Supporting information:

Effect of thermal history and shear on the viscoelastic response of iPP containing an oxalamide based organic compound.

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Supporting Information: 16 pages, 11 Figures
Molecular modelling protocol and findings

This section details the method by which the molecular weight distribution (MWD) of the dangling arms has been obtained. First, a log-normal distribution having an average molecular weight \( M_w \) of 310 kg/mol and polydispersity of 3.4 was constructed. Such a distribution is supposed to characterize the pure iPP melt. Nevertheless, since changes in the MWD of the iPP chains are not expected to occur by the addition of very low amounts (concentrations) of nucleating agent (OXA3,6), we have assumed that the MWD of the iPP chains in the systems containing OXA3,6 can be described by the same log-normal distribution. Second, the aforementioned MWD \( (<M_w>=310\text{kg/mol}, \text{PDI}=3.4) \) was split in two components: one comprising the high molecular weight tail of the distribution, and another one comprising the remaining distribution. The high molecular weight tail was assigned to the long dangling arms that undergo contour length fluctuations (CLF) while the second component was designated to the linear chains of the bulk that are not absorbed on the NA crystallites, according to the hypothesis described in the manuscript. Since the concentration of nucleating agent is low (i.e. 1 wt%) we have made the assumption that the dangling iPP arms are a volumetrically minor component in the melt in comparison with the non-absorbed linear chains. In this respect, we have set the volume fraction of dangling arms equal to 0.1.

Concerning the high molecular weight tail assigned to the dangling ends, two slightly different scenarios were examined. In the first one, the MWD designated to the dangling ends was considered to be log-normal with an average molecular weight of 950kg/mol and polydispersity of 1.5. The remaining of the distribution was assigned to the linear component. In the second scenario, starting from a cut-off value until the upper limit of the distribution (highest \( M_w \)), molecular weights were allocated to the dangling arms. The \( M_w \) cut-off value corresponded to the point of the distribution at which the cumulative sum of the weight (volume) fractions was equal to 0.9. Here, this cut-off value is ~700 kg/mol. The MWDs
corresponding to the first and second scenarios are shown in Figures S1A and S1B, respectively. There, blue and red solid lines correspond to the non-absorbed linear chains and the dangling ends, respectively. The black solid line shows the sum of the two MWDs of the linear and branched components while the black symbols denote the log-normal distribution of the pure iPP melt having \( <M_w> = 310 \) kg/mol and PDI=3.4. As regards the branched component, in either scenario, a given molecular weight, \( M_w,i \), was split into two dangling arms of equal molecular weight (i.e. \( M_w,i/2 \)).

The corresponding rheological predictions of the two aforementioned scenarios are shown in Figures S1C and S1D, respectively. Up to frequencies of \( 0.5 \) s\(^{-1}\), both scenarios predict very similar responses, which coincide or lie slightly above the response of the pure iPP melt. Nevertheless, at lower frequencies, the responses of both scenarios start to considerably deviate from the response of the pure iPP melt. As expected, the slow-down of the dynamics is more profound in the second scenario. (That is, a profound shoulder appears in G’ and G’’, and the complex viscosity manifests a sudden upturn.) This is because the MWD of the branched component (dangling arms) excludes molecular weights lower than the cut-off value of \(~700\) kg/mol, unlike the log-normal MWD of the branched component of the first scenario. Of course, the left side of the MWD of the branched component, in reality, cannot exhibit such an unrealistic upturn; there should be a fraction of low molecular weight dangling ends. Hence, the actual MWD of the dangling ends is presumably a mixture of the two distributions hypothesized. It is worth commenting on the high frequency responses (\( \omega > 50 \) s\(^{-1}\)) seen at Figures S1C and S1D. The theoretical response of the mixture (linear plus dangling ends) coincides with the one from the pure iPP melt. This is because dangling arms are assigned molecular weights only from the high molecular weight tail of the distribution. In reality, however, there will be some dangling arms of lower molecular weights. Such arms undergo
CLF as well; the fact that the experimental data of the the iPP + 1\% wt OXA3.6 melt lie above the data of the pure iPP at those high frequencies might reflect the CLF of those arms.

**Figure S1.** A and B: MWD for the two scenarios described in the text. C and D: Comparison of the corresponding predictions against small amplitude oscillatory shear data at 160 °C. Here, black colour refers to the pure iPP melt while green color refers to the iPP + 1 \% wt OXA3.6 melt. Regarding the model parameterization, it is the following: $\tau_e = 2.72 \times 10^{-7}$ s, $M_e = 5$ kg/mol, $\rho$ (170 °C) = 0.75 g/cm$^3$.

We now elaborate on how the split of a given molecular weight, $M_{w,i}$, into two dangling ends of equal molecular weight was achieved in the so-called branch-on-branch (BOB) software [1]. The latter does not directly provide the option of having linear chains in the melt that undergo CLF only, which is essentially the case considered here. (To have CLF as the only means of
tube escape mechanisms, *i.e.* slow reptative motions are forbidden.) Therefore, the input chain topology to the software was that of symmetric three arm stars. However, instead of splitting a given molecular weight and volume fraction into three equal parts, we allocated two $M_{w,i}/2$ fractions only to two arms. Further, two of the three arms were assigned a weight (volume) fraction of $w_i/2$ whereas the third star-arm was given a volume fraction equal to zero. To verify that this approach did not cause any abnormal behaviour to BOB, we compared software predictions against predictions obtained from the time marching algorithm (TMA), a similar tube model which, however, can directly treat linear chains undergoing CLF only [2].

Figure S2, compares the predictions of the two approaches. Concerning BOB, a melt of symmetric three arm stars was considered, with one arm having zero volume fraction; further, the remaining two arms were assigned molecular weights from a log-normal distribution having a PDI of 3.4 and an average molecular weight of 155 kg/mol (*i.e.* half the average $M_w$ of the average $M_w$ of the pure iPP system comprising linear chains only.) As regards TMA, a polydisperse melt of linear chains was considered, having a long-normal distribution of $<M_w> = 310$ kg/mol and PDI = 3.4. The corresponding monodisperse cases were considered too. As far as other parameters are concerned, like entanglement relaxation time, molecular weight, and modulus, the values used in both cases were exactly the same. (See discussion below.) Overall the comparison is good, which justifies that the current treatment of linear chains relaxing only by CLF does not impose any unusual behaviour to BOB. The slight discrepancy seen at the terminal regime can be attributed to the (1) slightly different way the two models treat the effect of CR and CLF on the terminal relaxation of the longest chains of the distribution or/and (2) the possibility that the constructed MWDs for the star spans and the linear chains are somewhat different.
Figure S2. Comparison of BOB and TMA predictions at 160 °C for monodisperse and polydisperse melts of linear chains that undergo tube escape by CLF only. The predictions of BOB are shown by solid lines while the predictions of TMA by symbols. Black colour refers to the monodisperse case while red colour to the polydisperse case. \( \tau_e = 2.72 \times 10^{-7} \) s, \( M_e = 5 \) kg/mol, \( G_N^0 = 0.445 \) MPa for TMA and \( \tau_e = 2.72 \times 10^{-7} \) s, \( M_e = 5 \) kg/mol, \( \rho \) (170 °C) = 0.75 g/cm³ for BOB.

In an earlier work we used the BOB software to capture the linear viscoelasticity of several iPP industrial grades [3]. For most grades, the experimental master curves were reported at 170°C therefore the tube model parameters were optimized at that temperature leading to \( \tau_e = 2.0 \times 10^{-7} \) s, \( M_e = 5 \) kg/mol, and \( \rho = 0.75 \) g/cm³. To be consistent with our earlier work, we shifted the aforementioned entanglement relaxation time according to the horizontal shift factors used to obtain a master curve of the present pure iPP melt at 220 °C. In particular the horizontal shift factors of the iPP melt follow the WLF equation: \( \log(a_T) = -c_1(T-T_0)/(c_2+T_0) \) where \( T_0 = 220 \) °C, \( c_1 = 3.5556 \) and \( c_2 = 149.7 \) °C. The entanglement relaxation time at 160 °C
was therefore obtained using the above WLF equation leading to the value 
\[ \tau_e (160^\circ C) = 2.72 \times 10^{-7} \text{ s}. \]
As regards the temperature dependence of the polymer density, we have used the expression 
\[ \rho(T) = \rho_0 - c_3 T \] where \( \rho_0 \) is the polymer density at 0 °C. Here \( \rho_0 = 0.95 \text{ g/cm}^3 \) and \( c_3 = 1.17647175 \text{ g} \cdot \text{C}^{-1} / \text{cm}^3 \) to be consistent with \( \rho(170^\circ C) = 0.75 \text{ g/cm}^3 \). The code was run using \( \rho(170^\circ C) = 0.75 \text{ g/cm}^3 \) and a vertical shift was applied to \( G' \) and \( G'' \) according to \( b_T = \rho(T) T T_0^{-1} / \rho(T_0) \) to reflect the changes in the polymer density due to changes in the temperature. In conclusion, the theoretical predictions shown at Figures S1 and S2 for 160 °C are obtained using the aforementioned procedure. The same applies to the model predictions shown at Figure S3 for 220 °C.
Detailed rheological behavior of iPP samples

**Figure S3.** Elastic modulus (top, left), Viscous modulus (top, right), complex viscosity (bottom, left), and phase angle (bottom, right) versus frequency for iPP containing various amounts of OXA3,6 determined at 220 °C at 1% strain. Please note, the images display two frequency sweeps per sample representing the high and low frequency range. Furthermore, the black dotted lines represent the model predictions, as is described in the section above.
Figure S4. Elastic modulus (top, left), Viscous modulus (top, right), complex viscosity (bottom, left), and phase angle (bottom, right) versus frequency for iPP containing various amounts of OXA3,6 determined at 160 °C at 1% strain. Samples were loaded at 220 °C. Please note, the images display two frequency sweeps per sample representing the high and low frequency range.
Optical morphology of OXA3,6 in iPP under various conditions.

**Figure S5.** Optical morphology of iPP + 0.5 wt% OXA3,6 (top) and iPP + 1.0 wt% OXA3,6 (bottom), directly after loading at 180 °C (left), upon melting of the OXA3,6 particles (middle) and after recrystallization of the particles during cooling at a rate of 5 °C/min (right).
Rheological data on OXA3.6 in iPP with different loading procedure.

Figure S6. Elastic modulus (top, left), Viscous modulus (top, right), complex viscosity (bottom, left), and phase angle (bottom, right) versus frequency for iPP containing 0.5 wt% OXA3.6 determined at 160 °C at 1% strain. Samples were loaded at 180 °C to maintain the OXA3.6 morphology induced during processing or at 220 °C to enforce generation of large OXA3.6 particles through recrystallization. Please note, the images display two frequency sweeps per sample representing the high and low frequency range.
Figure S7. Elastic modulus (top, left), Viscous modulus (top, right), complex viscosity (bottom, left), and phase angle (bottom, right) versus frequency for iPP containing 1.0 wt% OXA3,6 determined at 160 °C at 1% strain. Samples were loaded at 180 °C to maintain the OXA3,6 morphology induced during processing or at 220 °C to enforce generation of large OXA3,6 particles through recrystallization. Please note, the images display two frequency sweeps per sample representing the high and low frequency range.
Figure S8. Temperature dependency of the complex viscosity as a function of thermal history of the sample containing 1.0 wt% OXA3,6, taken at a frequency of 1 rad/s and 1% strain.
Equatorial SAXS patterns upon heating of iPP samples having OXA3,6 after shear

| Temperature | iPP + 0.5 wt% OXA3,6 | iPP + 1.0 wt% OXA3,6 |
|-------------|----------------------|----------------------|
| 180 °C      | ![Image]             | ![Image]             |
| 190 °C      | ![Image]             | ![Image]             |
| 200 °C      | ![Image]             | ![Image]             |
| 210 °C      | ![Image]             | ![Image]             |

**Figure S9.** Equatorial SAXS patterns obtained upon heating from 180 °C to 210 °C for iPP having 0.5 and 1.0 wt% OXA3,6. Scale bar is similar as to that in Figure 9 in the manuscript.
Pressure difference in slit-flow protocol 2

Figure S10. Pressure difference (ΔP) observed during the application of the 10 consecutive shear pulses in MPR protocol 2, for the pure iPP sample (left) and the iPP containing 0.5 wt% OXA3,6 (right).
WAXD diffractograms in slit-flow protocol 2

| Pulse nr. | pure iPP | iPP + 0.5 wt% OXA3,6 | iPP + 1.0 wt% OXA3,6 |
|----------|----------|---------------------|---------------------|
| 1        | ![Image](1) | ![Image](2) | ![Image](3) |
| 3        | ![Image](4) | ![Image](5) | ![Image](6) |
| 5        | ![Image](7) | ![Image](8) | ![Image](9) |
| 10       | ![Image](10) | ![Image](11) | ![Image](12) |

(110)  (040)  (130)

Figure S11. 2D-WAXS patterns depicting the rise in (110), (040), and (130) reflections of α-phase kebab crystallites, as observed directly after the application of shear pulses 1, 3, 5, and 10 applied in slit-flow protocol 2. Note that the same scaling of the scattering intensity is used for all images (as used for Figure 9 of the original manuscript).

References.

[1] Das, C.; Inkson, N.J.; Read, D.J.; Kelmanson, M.A.; McLeish, T.C.B. Computational linear rheology of general branch-on-branch polymers. *The Journal of Rheology*, 2006, 50 (2), 207–234

[2] van Ruymbeke, E.; Keunings, R.; Bailly, C. Prediction of linear viscoelastic properties for polydisperse mixtures of entangled star and linear polymers: Modified tube-based model and comparison with experimental results. *J. Non-Newtonian Fluid Mech.*, 2005, 128, 7-22

[3] Wilsens, C.H.R.M.; Hawke, L.G.D.; Troisi, E.M.; Hermida-Merino, D.; de Kort, G.; Leoné, N.; Saralidze, K.; Peters, G.W.M.; Rastogi, S. Effect of Self-Assembly of Oxalamide Based Organic Compounds on Melt Behavior, Nucleation, and Crystallization of Isotactic Polypropylene. *Macromolecules*, 2018, 51 (13), 4882–4895