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Melt-Miscible Oxalamide Based Nucleating Agents and Their Nucleation Efficiency in Isotactic Polypropylene

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S Supporting Information

ABSTRACT: In this study, the performance of three aliphatic oxalamide based compounds as nucleating agent (NA) for isotactic polypropylene (iPP) has been evaluated. The NAs evaluated in this study contain two oxalamide motifs that are connected through linking spacers with 2, 3, or 4 methylene units in between the oxalamide groups, while containing flexible hexyl end-groups on the outside. It is demonstrated that the onset of crystallization in the presence of these NAs under quiescent conditions, generally observed around 120–125 °C, is strongly dependent on both the crystallization conditions and NA concentration. Although these oxalamide compounds are only moderately effective under quiescent conditions, they show promise for use under industrially relevant processing conditions that require high cooling and shear rates: When the NA is forced to undergo shear-induced self-assembly and shear-alignment during cooling, the onset of crystallization of the iPP phase is observed in SAXS at temperatures up to 140 °C.

INTRODUCTION

Isotactic polypropylene (iPP) is a commodity polymer that has shown significant commercial success because of its economically viable synthesis via Ziegler–Natta catalysis¹ in combination with its relatively high melting temperature and good combination of mechanical properties.^{2,3} The versatile nature of iPP, hence the ability to tailor its thermal and mechanical properties through copolymerization, has made it one of the most successful polymers in, for example, the packaging and insulation industries. In addition, iPP is widely studied in academia because of its ability to crystallize into various polymorphs, including the monoclinic (α -phase), trigonal (β -phase), orthorhombic (γ -phase), and mesophases.^{4–9} Though iPP is able to crystallize via homogeneous^{10,11} nucleation, additives are often accidentally or purposely introduced during synthesis or processing to accelerate the nucleation process and to control the ensuing crystal morphology. Examples of nucleating agents (NAs) for polypropylene include amide based organic molecules,¹² metal salts, and inorganic powders,¹³ among others. A well-known class of NAs includes the nanofibril network-forming sorbitol-based compounds that act as hybrid shish for the growth of monoclinic crystal kebabs.¹⁴ Such characteristic hybrid shish-kebab morphologies generally yield products with high clarity and low haze due to the small crystallite size.¹⁵ Another well-known class of NAs are salts of dicarboxylic acids, for example the calcium salt of suberic acid, that promotes the formation of the trigonal β -crystal phase. The resulting iPP products, predominantly

consisting of β -crystals, characteristically exhibit higher tensile strain and strength, and improved impact strength and toughness, compared to iPP containing monoclinic α -crystals.⁷ In addition to the introduction of NAs, the nucleation and crystallization of iPP can also be improved by the application of shear or flow during processing, in combination with high pressures.¹⁶ The application of sufficient flow during processing can promote the formation of point nuclei or fiber-like nuclei, resulting in spherulitic crystals and shish-kebab structures, respectively.^{17–21}

Recently, melt-soluble oxalamide-based compounds have been reported to successfully act as nucleating agents (NA) in polylactide,^{22,23} polypropylene,²⁴ and poly(hydroxyalkanoate)s.^{25,26} These agents are readily synthesized through the sequential reaction of bifunctional amines with oxalate derivatives, followed by the reaction with monofunctional amines (Figure 1). Because of this simple two-step condensation chemistry, both the side arms and the bridging linker between the oxalamide motifs can easily be varied and provide a toolbox to tailor the chemical structure of the NA for optimal nucleation efficiency for various polymers. Generally, the side arms of the NA promote dissolution and miscibility of these compounds in a polymer matrix, whereas the linking spacer in

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Figure 1. Schematic representation of the two-step synthesis route and final chemical structures of the nucleating agents (NA) used in this study. In the final structure, the side arms are displayed in red, the linking spacer in blue, and the oxalamide motifs in black.

between the oxalamide motifs influences the temperature at which melting and dissolution occurs in the polymer melt.²⁷ When selected judiciously, these NAs dissolve during the melt-processing and self-assemble upon cooling, driven by the hydrogen bonding of the oxalamide motifs. In turn, these self-assembled NAs provide a surface for nucleation of the polymer.

In this paper we report on the design process and parameters involved in the development and optimization of tailor-made aliphatic oxalamide-based NAs for *i*PP. We focus on varying the linking spacer between the oxalamide motifs and how it affects the self-assembly of the NA, its ensuing morphology, and its efficiency to nucleate the *i*PP homopolymer. Special attention is given to the effect of processing conditions to predict the performance of these NAs after processing. To minimize effects of unknown additives in the crystallization of *i*PP, for our studies, we make use of *i*PP material obtained directly after polymerization, thus containing no additives.

EXPERIMENTAL SECTION

Synthesis of Nucleating Agents. The NAs were synthesized in a two-step condensation reaction, as is shown in Figure 1. The compounds were synthesized through the dropwise addition of a solution of, for example, ethane-1,2-diamine (6.1 g, 0.1 mol) in THF (60 mL), to a 10-fold excess of diethyloxalate (146 g, 1 mol). The desired intermediate, ethyl 2-[2-[(2-ethoxy-2-oxo-acetyl)amino]ethylamino]-2-oxo-acetate (OXA2), precipitated over time while the mixture was stirred at room temperature. After 24 h of reaction time, the intermediate was isolated through filtration and dissolved in chloroform. After hot filtration, the chloroform was evaporated, and the intermediate was dried *in vacuo* at 80 °C overnight. In the second reaction step, 5 g of intermediate OXA2 was dissolved in 200 mL of chloroform together with 3.91 g of hexylamine, and the mixture was left to stir under refluxing conditions. Over time, the final product formed as a precipitate and was isolated through filtration after 48 h of reaction. After washing the sample twice with chloroform and twice with diethyl ether, the obtained crystals were dried *in vacuo* at 80 °C overnight. The other NAs were synthesized using the same procedure, but propane-1,3-diamine, as well as butane-1,4-diamine for the

linking spacer, was used. For more details related to the synthesis of the NA, we refer to our previous publications.^{24,27} All compounds were used as synthesized, without further purification.

Material Preparation and Blending Process. The developed compounds were melt-blended with Borealis *i*PP, obtained straight from the reactor (T1410, powder). Antioxidant Irganox 1010 (1 wt %) was added to all samples to limit degradation during processing. Both the NA and the *i*PP were dried at 80 °C overnight *in vacuo* prior to processing. The concentration of NA was varied from 0.01 wt % to 1 wt % and the samples were physically mixed prior to introduction in the extruder. Extrusion and blending was performed in an Explore twin-screw extruder with a barrel size of 4 g at 220 °C for 5 min at 100 rpm. After extrusion, the samples were cooled to room temperature and analysis was performed on the extrudates, unless mentioned otherwise.

Characterization Methods. DSC characterization was performed on the samples using a TA Instruments Q1000 DSC. All samples containing *i*PP were measured at heating and cooling rates of 10 °C/min up to a maximum temperature of 220 °C, unless mentioned otherwise. For the pure nucleating agents, the DSC experiments were performed up to a temperature above their melting temperature, which is up to 300 °C for OXA 2,6. The crystallization exotherm observed during cooling of the samples was used to define peak crystallization temperature (T_c) and onset of crystallization temperature (T_{ons}). The peak crystallization temperature is considered the peak value of the crystallization exotherm, whereas the intersection of the tangents of the baseline and the crystallization curve is considered to be the onset temperature for crystallization.

Polarization optical micrographs were taken between cross-polarizers on an Olympus BX53 microscope mounted with an Olympus DP26 camera and a Linkam hotstage. The samples were heated to the desired temperature (generally 200 or 220 °C) at a rate of 30 °C/min. After leaving the samples for 3 min in this isothermal condition, the samples were cooled at a specified cooling rate (generally 10 °C/min) until crystal-

lization was observed. Optical micrographs depicting the morphological changes were recorded during cooling.

Online 2D small-angle X-ray scattering (SAXS) experiments following the crystallization process were performed at the DUBBLE beamline (BM26B) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. As is reported by Bras and co-workers²⁸ and Portale and co-workers,²⁹ this beamline is particularly optimized for polymer science. Samples were mounted in a Linkam CSS-450 shear-cell, which was placed in the X-ray beam (wavelength was 0.1 nm). During the crystallization process, SAXS images were collected with a 2D Pilatus 1 M detector (169 mm × 179 mm active area) placed at 6 m distance from the sample. A standard rat tail tendon collagen fiber was used to calibrate the modulus of the scattering vector q -scale, using the position from diffraction peaks where $q = 4\pi \sin \theta / \lambda$ with θ being half of the scattering angle. All samples were cooled from 200 °C at a rate of 10 °C/min to the desired temperature. For samples that were not measured under quiescent conditions, a nominal shear pulse (60 s⁻¹, 3 s) was applied at a temperature between 200 and 170 °C, during continuous cooling. The shear pulse was evaluated at the optical window, located in-between the edge and the center of the circular sample. The maximum value in the Lorentz corrected 1D-SAXS pattern, obtained after integrating the meridional scattering signal, was identified as the long period (L_p) of the samples. The Lorentz correction has been applied through multiplying the measured intensity distribution by a factor q^2 .

The build-up in complex viscosity of the *i*PP blends during crystallization was followed during continuous cooling from 200 to 80 °C in a TA Instruments ARG2 rheometer. A parallel plate geometry having a diameter of 25 mm and gap of 500 μm was used to study the temperature dependence of the complex viscosity. The stress (100 Pa) and angular frequency (3 rad/s) were chosen such that the experiments were performed in the linear viscoelastic regime. To probe the effect of shear induced self-assembly and/or shear induced orientation of the NA in the *i*PP melt on the crystallization process, a shear pulse (60 s⁻¹, 3 s) was applied at 170 °C during cooling.

RESULTS AND DISCUSSION

Thermal Behavior and Phase Morphology of the NAs in *i*PP. The chemical structure and melting temperatures of various nucleating agents (NAs) evaluated in this study are listed in Figure 2. The names of the NAs, OXA X,Y, were chosen such that X reflects the number of methylene units in the linking spacer between the oxalamide groups and Y reflects the number of methylene units in the side arms. For the NAs

Nucleating agent		T_m (°C)
OXA 2,6		287
OXA 3,6		231
OXA 4,6		247

Figure 2. Chemical structure and the peak melting temperature (T_m), determined at a heating rate of 10 °C/min in DSC analysis, of the three NAs OXA 2,6, OXA 3,6, and OXA 4,6.

studied in this work, X is 2, 3, or 4 methylene units, while Y is kept constant at 6 methylene units.

The melting and crystallization behavior of the compounds in their pure state was evaluated using DSC analysis. For these three oxalamide-based compounds, one or two crystal-to-crystal transitions are observed prior to melting and during cooling after crystallization (Figure 3). The first crystal-to-crystal transition is observed around 50 °C for all three NAs and is associated with a release in constrained motion of the carbons next to the oxalamide groups, thereby weakening the hydrogen bonding.²⁵ Only for OXA 4,6 is a second phase transition observed at 164 °C. This phase transition is expected to be a structural reorganization induced by an increase in mobility of the linking spacer, as is also observed in comparable bisamide analogues.^{30,31} A similar phase transition was observed in comparable compounds having 6 methylene units between the oxalamide motifs.^{25,32} The absence of a second phase transition prior to melting of OXA 2,6 and OXA 3,6 is attributed to their short linking spacer-length that is expected to restrict their mobility, thereby preventing a strong increase in molecular motion upon heating. Final melting transitions of the NAs are observed at 287 °C (OXA 2,6), 231 °C (OXA 3,6), and 247 °C (OXA 4,6). The suppression in melting temperature of OXA 3,6 compared to OXA 2,6 and OXA 4,6 is likely a result from nonoptimal hydrogen bonding and a variation in crystal packing originating from the odd diamine spacer length.^{33–35} For reference, a detailed overview of the transition temperatures and enthalpies observed during heating and cooling of the NAs is provided in Table S1 and Table S2 of the Supporting Information.

Melt-extrusion was performed on *i*PP/NA blends to evaluate the effect of the variation in linking spacer length on the dissolution, the resultant morphology upon crystallization, and nucleation efficiency of the NAs in *i*PP. In the *i*PP/NA blends containing 1 wt % of NA or less, molecular miscibility between the *i*PP melt and NA is observed: The suppression in both the melting and self-assembly temperature of the NAs in the *i*PP melt is observed, with decreasing NA concentration, and is attributed to the dissolution of NA in *i*PP melt. The miscibility has been probed using polarization optical microscopy and DSC. The self-assembly temperature of the NA in samples having 0.1–1 wt % NA was determined from the second DSC cooling runs, performed at a cooling rate of 10 °C/min. We refer to the Supporting Information for the procedure used for determining the self-assembly temperature of the nucleating agents from the *i*PP melt. The DSC traces of *i*PP blends having different concentrations of OXA 4,6 are shown in Figure S1. No exotherm corresponding to the self-assembly of NA could be observed in DSC analysis for samples containing less than 0.1 wt % of NA. Therefore, for these samples, the self-assembly of the NA was determined using polarization optical microscopy only. Figure 4 shows the temperature dependency of the self-assembling process of various concentrations of the three NAs. In general, four characteristic regions can be identified in Figure 4. Region A denotes the temperature window where the *i*PP/NA blends are molecularly mixed. Upon cooling, the NA self-assembles into crystals, thereby entering region B where the NA resides in the solid-state in the polymer melt. Further cooling to region C eventually results in the interfacial crystallization of *i*PP on the surface of the NA crystals. Region D indicates the temperature range in which crystallization of *i*PP occurs, independent of the NA concentration. Figure 5 shows the characteristic polarization

Figure 3. DSC thermograms showing the second heating (A) and second cooling (B) run of the NAs OXA 2,6 (black line), OXA 3,6 (red line), and OXA 4,6 (blue line). Both the heating and cooling runs were performed at a rate of 10 °C/min.

Figure 4. Phase diagram showing the self-assembly of OXA 2,6, OXA 3,6, and OXA 4,6 in iPP/NA blends during cooling (10 °C/min), as a function of NA concentration. The dotted lines showing the trend are added to guide the eye. The self-assembly temperatures of the NA were determined via DSC analysis during cooling at a rate of 10 °C/min and confirmed using polarization optical microscopy. Optical microscopy was used to determine the self-assembly temperature for blends with NA concentrations lower than 0.1 wt %. The letters A–D refer to various regions observed in the phase diagram. For guidance, arrows depicting the crystallization processes piloted in Figure 5 panels A and B are drawn in the phase diagram.

optical micrographs depicting the morphological changes in blends having a low NA concentration (Figure 5A, 0.05 wt % OXA2,6) and blends with a high NA concentration (Figure 5B, 0.5 wt % OXA 4,6).

From Figure 4 it is evident that self-assembly of the NA is dependent on both the chemical structure and the concentration of the selected NA. In turn, the morphology and distribution of the self-assembled NA structures are also dependent on the cooling process. For example, in the iPP/NA blend containing 1 wt % OXA 2,6, the onset for self-assembly is already observed at 230 °C. The growth of the NA crystals, starting at such a high temperature, yields only a few crystals that continuously grow over time during the cooling process. As a result, by the time heterogeneous nucleation and crystal growth of the iPP phase is initiated, the NA is present in

the form of large micrometer-sized aggregates providing a low surface-to-volume ratio for heterogeneous nucleation. This is also the case for OXA 3,6 and OXA 4,6 blends having high NA concentrations (Figure 5b).

We observe that decreasing the NA concentration results in the self-assembly of the NA at lowered temperatures, thereby positively decreasing the NA crystal size and the resultant morphology on cooling, as is discussed in the section below. The cause for the formation of smaller crystallites is attributed to the self-assembly at higher supercooling, combined with the increased viscosity of iPP melt limiting chain diffusion for the crystal growth of NA. For example, in the optical micrographs in Figure 5A, no growth of NA crystals is observed on cooling the iPP/NA blend containing 0.05 wt % OXA 2,6 from the melt. Optically, the presence of the NA can only be realized by the evolution of a fibrillar crystal morphology of the iPP phase, starting at 134 °C. This fibril growth indirectly indicates that OXA 2,6 has self-assembled during cooling and effectively provides a surface for heterogeneous nucleation, while having crystal dimensions below the resolution of the optical microscope. Unlike OXA 2,6 iPP/NA blends, iPP/NA blends containing 0.1 wt % of OXA 3,6 or OXA 4,6 or less do not exhibit any self-assembly or enhanced nucleation efficiency. This indicates that OXA 3,6 and OXA 4,6 require a minimum concentration of 0.1 wt % to self-assemble on cooling at a rate of 10 °C/min. Furthermore, this also confirms that the increase in nucleation efficiency requires phase separation followed by crystallization of NA in the polymer matrix.

From the data described above, it may be clear that the NA morphology after phase separation is highly dependent on both the concentration and the self-assembly temperature (hence, on the supercooling). In fact, the self-assembly of the NA from the iPP melt seems to be highly analogous to the nucleation and growth of polymers: self-assembly at low undercooling results in a low number of nuclei and allows for the growth of large aggregates, whereas a large supercooling gives rise to a higher number of nuclei and generally yields crystallites with smaller size.³⁶

It should be noted that the control over the NA morphology after self-assembly is of crucial importance for the nucleation efficiency of the NA: Ideally, we would like to generate self-assembled NA aggregates with as high as possible surface-to-volume (S/V) ratio, since the NA surface governs the nucleation of the iPP phase. For example, the well-known sorbitol-based nucleating agents are reported to self-assemble

Figure 5. Optical micrographs, viewed between cross-polars, were recorded during cooling (10 °C/min) of an *i*PP/NA blend containing (A) 0.05 wt % OXA 2,6 and (B) 0.5 wt % OXA 4,6. For all *i*PP/NA mixtures, self-assembly of the NA occurs during cooling, followed by surface induced nucleation and growth of *i*PP crystals. Though the self-assembly of OXA 2,6 is not directly observed in polarization optical microscopy, the presence of NA is detected by the fibrillary-shaped *i*PP crystal growth starting at 134 °C. This fibrillar crystal morphology of *i*PP is expected to be the result of interfacial crystallization on the surface of NA crystals that are too small to be detected by light microscopy.

Figure 6. (a) Peak crystallization temperature and (b) onset of crystallization of the *i*PP phase as a function of NA concentration, as observed during the DSC cooling run (10 °C/min). The black dotted line indicates the peak and onset of crystallization for the extruded *i*PP that contains no NA.

into one-dimensional nanofibrils that are present as a network in the *i*PP phase.¹⁵ Because of their nanofibrillar network, imposed by the crystallographic restrictions of the sorbitol-based molecules that possess low, though evident, symmetry and directionality in assembly,^{37,38} these nucleating agents exhibit a large S/V ratio. As a result, a high number of *i*PP nucleation sites are provided, resulting in almost instantaneous nucleation and crystal growth upon cooling. In contrast, for the oxalamide-based NAs tested under quiescent conditions, the S/V ratio is dependent on the NA concentration: As discussed in the previous section, increasing the NA concentration effectively increases the NA aggregate size and thereby decreases the effective S/V ratio.

To probe this effect of the NA morphology on the crystallization behavior, we have evaluated the onset of crystallization and the crystallization peak of the *i*PP phase, as a function of NA concentration. Figure 6a shows the peak crystallization temperature observed in the second DSC cooling run, performed at 10 °C/min. Similarly, Figure 6b shows the onset of the crystallization process, determined from the same data curves. The onset and peak crystallization temperatures of *i*PP are extracted from the DSC traces used for determining the self-assembly temperature of the nucleating agents from the blends (Figure S1 of the Supporting Information).

The black dotted lines incorporated in Figure 6a,b indicate the peak crystallization temperature and the onset of

crystallization for pure *i*PP in the absence of NA. For OXA 2,6 it can be observed that both the onset of crystallization and the peak crystallization temperature decreases with increasing NA concentration. This indicates that the number of nuclei growing on the NA surface after self-assembly decreases with increasing concentration of OXA 2,6.

Interestingly, OXA 2,6 seems to exhibit the highest nucleation efficiency at concentrations between 0.01 and 0.05 wt %. This is not the case for OXA 3,6 and OXA 4,6, which do not self-assemble below a concentration of 0.1 wt %, as observed earlier. The DSC cooling traces of *i*PP containing 0.05 wt % OXA 3,6 and OXA 4,6, showing that the *i*PP nucleation is not hindered by the molecularly dissolved nucleating agents, are supplied in Figure S2 of the Supporting Information. Even though OXA 3,6 and OXA 4,6 do not self-assemble in concentrations below 0.1 wt %, they show an improved peak crystallization temperature and onset of crystallization at concentrations above 0.1 wt %, compared to OXA 2,6. For example, the onset of crystallization is observed at 124 °C at a concentration of 0.3 wt % OXA 4,6, whereas the onset of crystallization occurs 2 °C lower at 122 °C for the blend containing 0.3 wt % OXA 2,6. Increasing the NA concentration in blends containing OXA 3,6 or OXA 4,6 results in a further increase in the observed onset of crystallization. In contrast to the blends containing OXA 2,6, this indicates that the total number of nuclei growing on the available NA surface increases

Figure 7. Effect of NA morphology observed during cooling at various cooling rates in an *iPP* sample containing 0.5 wt % OXA 4,6. The cooling rates were only varied between 220 and 180 °C, which is the temperature window where self-assembly of OXA 4,6 occurs at this concentration. Cooling from 180 to 134 °C was performed at 10 °C/min and the sample was kept isothermal to evaluate the crystalline morphology of the *iPP* phase.

with increasing concentration of OXA 3,6 and OXA 4,6. For this data it may be clear that the S/V ratio of the NA after self-assembly, and hence the total number of nuclei per volume of NA, is highly dependent on both the chemical structure and the NA concentration.

To probe the effect of the NA on the crystal phase of the *iPP* after crystallization, WAXD studies have been performed on samples containing 0.5 wt % NA. The samples were heated to 200 °C and consecutively cooled at a rate of 10 °C/min to room temperature. After the samples were cooled, WAXD analysis was performed. In general, it is observed that the *iPP* phase in blends containing OXA 2,6 and OXA 3,6, despite the differences in NA morphology after self-assembly, crystallizes into the α -form. In contrast, the *iPP* containing OXA 4,6, crystallized under the same crystallization conditions, shows approximately 45% of the β -crystalline fraction (55% overall crystallinity). WAXD of the samples are provided in the Supporting Information section (Figure S3).

Effect of Cooling Rate on NA Morphology and Its Nucleating Efficiency. In the previous section, we evaluated the nucleation efficiency for various concentrations of NA in *iPP*. The main observation is that the nucleation efficiency, under quiescent conditions, is highly dependent on the resultant morphology of the nucleating agent, which in turn is dependent on the concentration of the NA. In addition, we observe that the NA morphology is also highly dependent on the processing conditions: Figure 7 shows the variation in OXA 4,6 morphology (0.5 wt %) after cooling from 220 to 180 °C with cooling rates varying from 1 to 30 °C/min. To recall, in this temperature window, the self-assembly of OXA 4,6 occurs at this concentration. This indicates that through varying the cooling rate, we also vary the time available for the NA to self-assemble. After the samples reached 180 °C, they were cooled at a constant rate (10 °C/min) to 134 °C and kept isothermal. During the isothermal crystallization at 134 °C, the crystallization process was recorded using polarization optical microscopy. In addition, an air-quenched sample was prepared through heating to 220 °C for 3 min, followed by removing the sample from the hot-stage and subsequently cooling it to room temperature in air. To investigate the resultant morphology of the nucleating agent in this air-quenched sample, the polypropylene crystals were molten by heating the air-quenched sample to 190 °C. To ensure complete melting of the *iPP* crystals, the sample was left under isothermal condition for 3 min leaving behind the NA aggregates. The resultant

sample with the NA aggregates was subsequently cooled to 134 °C (10 °C/min) and kept under isothermal conditions to record the optical micrographs between cross-polars during the crystallization process.

From Figure 7 it can be clearly seen that applying low cooling rates, for example 1 °C/min, results in the growth of large NA aggregates. Increasing the cooling rate decreases the aggregate size of the NA and increases the number of aggregates formed during cooling. In fact, the air quenched sample results in the formation of NA aggregates with presumably nanodimensions, since they are not visible by optical microscopy. Interestingly the onset of crystallization is observed at the same time for all tested samples at 134 °C and crystal growth proceeded at the same rate. Furthermore, what can clearly be observed for the samples that were cooled at a rate of 1 and 10 °C/min is that the *iPP* nucleation and crystal growth occurs on the surface of the OXA 4,6 crystal aggregates. However, due to the poor distribution of the nucleation sites at the aggregate surfaces, only part of the visible *iPP* phase is nucleated. For the morphologies generated at higher cooling rates, the NA is finely dispersed, and almost instantaneous nucleation and crystal growth is observed throughout the viewed area. This is clearly visible from the optical micrographs taken for the air-cooled sample in Figure 7.

DSC analysis was performed under the same conditions to identify the effect of the nucleating agent morphology on the crystallization curve during cooling, and the resultant DSC crystallization thermograms are shown in Figure 8. The DSC crystallization curves for *iPP* without NA (thus only containing 1 wt % Irganox 1010) and the blend containing 0.5 wt % of OXA 3,6 are supplied in the Supporting Information (Figure S4). From this data it is observed that allowing the nucleating agent to self-assemble at increasing cooling rates increases both the onset and peak crystallization temperature. The increase in nucleation efficiency at increasing cooling rates can directly be correlated to the improved S/V ratio of the nucleating agent; the improved S/V ratio results in the formation of more nuclei per volume NA upon cooling and hence, a faster increase of the crystalline fraction over time. To have further insight on the origin of the nucleation efficiency it is important to have atomistic level understanding on the structure evolution of the nucleating agent. This requires further investigation which at present is beyond the scope of the manuscript.^{39,40}

Effect of Shear on NA Morphology and Nucleation Efficiency. From the sections above it can be concluded that

Figure 8. DSC crystallization peaks observed during the cooling of *i*PP/NA blends containing 0.5 wt % OXA 4,6. Prior to crystallization of the *i*PP phase, the samples were cooled from 220 to 180 °C at a rate of 1, 3, 10, or 30 °C/min to vary the NA morphology. After an isotherm of 3 min, the crystallization transition of the *i*PP phase was recorded during continuous cooling at a rate of 10 °C/min.

the oxalamides under investigation show higher S/V ratio with increasing cooling rates, under quiescent conditions. To relate to the nucleation ability of the NAs under processing conditions, the self-assembly of the NAs under shear have been evaluated in polarization optical microscopy mounted with a Linkam shear-cell (Figure 9). Figure 9B shows that on

Figure 9. NA morphology observed at 170 °C of an *i*PP sample containing 0.5 wt % YD4,6. The samples were cooled at a rate of 10 °C/min from 220 °C. Micrograph A depicts the resultant morphology on cooling without application of any shear, micrograph B depicts the morphology after applying a shear pulse (3 s, 60 s⁻¹) at 180 °C, and micrograph C depicts the morphology after continuous shearing (60 s⁻¹) of the sample while cooling from 220 to 180 °C at 10 °C/min.

applying a shear pulse at 180 °C (60 s⁻¹, 3 s) during cooling (10 °C/min) promotes; (1) self-assembly of the nucleating agent in the shear direction, (2) shear alignment of the NA aggregates, and (3) a decrease in the overall aggregate size. A further improvement on the NA morphology along the shear direction is observed after the continuous application of shear (60 s⁻¹) while cooling from 220 to 180 °C at 10 °C/min (Figure 9c). The shear-promoted self-assembly in combination with shear-alignment of NAs is not uncommon, for example, similar behavior has been reported for the self-assembly of DMDBS or calcium/lanthanum complexes.^{41,42}

To follow the effect of shear-induced self-assembly and shear-alignment of the NA on the crystallization process of *i*PP, 2D-SAXS experiments were performed at the DUBBLE BM26b beamline at the ESRF in Grenoble (France). *i*PP/NA blends containing various amounts of NAs were prepared and mounted on a Linkam shear-cell, which in turn was placed in the X-ray beam. The samples were heated at 10 °C/min to 200 °C and were left for 5 min prior to cooling at a rate of 10 °C/min to 80 °C. A shear pulse was applied at a temperature

between 200 and 170 °C (60 s⁻¹, 3 s), while continuously cooling the sample at a rate of 10 °C/min, to induce the self-assembly of the NA and/or promote shear alignment of the aggregates along the shear direction. The shear pulse was applied above the melting temperature of the *i*PP phase to minimize the effects of flow-induced crystallization and to be able to focus on the effect of the nucleating agent on the *i*PP crystallization and its ensuing crystal morphology.⁴³ 2D-SAXS patterns were collected during cooling to evaluate the crystallization morphology of *i*PP. For comparison, a sample with DMDBS as nucleating agent was used. Figure 10A shows the protocol designed to control the thermal history. Figure 10B shows evolution of the long period during cooling the samples having 0.3 wt % NA, calculated from the meridional SAXS intensity. For the data in Figure 10B, the shear pulse was applied at 170 °C, while cooling at a rate of 10 °C/min. The long period at different temperatures was identified as the peak value after integration of the Lorentz corrected meridional data. Figure 10C depicts characteristic 2D SAXS patterns taken for the various samples during continuous cooling.

In Figures 6 and 8 we have observed that the quiescent crystallization of *i*PP in the presence of the oxalamide-based NAs increases the onset of crystallization from 115 °C to roughly 122–125 °C. The increase in the onset of crystallization is found to be dependent of the cooling rate, the chemical structure of the NA, the NA concentration, and the ensuing NA morphology. From the SAXS data obtained for pure *i*PP (without NA), the onset of crystallization is observed during cooling between 115–110 °C, which is in good agreement with the DSC data. This indicates that all molecular orientation, imposed by the shear pulse applied at 170 °C, has relaxed prior to crystallization of the *i*PP phase. Indeed, from Figure 10C we can observe an isotropic distribution in scattering intensity, thereby confirming the absence of shear-induced crystallization. Similarly, for the sample containing 0.3 wt % OXA 2,6, the application of the shear pulse has no significant effect on the crystallization of *i*PP since isotropic crystallization is observed upon cooling. However, in the presence of OXA 2,6, the onset in scattering intensity occurs around 120 °C. This value, correlating to the onset of crystallization, is in good agreement with the values obtained under quiescent conditions (Figure 6). For this sample it is likely that the nucleating agent was not molten while heating the sample to maximum 200 °C. To recall, the self-assembly temperature of OXA 2,6 at 0.3 wt % concentration lies well above 200 °C (Figure 4). As observed earlier, the OXA 2,6 crystals at these concentrations will be present as large micro-sized aggregates and will exhibit a poor nucleation efficiency due to their low S/V ratio. Furthermore, the isotropic SAXS pattern indicates that these aggregates are hardly influenced by the shear pulse and are not likely to align in the shear direction.

In contrast, when a shear pulse is applied at 170 °C in blends containing OXA 3,6 and OXA 4,6, upon continuous cooling at a rate of 10 °C/min, the onset of crystallization is already observed between 140 and 135 °C. This corresponds to a 10 to 15 °C increase in the onset of crystallization compared to crystallization under quiescent conditions. It is expected that this synergistic increase in the crystallization temperature after shearing blends containing OXA 3,6 and OXA 4,6 can be related to the shear-induced/shear-aligned NA morphology, as observed in Figure 9. In addition the application of shear further aligns nucleating agents and the chain segments along

Figure 10. (A) Schematic drawing of the thermal history designed to obtain oriented *i*PP morphologies after the application of shear in the *i*PP melt. The steps in experiment were performed as following: 1, heating (10 °C/min); 2, 5 min isotherm (200 °C); 3, cooling (10 °C/min) to 80 °C; 4, shear pulse (3 s, 60 s⁻¹, at 170 °C) applied during cooling run 3. (B) Peak value of the long period of the oriented *i*PP crystals growing during cooling at a rate of 10 °C/min, calculated from the meridional azimuthal intensity distribution after Lorentz correction. (C) Selection of the 2D SAXS patterns used for the determination of the long period. The shear-direction is indicated by white arrows for each experiment.

the flow direction which, similar to sorbitol derivatives, also suppresses the nucleation barrier and enhances the crystallization process.⁴⁴

When the shear-pulse is applied at a too high temperature, for example at 200 °C, no self-assembly nor shear-alignment of the nucleating agent aggregates is induced: Instead, isotropic self-assembly of the nucleating agents occurs upon cooling and no improvement in crystallization temperature (compared to quiescent crystallization) is observed upon further cooling. An example of such behavior is shown in Figure 11 for the sample containing 0.5 wt % of OXA 3,6: The growth of oriented *i*PP crystals is clearly observed at 140 °C after shearing at 170 °C, whereas the crystallization of the polymer is only observed at 120 °C when the shear pulse is applied at 200 °C.

For the 2D-SAXS patterns recorded for blends containing OXA 3,6 and OXA 4,6, after the application of shear at 170 °C, the observed scattering intensity exhibits lobes along the shear direction. This indicates that the *i*PP crystals grow perpendicular to the shear direction of the sample, which results in the crystals being periodically ordered along the shear direction. Such scattering is characteristic for semicrystalline polymers that exhibit a (hybrid) shish-kebab morphology.^{45,46} In addition, daughter lamella can be detected by the presence of

Figure 11. 2D SAXS patterns obtained during cooling and crystallization of *i*PP containing 0.5 wt % OXA 3,6 in the shear-cell setup. Isotropic crystal growth is observed at 120 °C when the shear pulse is applied at 200 °C. In contrast, when the shear-pulse is applied at 170 °C, oriented crystal growth of the *i*PP phase is already observed at 140 °C.

the weak horizontally spaced lobes in scattering intensity, perpendicular to the shear direction.⁴⁷

For the blend containing DMDBS, the SAXS images show the onset in crystal growth resulting from an hybrid shish-kebab morphology at 135 °C, after the application of shear at 170 °C prior to cooling. This onset of crystallization of *i*PP in the presence of 0.3 wt % DMDBS is in accordance with the

previous observations of Balzano and co-workers.⁴¹ DSC experiments under quiescent conditions (without the application of shear) were performed to identify the onset of crystallization during quiescent conditions (0.3 wt % DMDBS) and yielded an onset value of 132 °C. This indicates that the alignment of the DMDBS network can be achieved through the application of a shear pulse, but does not significantly influence on the onset of crystallization of the *i*PP phase compared to *i*PP/DMDBS blends crystallized under quiescent conditions. On comparing the performance of DMDBS with the oxalamide based nucleating agents it can be concluded that DMDBS exhibits superior nucleation efficiency under quiescent conditions due to its high S/V ratio. However, due to the improved shear induced/aligned NA morphology of the OXA 3,6 and OXA 4,6 blends, the onset of crystallization temperature is comparable to DMDBS in blends that are subjected to shear prior to or during cooling.

To make the demarcation between crystallization arising from the (a) *i*PP under quiescent conditions, (b) *i*PP after application of the shear pulse, (c) *i*PP in the presence of the nucleating agent under quiescent condition and, (d) *i*PP in the presence of the nucleating agent after application of the shear pulse, rheological studies have been performed.

To remove the sample history, the samples were loaded in the rheometer at 200 °C, having a parallel plate–plate setup, and subsequently cooled at a rate of 5 °C/min to 80 °C. During cooling, the buildup of the complex viscosity was monitored, and when required, a shear pulse was applied at 170 °C (60 s^{−1}, 3 s). This protocol was applied for pure *i*PP samples and for samples containing 0.5 wt % OXA 3,6 or OXA 4,6. It has to be noted that the shear pulse applied under these conditions in the rheometer results in a radial distribution of the shear rate in the sample, as is also the case for the experiments in the Linkam CSS-450 shear-cell. This implies that the experimental data obtained in the rheometer are averaged values of various shear rates, whereas the SAXS data obtained from the Linkam CSS-450 shear-cell are obtained at a fixed point, hence at a fixed shear rate.

Figure 12 shows the increase in complex viscosity for the pure *i*PP samples and the samples containing 0.5 wt % of OXA 3,6. The data obtained for the sample containing 0.5 wt % OXA 4,6 is provided in Figure S5 of the Supporting Information. From the data in Figure 12 it is apparent that the application of a shear pulse at 170 °C does not influence the crystallization of pure *i*PP compared to crystallization under quiescent conditions (ignoring possible effects of the oscillations used to track the changes in elastic and viscous modulus). The onset in the buildup of the complex viscosity is associated with the crystallization of *i*PP. The introduction of 0.5 wt % OXA 3,6 shifts the onset of crystallization from 123 to 127 °C, when no shear pulse is applied during cooling. The application of a shear pulse at 170 °C during continuous cooling, in the *i*PP/NA blend containing 0.5 wt % OXA 3,6, results in a further increase in the onset of crystallization to 132 °C. This data confirm that the increase in the onset of crystallization of the *i*PP, after the application of shear, in oxalamide nucleated blends is solely due to the shear-alignment and shear induced self-assembled morphology of the NAs.

CONCLUSIONS

We have evaluated the effect of three different oxalamide-based nucleating agents, OXA 2,6, OXA 3,6, and OXA 4,6, on the nucleation and crystallization of *i*PP. The observations are that

Figure 12. Change in complex viscosity of pure *i*PP and *i*PP containing 0.5 wt % OXA 3,6, observed during cooling and crystallization in the rheometer. The onset of crystallization is defined as the intersection of the tangential lines of the complex viscosity before and during the crystallization process. Note: the shear pulse in this protocol (60 s^{−1} for 3s) is applied at 170 °C.

these NAs are soluble in the melt of *i*PP and self-assemble into fibrillar crystals upon cooling. These self-assembled structures can promote the nucleation process of *i*PP at concentrations as low as 0.01 wt %, as is the case for OXA 2,6. However, increasing the concentration of OXA 2,6 resulted in a decrease in the onset of crystallization, indicating that the number of nuclei provided by OXA 2,6 decreases with increasing concentration. In contrast, OXA 3,6 and OXA 4,6 improve the nucleation efficiency of *i*PP at or above concentrations of 0.1 wt %. For these nucleating agents, in contrast to OXA 2,6, the onset of crystallization shifts to higher temperatures when the concentration is increased. The effectiveness of the three nucleating agents on crystallization is strongly related to the morphology after self-assembly. The dispersion of nanosized NA crystals yields a high surface to volume ratio of the nucleating agent aggregates and thereby increases the number of nuclei per NA volume. As a result, these nucleating agents are more effective when used in low concentrations or at high cooling rates, since these conditions promote the formation of nanosized crystallites. For blends containing such nanosized NA crystals, a maximum increase of 10 °C in onset of crystallization is observed compared to pure *i*PP. To reflect, with the use of too high NA concentrations or too low cooling rates, the NA self-assemble into micrometer-sized crystallites which exhibit a significant decrease in the surface-to-volume ratio and onset of crystallization. The application of shear above the *i*PP melting temperature was shown to promote shear-induced self-assembly and shear-alignment of the NA upon cooling. *i*PP blends containing OXA 3,6 or OXA 4,6 that were subjected to shear at the judicious temperature (170 °C for 0.3–0.5 wt %) upon cooling, displayed a further increase in the onset of crystallization to values up to 140 °C. Overall, this work indicates that these oxalamide-based nucleating agents exhibit an improved nucleation efficiency, at least equivalent to DMDBS, with increasing cooling rates and under shear conditions. This makes these compounds interesting candidates for use under industrial processing conditions, since high cooling and shear rates are often desired.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.6b03120.

Additional information on the phase transitions and transition enthalpies of the NAs (Table S1 and S2); determination of peak crystallization temperatures of iPP, and self-assembly temperatures of nucleating agents (Figure S1); DSC thermograms of iPP/NA blends having very low concentrations of nucleating agent (Figure S2); wide angle diffraction patterns and crystallinity of the nucleated iPP samples (Figure S3); effect of cooling rate on the self-assembly of nucleating agent and its influence on the crystallization of iPP (Figure S4); and increase in complex viscosity during crystallization in the rheometer for the iPP blend containing 0.5 wt % OXA 4,6 (Figure S5) (PDF)

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Notes

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