample needed about two minutes to stabilize after the temperature was changed to the desired crystallization temperature.

The crystallization half time $(t_{1/2})$ and the induction time (t_0) are important parameters that are frequently used for the characterization of isothermal crystallization^{3, 8}. As can be seen in Fig. 2a, the rheological moduli (G', G'') show an Sshape behavior on a log-scale and reach a maximum plateau which enables to the use of G' to calculate $t_{1/2,rheo}$ of crystallization. To calculate $t_{1/2,rheo}$, the values for G' were normalized and the time value at one half of the maximum value for G' was taken as a $t_{1/2, rheo}$ (see Fig. 4a and b). The induction time value was taken as the value that makes the Avrami fit reach a correlation coefficient (R^2) that is at least 0.9990 ensure a good fit⁶. The change is only 25 s in the induction time by a 1.7 °C increase in temperature.

The gel point, as seen in Fig. 2a, is the point where the moduli change from a liquid like response to a solid-like response (G'=G''). It was used to evaluate the influence of crystallization temperature on the initial crystallization.



Figure 2. The isothermal crystallization of HDPE was measured via RheoNMR at $\gamma_0=1\%$, $\omega=1$ rad/s; a) rheological moduli (*G'*, *G''*) and crystallinity (*X_c*) as a function of time at 123.9 °C, b) rheological moduli versus time at different temperatures, c) crystallinities, which were fitted by an Avrami model, versus time at different temperatures.

In Fig. 2b and c, the isothermal crystallization for HDPE was investigated to determine the crystallization kinetics as a function of temperature. The S-shape of the

rheological moduli reflects the viscoelastic properties of the undercooled melt with short plateaus and the later time long plateaus associated with the final spherulitic structures. The shapes of the rheological curves at different temperature were similar, that which shows the crystallization mechanism remains unchanged. Figure 2b shows the excellent overlay with only a small difference in the times of the short plateaus indicating the slight differences in the viscoelastic properties of the supercooled melt due to the different crystallization temperatures. Increasing the temperature slowed down the isothermal crystallization as expected. At lower temperatures, there is an increased tendency for slippage at geometry walls in the later stages of crystallization. The results from NMR show the maximum attainable crystallinity at 2250 s (see Fig. 2c), which decrease slightly with increasing crystallization temperature due to slower crystallization. In Fig. 2c, X_c shows behavior that looks like it is decreasing during cooling, but is in fact an artifact due to the signal intensity change.

For more detailed analyses, an Avrami model was fitted to the data to evaluate the kinetics (see Fig. 3).



Figure 3. Results for the Avrami fit to the data presented in Figure 2c.



Figure 4. a) Normalized *G'* as a function of the time and b) half times, c) gelation times and crystallinities at gel point as a function of the different temperature for the crystallization of HDPE.

The rate parameter *K* decreases by a factor of \sim 3 when the temperature is changed by 1.7 °C, whereas the exponent *n* increased from 2.3 to 3.2 indicating potantial change from 2-dimensional growth of the cystals to 3-dimentional growth (see Fig. 3). It is important to mention that Zhuravlev *et al.*⁹ observed homogenous nucleation only below

90 °C with an extremely high cooling rate of 10,000 K/s. Therefore, the nucleation mode can be assumed to be heterogeneous for isothermal crystallization of HDPE with a \sim 30 K/min cooling rate via RheoNMR.

Fig. 4b and c show values for $t_{1/2,rheo}$ and t_{gel} , which provide information about the effects of the temperature on crystallization. The $t_{1/2,rheo}$ values for crystallization increased monotonically from 435 s to 761 s, and t_{gel} changed from 276 s to 393 s with a 1.7 °C increased in temperatures due to slower crystallization. The $X_{c,gel}$ changed from 0.7 to 1.9% with increasing temperature.



Figure 5. Direct correlation between macroscopic mechanical properties (rheological moduli (G', G'')) and microscopic molecular dynamics (crystallinity) as a function of temperature for HDPE.

Direct correlation of the changes in the macroscopic mechanical properties (rheological moduli) and the microscopic molecular dynamics (crystallinity) is shown in Fig. 5. Here it can be seen that for the moduli at lower temperatures (123.6 and 123.9 °C) were higher than at high temperatures (124.9 and 125.3 °C) between 0% to 30% crystallinity, which could be due to differences in the morphology of the crystals.

It is important to separate the effect of shear-induced nucleation from subsequent crystal growth. Applying steady shear in the melt state causes the formation of precursors in the form of liquid fibrils¹⁰, which can then be cooled to observe quench crystallization

under small amplitude oscillatory shear¹⁰. By applying steady shear (2/s for 11s) to the sample before crystallization, the actual conditions for processing were mimicked in Fig. 6a.



Figure 6. The isothermal crystallization is compared with a pre-shear experiment at $\gamma_0=1\%$, $\omega=1$ rad/s at 123.6 °C for HDPE; a) rheological moduli (*G'*, *G''*) and crystallinity (*X_c*), which were fitted using an Avrami model, as a function of time, b) direct correlation between rheological moduli (*G'*, *G''*) and the percent crystallinity.

In Fig. 6a, it can be seen that with preshear enhanced crystallization. The $t_{1/2,rheo}$ and t_0 decrease by 42 s and 17 s, respectively with pre-shear. The rate parameter increase by a factor of ~ 1.2 and the exponent *n* increased from 2.8 to 3.2 with pre-shear (see Table 1), while attaining the same final crystallinity. Pre-shearing did slight increase the rate of crystallization, but did not change the dependence of *G'*, *G''* on the degree of crystallinity (see Fig. 6b). This indicates that the morphology of the sample was not affected by the applied pre-shear when the sample was molten.

X _c =25%	K [1/s]	n [-]
Xc	3.3×10 ⁻³	2.8
X_c with pre-shear	4.1×10-3	3.2

Table 1. Results for the Avrami fit to the data presented in Figure 6a.

CONCLUSION

The novel characterization technique low-field RheoNMR provides the full rheological shear characterization with simultaneous monitoring of the molecular dynamics to avoid thermal conditions (temperature gradient, absolute temperature difference). Macroscopic material properties and microscopic molecular dynamics can be correlated via this method. To display the possibilities of this new method, study on the isothermal crystallization of PE including the temperature dependency and effect of preshear on the crystallization kinetics were presented. The increasing the degree of crystallinity the isothermal during crystallization experiment was measured via TD NMR and the data was evaluated via using the CPMG echo sequence. Kinetic parameters (K, n) were determined by fitting an Avrami model up to 50% of the final crystallinity. Α 1.7 °C increase in temperature caused a factor of ~3 decrease in K. And the change in the value for exponent n indicates a potential change in the type of crystal growth from disks ($n\approx 2$) to spherical ($n\approx3$). The nucleation mode was assumed to be a heterogeneous nucleation based on the literature due to the low cooling rate of the device. The $t_{1/2, rheo}$ values showed an increase monotonically from 435 s to 761 s, and tgel changed from 276 s to 393 s with a 1.7 °C increase in temperatures. The $X_{c,gel}$ changed 0.7 to 1.9% with increasing from temperature. The results showed the crystallization was slower when the crystallization temperature increased. Applying a short time pre-shear in the melt

state enhances the crystallization, but did not change the dependence of the rheological moduli on the degree of crystallinity, which may indicate that the morphology of the sample was not affected. This unchanged morphology should be confirmed via XRD as a next step. Low-field RheoNMR enables a clear evaluation of temperature and pre-shear effects on the isothermal crystallization kinetics. Furthermore, this new characterization technique can be used to study gelation or curing reactions and, in the case of polymer crystallization, the influence of pre-shear, high strain amplitude, temperature, additives, M_w , PDI and branch or tacticity characteristics on the isothermal crystallization process.

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