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Doctoral Dissertation

Novel technologies to accelerate flow-induced
crystallization of polymer materials

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Abstract

The crystallization behavior of a crystalline polymer during/after flow is significantly important. Depending on the conditions including temperature, shear rate, and residence time, the growing structures varied from spherulite to orientation structures such as row-nucleated and shish-kebab structures. As known, precise morphology control is essential to the properties of final products. Shear flow influences crystallization, which significantly enhances the crystallization rate and generates orientated crystallites. The present study focused on polypropylene (PP), which is one of the most popular materials and proposes a technology to promote the flow-induced crystallization of PP. The enhanced crystallization rate and molecular orientation of PP have been achieved by the addition of a fibrous nucleating agent or long-chain branched polymers even an immiscible blend system with an applied shear history. Additionally, the crystallization behavior of bio-based polymers, such as poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH), produced from renewable resources and used in various applications, was also investigated. The investigation results are shown in the details.

Keywords: Polypropylene, Low-density polyethylene, Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate), Fibrous nucleating agent, Flow-induced crystallization

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Khunanya Janchai

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Chapter 1

General Introduction

1.1 Polymer materials

Polymer materials are substances made up of long chains of repeating units called monomers. These materials have unique properties that make them suitable for various applications. Their molecular structure can be categorized based on their composition, molecular weight, and the nature of their polymerization.

1.1.1 Polymer synthesis.

- Polymer can be synthesized by following two major strategies, denominated step polymerization and chain polymerization.
- Stereospecific polymerization is a special polymerization type that leads to controlled tacticity polymers.

1.1.1.1 Step polymerization

Step polymerization, also known as step-growth polymerization, is a key method for synthesizing polymers. This process involves the formation of polymers through a series of steps where monomers react to form covalent bonds, usually resulting in the elimination of small molecules like water or methanol. In other cases, without any elimination of any by-product; in other words, the molecular weight of the product is equal to the sum of the molecule weight of the reactants.

This is the case, for instance, for the opening of an epoxide ring by amine function [1].

Applications

Textiles: Polymers like polyamide and polyester are used in the production of fibers and fabrics.

Plastics: Polyester and polyamide polymers are used in various plastic products, including containers and automotive parts.

Biomedical Devices: Polymers such as poly(lactic acid) are used in medical implants and biodegradable products.

1.1.1.2 Chain polymerization

Chain polymerization, also known as chain-growth polymerization, is a widely used method for synthesizing polymers where the growth of polymer chains proceeds through a sequence of reactions involving an initiator and monomers. Chain polymerization involves three main stages: initiation, propagation, and termination. Each stage plays an important role in the formation of a high-molecular-weight polymers [1].

Initiation:

- Initiator: The process starts with the use of an initiator, which is a chemical compound that generates active species capable of starting

polymerization. Common initiators include free radicals, cations, or anions.

- **Activation:** The initiator reacts with the monomer to create a reactive site, such as a free radical or an ionic species, that can open the monomer's double bond, leading to the formation of a growing polymer chain.

Propagation:

- **Chain Growth:** The active site on the growing polymer chain reacts with additional monomers, adding them to the chain and extending its length. This step involves the continuous addition of monomers to the growing chain end.
- **Chain Length:** During propagation, the polymer chain grows rapidly as long as monomers are available and the conditions are favorable. The chain length increases as monomers are added sequentially.

Termination:

- **End of Growth:** The polymerization process ends when the active site of the chain is deactivated or terminated.
- **Combination:** Two growing polymer chains combine to form a single, longer chain.
- **Disproportionation:** A hydrogen atom is transferred from one polymer chain to another, resulting in the formation of two terminated chains.

Initiation and propagation reactions for the $\text{CH}_2=\text{CHR}$ monomer are shown in Figure 1.1.

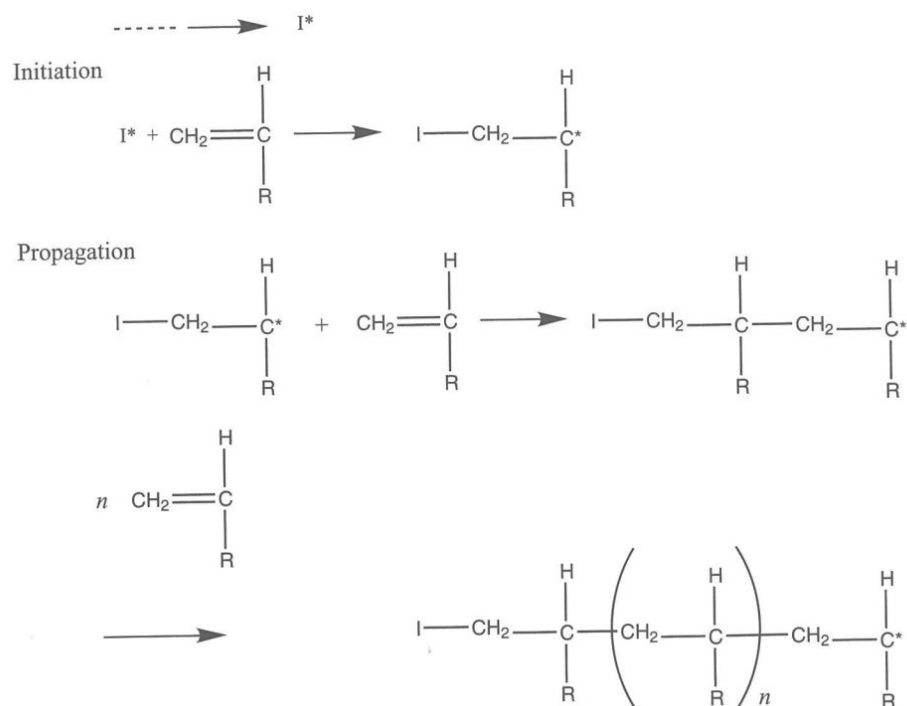
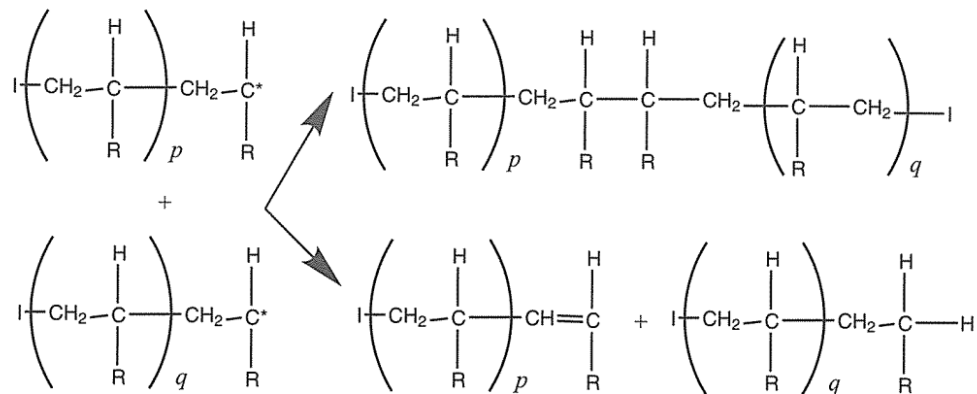


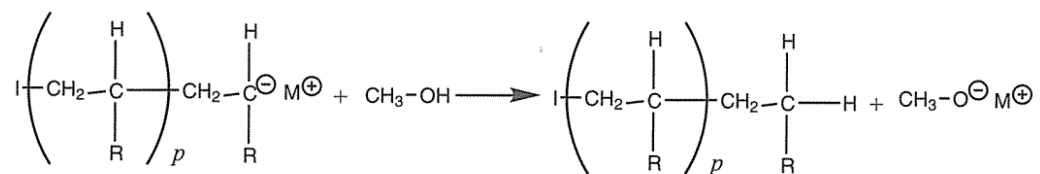
Figure 1.1 Scheme of the initiation and propagation reactions during the chain polymerization of a $\text{CH}_2=\text{CHR}$ monomer [2].

Figure 1.2 gives a few examples of termination reactions for the different types of chain polymerization.

Free radical



Anionic



Cationic

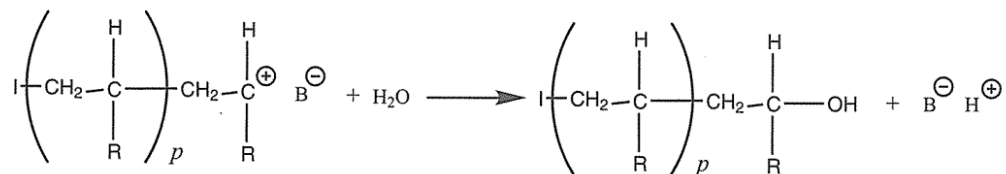


Figure 1.2 Examples of termination reactions observed in polystyrene (R=Phenyl) for the different types of chain polymerization: free radical, anion, and cationic [2].

Applications

Plastics: Chain polymerization is used to produce a wide variety of synthetic plastics, including polyethylene, polypropylene, and polystyrene.

Elastomers: Polymers like natural rubber and synthetic rubbers are synthesized via chain polymerization and are used in tires and flexible materials.

Fibers: Polyester, polyamide, and acrylic fibers are made using chain polymerization and are used in textiles and industrial applications.

1.1.2 Polymer properties

Polymer properties are a broad and diverse set of characteristics that define how a polymer behaves and performs in different applications. These characteristics are determined by the polymer's chemical composition, molecular weight, and processing methods.

Crystallinity: The degree to which polymer chains are ordered affects physical properties:

- Crystalline Regions: Ordered, regular arrangements of polymer chains lead to higher density, melting points, and mechanical strength.
- Amorphous Regions: Disordered, random arrangements result in flexibility, transparency, and lower density.

Tacticity: The arrangement of side groups along the polymer chain affects properties:

- Isotactic: All side groups are on the same side of the polymer chain, leading to high crystallinity (e.g., isotactic polypropylene).
- Syndiotactic: Side groups alternate sides, which also enhances crystallinity.
- Atactic: Side groups are randomly arranged, resulting in an amorphous, less crystalline polymer (e.g., atactic polystyrene).

The stereoregular polymer with controlled tacticity of PP depends on the position of methyl groups: isotactic, syndiotactic, and atactic, as shown in Figure 1.3.

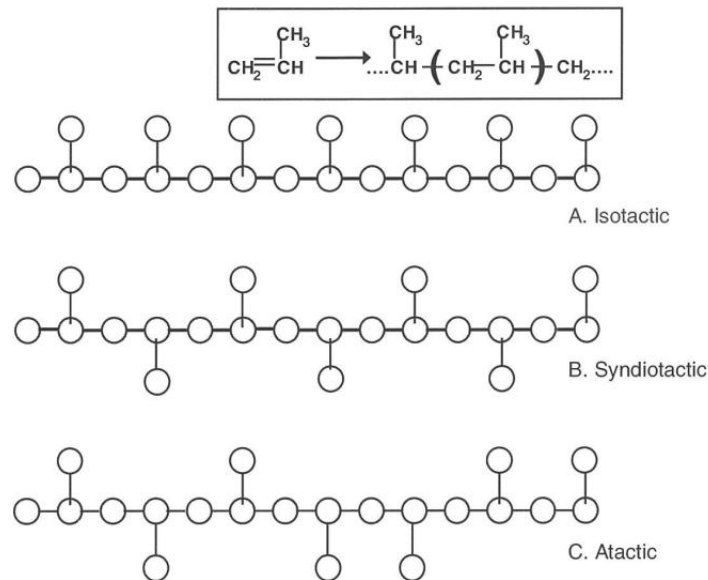


Figure 1.3. Molecular structures of polypropylene: A. Isotactic, B. Syndiotactic, and C. Atactic [3].

1.2 Crystallization process

When a crystalline polymer crystallizes from the melt, typically during the cooling process, lamellae organize around primary nuclei to form a spherulitic texture. These spherulites continue to grow until they encounter adjacent spherulites, at which point growth ceases. The final size of the spherulites and their crystalline orientation significantly influence their physical, mechanical, and optical properties. Figure 1.4. shows an illustration of the heterogeneous nucleation (nucleated system) versus that of a non-nucleated one.

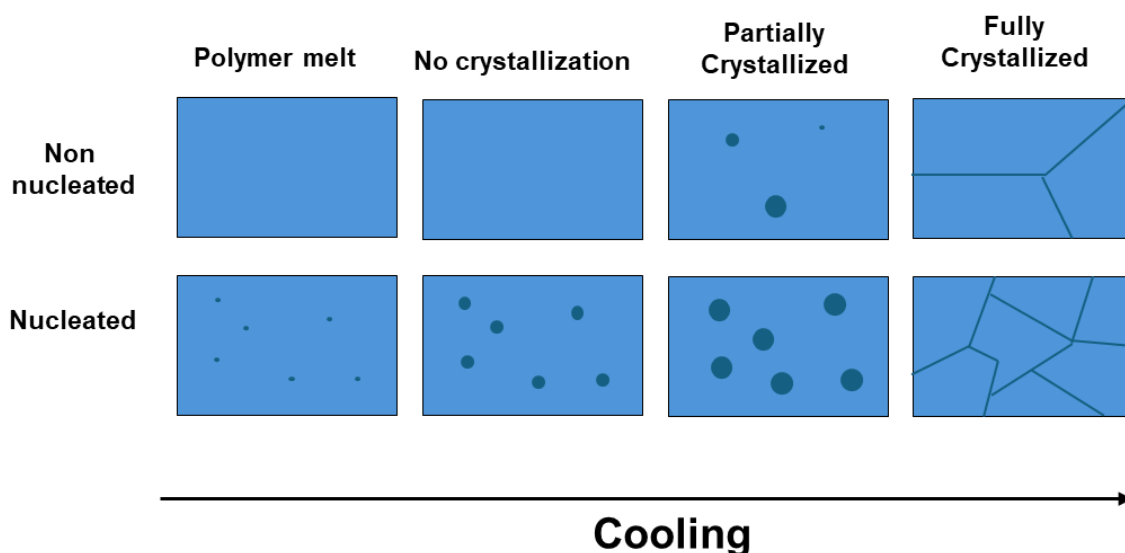


Figure 1.4 Illustration of the crystallization process of non-nucleated and nucleated systems.

1.3 Polymer crystallization

Polymer crystallization involves a two-step process: nucleation and crystal growth. The formation of stable nuclei is essential to initiate the crystallization of a polymer. The development of stable nuclei is governed by the thermodynamic principle; i.e., the change in Gibbs free energy from the melt to the nuclei must be favorable, $\Delta G = G_{\text{nuclei}} - G_{\text{melt}} < 0$. The free energy change can be expressed as $\Delta G = \Delta G_b + \Delta G_s$, where ΔG_b is the bulk free energy change (a negative value) and ΔG_s the surface free energy change (a positive value). The nucleation process is determined by the competition between bulk and surface energy change (bulk energy should overcome the surface one to generate stable nuclei). The flow in terms of the thermodynamic point of view raises the free energy to a melt. Therefore, it promotes nucleation. Flow field can not only accelerate crystallization kinetic but also change the crystallization

morphology from isotropic spherulites to highly oriented shish-kebab structure.

1.4 Flow-induced crystallization

Polymer processing techniques such as fiber spinning, injection molding, and film blowing invariably involve complex flow conditions. Flow-induced crystallization significantly influences the structural development and ultimate characteristics of semicrystalline polymer products, hence affecting mechanical properties such as modulus and strength.

Figure 1.5 illustrates the typical morphologies of crystallization resulting from different flow histories. In terms of morphological changes, the flow history has a noticeable impact on accelerating the crystallization process and altering crystal morphology, transforming it from a spherulite texture to an oriented shish-kebab structure. In the absence of flow, polymers typically form spherulite texture during crystallization as shown in Figure 1.5a. Weak flow is considered to increase the nucleation density by orienting polymer chains, which results in a significantly higher density of elliptical crystallites. Additionally, the lamellar stacks tend to align preferentially in the direction of the flow, as shown in Figure 1.5b. Strong flow can significantly elongate polymer chains, leading to the formation of oriented or rodlike nuclei, which subsequently develop into a shish-kebab structure, as shown in Figure 1.5c.

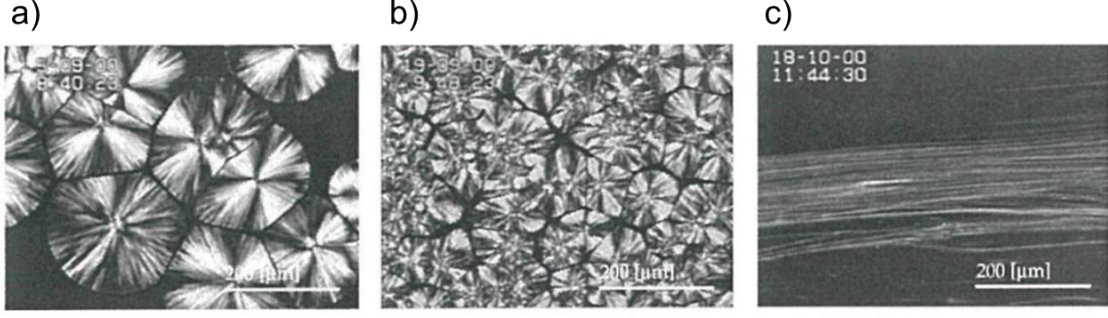


Figure 1.5. Typical morphologies of flow-induced crystallization with (a) no flow, (b) weak flow, and (c) strong flow [4,5].

Flow-induced crystallization is notably influenced by the presence of high molecular-weight-fractions (HMW) [6,7]. Based on the research on flow-induced crystallization, a high-molecular-weight fraction plays an important role in shish formation, at which the Weissenberg number Wi_R associated with the Rouse relaxation is larger than unity (eq. (1-1)) [8-12] to show flow-induced crystallization. Furthermore, the Rouse time τ_R is proportional to the square of the molecular weight M , which is often expressed using the average molecular weight between entanglement couplings, i.e., M_e , as denoted in eq. (1-2):

$$Wi_R \equiv \dot{\gamma}\tau_R > 1, \quad (1-1)$$

$$\tau_R = \tau_e \left(M / M_e \right)^2, \quad (1-2)$$

where τ_e is the equilibrium time between neighboring entanglements.

During the flow-induced crystallization process, shish-kebab structures are often developed. The formation of shish-kebab structures under flow conditions is attributed

to nucleation lines that orient parallel to the flow direction, with the lamellar crystals subsequently growing in a direction perpendicular to the flow, as shown in Figure 1.6. The crystallization of extended chains is promoted by both thermodynamic and kinetic factors. Thermodynamically, the entropy of extended chain conformations is lower than that of folded chains, hence elevating the melting point of the resultant crystals. Kinetically, an extended chain, being nearer to its crystalline state, encounters a lower kinetic barrier compared to a chain in a random configuration. As a result, the crystallization of extended chains initially leads to the formation of shish structures. They shish act as nucleating templates for coiled chains, which subsequently crystallize into folded-chain crystals, i.e., lamellae [13-18].

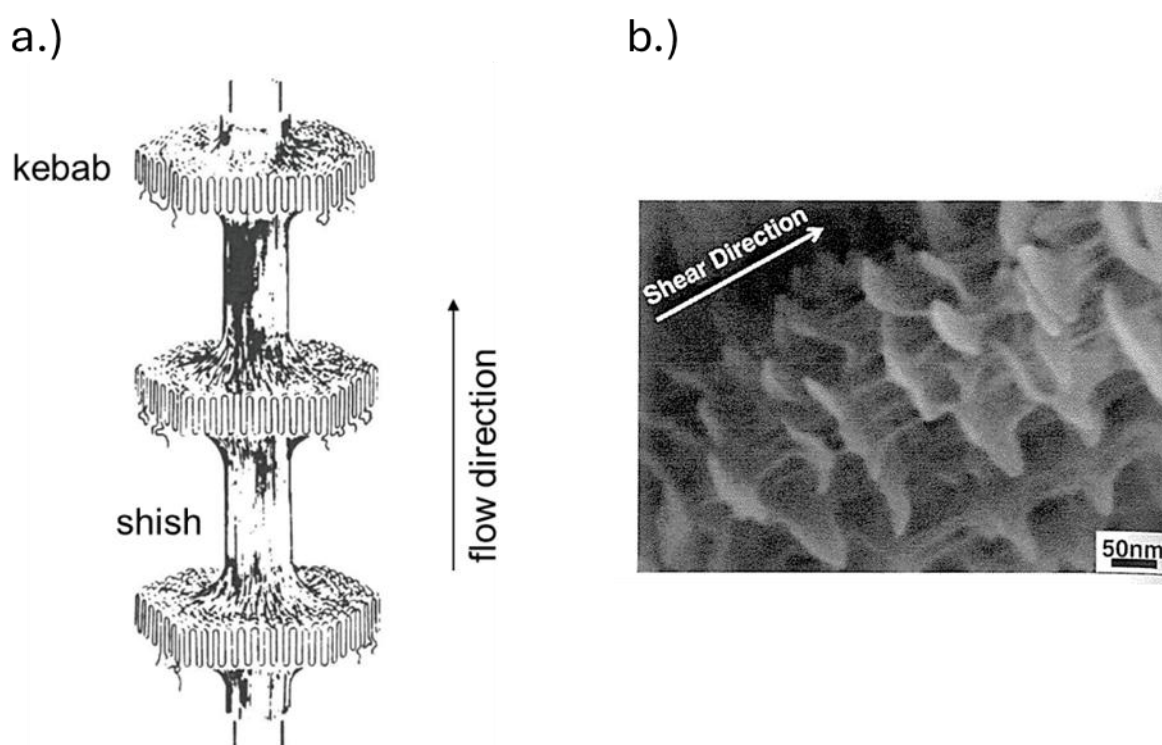


Figure 1.6 (a) Schematic illustration of shish-kebab structure [19,20] and (b) SEM images of toluene-extracted UHMWPE crystallites with shish-kebab having multiple shish [4].

1.5 Objective of the study

The main objective of this research is to propose new ideas for enhancing the crystallization of polymer materials with a flow history.

In the research, crystallization behavior was evaluated using a home-made machine. This machine is mainly composed of a parallel-plate shear stage made of quartz with covered in a temperature-controlled chamber and photo-detector. Using this machine, the growth of crystallization after flow history can be monitored with the evaluation of orientation growth as well as morphology development. In addition, I evaluated molecular orientation using two-dimensional wide-angle X-ray diffraction (2D-WAXD) and infra-red dichroism. Rheological properties were also evaluated using a cone-and-plate rheometer.

This research is useful not only in academia but also in controlling processing conditions in industry. Currently, we are mainly conducting research on polypropylene (PP) and polyethylene (PE). Since the methods must be independent of the polymer species, they can be applied to other crystalline polymers.

References

- [1] Robert J. Y, and Peter A.L. Polymer introduction. 2nd ed. CRC Press (2011)
- [2] Jean-Louis. H, Francoise L, and Lucucien M. Polymer materials. Macroscopic Properties and Molecular Interpretations. John Wiley & Sons (2011)
- [3] Ed., Pasquini N, Polypropylene handbook 2nd ed. Hanser (2005)
- [4] Ewa P, and Gregory C. R Handbook of polymer crystallization. John Wiley & Sons, (2013)
- [5] Zhen W, Zhe M, and Liangbin L. Flow-induced crystallization of polymers: molecular and thermodynamic considerations, *Macromolecules*, 49, 1505-1517 (2016)
- [6] Sugimoto M, Masubuchi, Takimoto J, and Koyama K. Melt rheology of polypropylene containing small amounts of high-molecular-weight chain. 2. uniaxial and biaxial extensional flow, *Macromolecules* 34, 6056–6063 (2001)
- [7] Kida T, Kimura T, Eno A, Janchai K, Yamaguchi M, Otsuki Y, Kimura T, Mizukawa T, Murakami T, Hato K, and Okawa T. Effect of ultra-high-molecular-weight molecular chains on the morphology, crystallization, and mechanical properties of polypropylene, *Polymers* 13, 4222 (2021)
- [8] Balzano L, Kukalyekar N, Rastogi S, Peters GWM, and Chadwick JC. Crystallization and dissolution of flow-induced precursors, *Phys Rev Lett*, 100, 048302 (2008)
- [9] Mykhaylyk OO, Chambon P, Impradice C, Fairclough JPA, Terrill NJ, and Ryan AJ. Control of structural morphology in shear-induced crystallization of polymers, *Macromolecules*, 43, 2389-2405 (2010)

- [10] Hamad FG, Colby RH, and Milner ST. Onset of flow-induced crystallization kinetics of highly isotactic polypropylene, *Macromolecules*, 48, 3725-3738 (2015)
- [11] Wingstrand SL, Shen B, Kornfield JA, Mortensen K, Parisi D, Vlassopoulos D, and Hassager O. Rheological link between polymer melts with a high molecular weight tail and enhanced formation of shish-kebabs, *ACS Macro Lett*, 6, 1268-1273 (2017)
- [12] Zhang Q, Li L, Su F, Ji Y, Ali S, Zhao H, Meng L, and Li L. From molecular entanglement network to crystal-cross-linked network and crystal scaffold during film blowing of polyethylene: an in situ synchrotron radiation small- and wide-angle x-ray scattering study, *Macromolecules*, 51, 4350-4362 (2018)
- [13] Nazari B, Tran H, Beauregard B, Flynn-Hepford M, Harrell D, Milner ST, and Colby RH. Two distinct morphologies for semicrystalline isotactic polypropylene crystallized after shear flow, *Macromolecules*, 51, 4750-4761 (2018)
- [14] Yamaguchi M, Fukui T, Okamoto K, Sasaki S, Uchiyama Y, and Ueoka C. Anomalous molecular orientation of isotactic polypropylene sheet containing N,N'-dicyclohexyl-2,6-naphthalenedicarboxamide, *Polymer*, 50, 1497-1504 (2009)
- [15] Phillips AW, Bhatia A, Zhu P, and Edward G. Shish formation and relaxation insheared isotactic polypropylene containing nucleating particles, *Macromolecules*, 44, 3517-3528 (2011)
- [16] Patil N, Invigorito C, Gahleitner M, and Rastogi S. Influence of a particulate nucleating agent on the quiescent and flow-induced crystallization of isotactic polypropylene, *Polymer*, 54, 5883-5891 (2013)
- [17] Rungswang W, Thongsak K, Prasansuklarb A, Plailahan K, Saendee P, Rugmai S,

and Cheevasrirungruang W. Effects of sodium salt and sorbitol-derivative nucleating agents on physical properties related to crystal structure and orientation of polypropylene, *Ind Eng Chem Res*, 53, 2331-2339 (2014)

[18] Seemork J, Siriprumpoonthum M, Lee Y, Nobukawa S, and Yamaguchi M. Effect of die geometry on drawdown force of polypropylene at capillary extrusion, *Adv Polym Technol*, 34, 21477 (2015)

[19] Ward IW, *Structure and properties of orientation polymer*. Chapman & Hall, (1975)

[20] Ed., Pasquini N, *Polypropylene handbook* 2nd ed. Hanser (2005)

Chapter 2

Effect of fibrous nucleating agent on shear-induced crystallization of polypropylene

2.1 Introduction

2.1.1 Polypropylene morphology

Polypropylene (PP) is widely regarded as one of the most essential crystalline polymers due to its notable combination of properties, including high stiffness, excellent resistance to stress cracking, substantial thermal stability, and easy processing. Like many other semicrystalline polymers, PP exhibits a complex, hierarchical morphology as shown in Figure 2.1. Under typical processing conditions without the presence of a flow field, polypropylene (PP) generally forms a spherulitic structure, as illustrated in Figure 2.2. This spherulite texture, while common, results in poor rigidity, which poses limitations on its potential applications. Strategies to enhance the crystallinity and rigidity of PP have therefore become important in expanding its use in more demanding engineering applications.

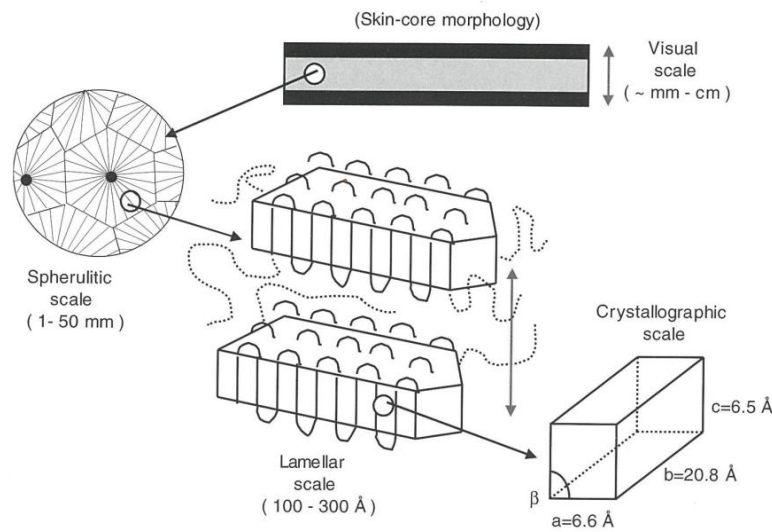


Figure 2.1. Characteristic hierarchy of morphology scales in PP [1]. The skin-core morphology of an injection molded product is used to illustrate hierarchical morphology

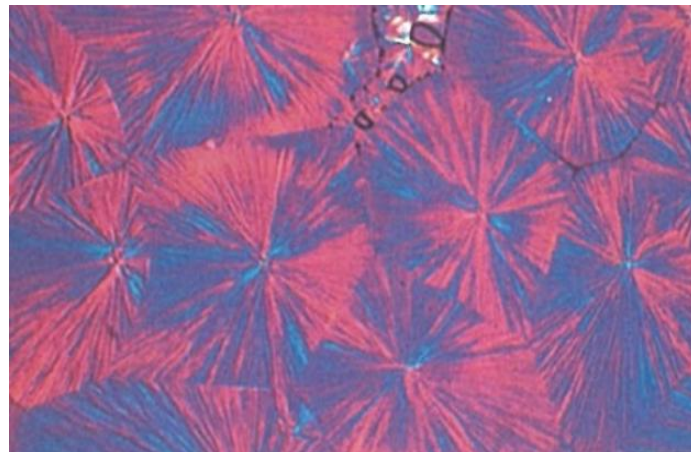


Figure 2.2. Spherulite texture of PP detected by a polarized optical microscope [2].

One approach to improving the modulus of PP is by developing a highly oriented molecular structure, such as the shish-kebab structure. Recent research on flow-induced crystallization has shown that the high-molecular-weight fraction plays a crucial role in the development of shish structures [3,4]. This phenomenon occurs particularly when the Weissenberg number, related with the Rouse relaxation time Wi_s , is larger than 1

[5-9], as discussed in Chapter 1. This correlation highlights the critical role of molecular weight distribution in promoting the formation of oriented crystalline structures during flow-induced crystallization. Furthermore, research has shown that the formation of shish, or extended chain crystals, can be effectively substituted using fibrous nucleating agents. These agents facilitate the nucleation process, promoting the development of highly oriented crystalline structures like that achieved through flow-induced crystallization.

2.1.2 Nucleating agent

A variety of additives are employed to modify the properties of polymers. In the case of PP, nucleating agents are frequently utilized due to their capacity to significantly accelerate the crystallization rate. Moreover, they have the ability to selectively and profoundly influence the solid-state morphology that develops during processing, resulting in improved material properties. Additionally, nucleating agents enhance the physical, mechanical, and optical properties of PP. Compounds derived from 1,3:2,4-dibenzylidene-D-sorbitol (DBS) are particularly effective in achieving these improvements, demonstrating their utility in polymer modification. DBS, an amphiphilic molecule derived from the sugar alcohol D-glucitol, exhibits a distinct butterfly-shaped structure due to the presence of two hydroxyl groups, as shown in Figure 2.3. These DBS molecules have a strong tendency to interact through hydrogen bonding and can self-assemble into a fibrillar structure, as shown in Figure 2.4. This self-assembly enables DBS to effectively function as a shish, facilitating the formation of highly oriented crystalline structures [10-12]. DBS molecules are also capable of self-assembling within the melt state of crystalline polymers like PP. This self-assembly

process contributes to the formation of a fibrillar network, which can influence the crystallization behavior and improve the mechanical properties of the polymer during processing.

DBS and its derivatives dissolve in a polymer melt and form nucleating particles during cooling. DBS is known to show the lattice matching with PP crystals. Therefore, it is widely used as a nucleating agent.

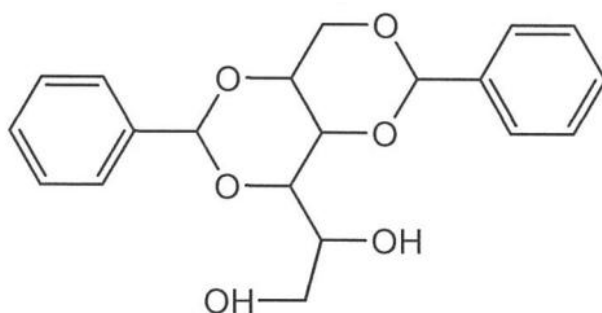


Figure 2.3. Structure of 1,3:2,4-dibenzylidene-D-sorbitol (DBS).

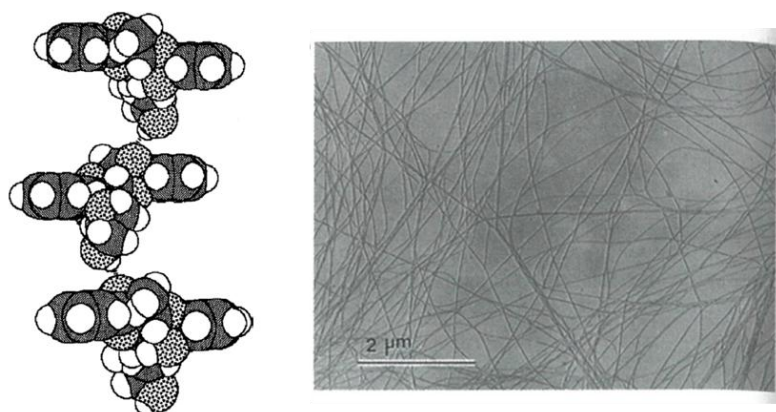


Figure 2.4. Structure model (left) and fibrillar structure of DBS (right) crystallized from tetrahydrofuran [2].

MDBS, a derivative of the DBS family, features two additional methyl groups attached to the para positions of each terminal phenyl ring. The fibrillar structure of both MDBS and DBS plays a critical role in the crystallization process under flow conditions, functioning as a pseudo-shish [12]. As a result, the incorporation of MDBS significantly influences the structure and properties of PP. However, the specific effects of MDBS (or DBS) on the crystallization behavior of PP in the presence of a flow field have not been clarified yet.

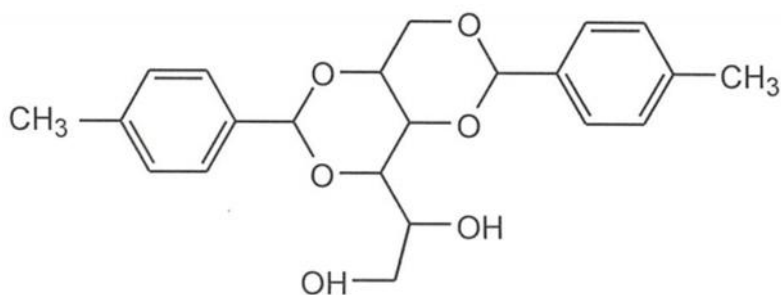


Figure 2.5. Structure of 1,3:2,4-bis-O-(4-methylbenzylidene)-D-sorbitol (MDBS).

2.2 Experimental Procedure

2.2.1 Materials

The polymer utilized in this study is an isotactic polypropylene homopolymer (PP, PM900A) sourced from SunAllomer Ltd. The specific characteristics of this polymer are presented in Table 2.1.

Table 2.1 Characteristics of PP

Information	Value, unit	Test standard
melt flow index	30 g/10min	JIS K7210
number average molecular weights	35,000	size exclusion chromatography
weight average molecular weights	179,000	
z average molecular weights	491,000	

The polymer was blended with a sorbitol-derived crystalline nucleating agent, namely 1,3:2,4-bis-o-(4-methylbenzylidene)-D-sorbitol (MDBS), supplied by New Japan Chemical Co., Ltd. MDBS has a melting point in the range of 260–265 °C. Tris(2,4-di-tert-butylphenyl)phosphite (Irgafos 168) and pentaerythritol tetrakis(3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionate) (Irganox 1010), both provided by BASF SE, were utilized as thermal stabilizers in this study. Calcium stearate, sourced from Nitto Kasei Kogyo K. K., was employed as an acid neutralizing agent [13]. PP containing 0.4 weight percent of MDBS was produced using a co-rotating twin-screw

extruder (model KZW15TW-45MG-NH, Technovel Corp.) operated at a processing temperature of 240 °C. The extruder included a screw diameter of 15 mm and rotational speed of 250 rpm. A capillary rheometer (140 SAS-2002; Yasuda Seiki Seisakusho, Ltd.) was employed for extrusion at 180 °C to stabilize the structure of the MDBS in the PP. The strand was extruded downward from a circular die without stretching and cooled in air at 23 °C.

2.2.2 Sample preparation

The samples were fabricated into flat films with thicknesses of 100 and 900 μm utilizing a compression-molding machine at 180°C for 2 minutes.

2.3 Measurements

The frequency dependence of the oscillatory storage modulus (G') and loss modulus (G'') for both PP and PP/MDBS was evaluated using a cone-and-plate rheometer (AR2000ex; TA Instruments, Inc.) at 180°C. The cone employed had a 25 mm diameter, a 4° angle.

The thermal properties were analyzed in a nitrogen atmosphere using a differential scanning calorimeter (DSC; model DSC8500, PerkinElmer Inc.). Approximately 10 mg of the sample was placed in an aluminum pan, heated to 180°C for 5 minutes, and subsequently cooled at a rate of 30 °C/min to ascertain the crystallization temperature. A DSC machine also evaluated the degree of crystallinity. The measurement was carried out at 30 °C/min from 25 °C to 180 °C.

Crystallization behavior was examined using a polarizing optical microscope (POM) with a crossed-polarizer configuration (Leica DM2700P, Leica Microsystems,

Ltd.). The microscope had a quartz parallel-plate shear stage (CSS450, Linkam Scientific Instruments, Ltd.), as seen in Figure 2.6a. The parallel-plate stage was mounted within a temperature-regulated chamber, which had a 2.8 mm diameter window for light transmission. The center of the window was located 7.5 mm from the center of the plate. Additionally, the direction of the polarizer and analyzer relative to the flow direction is shown on the right side of Figure 2.6b. A photodetector (PM16-121, Thorlabs Inc.) was installed in place of one of the eyepieces to measure the light intensity after it passed through a 633 nm color filter. A camera was mounted on the other eyepiece to observe and analyze the morphology. The experimental procedures related to temperature and shear conditions are illustrated in Figure 2.7. The sample film was placed between the plates and heated to 170 °C to completely melt the film. Subsequent to modifying the gap to 100 μm , the sample plates were cooled to 130 °C to facilitate the microscope's focus. Subsequently, the sample was reheated at 180 °C for 5 minutes to ensure complete melting before the cooling process. The samples were subsequently chilled at a consistent rate of 30 °C/min from 180 °C. Shear was applied during non-isothermal process from 180 °C to 160 °C at various shear rates of 0, 1, 5, 10, 50, and 100 s^{-1} by rotating the bottom plate; the shear rate was determined in the center of the observation window.

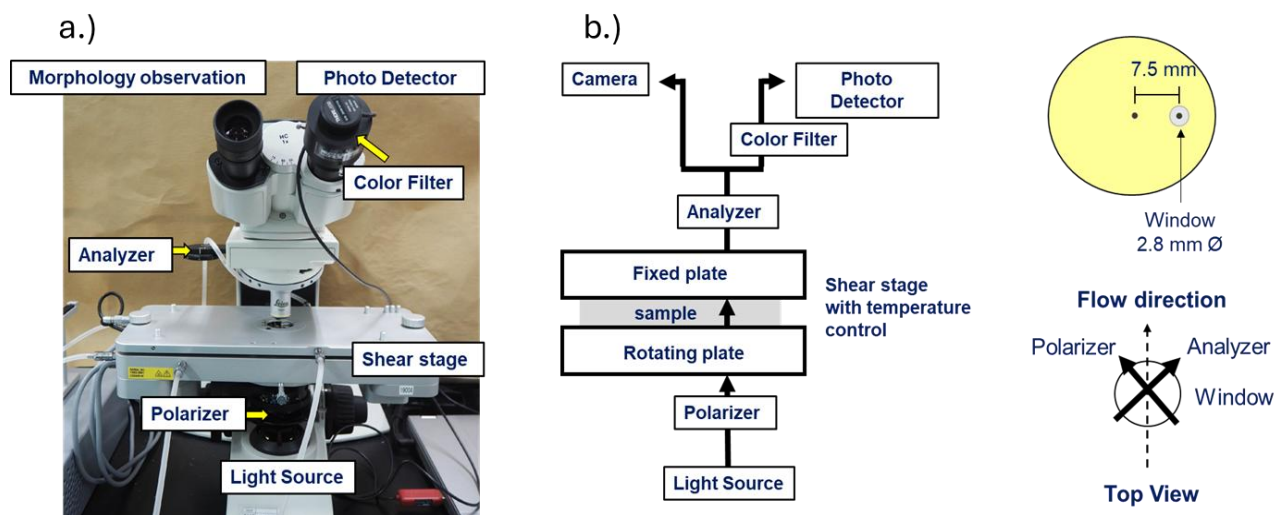


Figure 2.6. (a) A polarizing optical microscope (POM) fitted with a parallel-plate shear stage and (b) a schematic representation of the apparatus utilized to assess crystallization behavior.

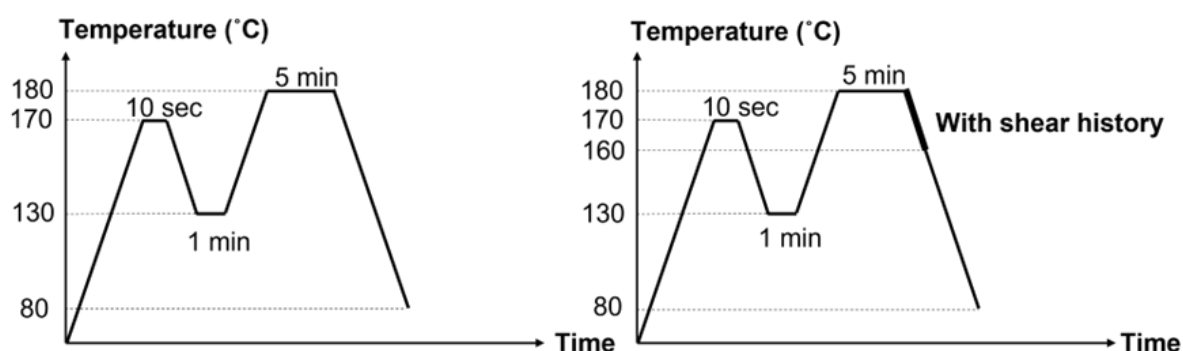


Figure 2.7. Experimental protocols. (a) Without shear history and (b) with shear history.

The sample film was taken out from the plates following crystallization for further analysis. The orientation of the PP chains was assessed using a Fourier-transform infrared (FTIR) spectroscopy system (Spectrum 100; PerkinElmer) equipped with a polarizer. Additionally, two-dimensional wide-angle X-ray diffraction (2D-WAXD) and

small-angle X-ray scattering (2D-SAXS) patterns were obtained using an X-ray diffraction (XRD) system (SmartLab; Rigaku). The samples were irradiated with a graphite-monochromatized Cu K α radiation beam, operated at 45 kV and 200 mA. The exposure times for WAXD and SAXS were set to 3 and 30 minutes, respectively, with a beam spot diameter of 1.5 mm. The orientation functions derived from FTIR and WAXD were determined by adjusting the position of the sample film during analysis.

The drawdown force was examined using a capillary rheometer (model 140 SAS-2002, Yasuda Seiki Seisakusyo), which was attached to a tension detector (DT-413 G-04-3, Nidec Shimpo) and a series of revolving winding rollers. The barrel and circular die were kept at a temperature of 180 °C for the whole experiment. Two circular dies with L/D ratios of 10/1 (mm) and 40/1 (mm) were used. The experiments were conducted at draw ratios of 7.5 and 11.0, which were defined as the ratio of the strand's stretching speed by the winding rollers to the average extrusion speed at the die exit, with an apparent shear rate of 124 s⁻¹ at the die wall.

2.4 Results and Discussion

2.4.1 Rheological properties

The rheological properties were investigated using a cone-and-plate rheometer. Figure 2.8 illustrates the dependence of the oscillatory shear moduli specifically the storage modulus G' and loss modulus G'' on angular frequency ω at 180 °C. For pure PP, G'' was proportional to ω , and the slope of G' was much larger than that of G'' , consistent with a typical rheological behavior observed in the terminal region. In

contrast, the sample containing 4000 ppm of MDBS (PP/MDBS) showed a plateau in G' at low frequencies, indicating the formation of an MDBS network within the system. These results agree with the previous reports [11,14].

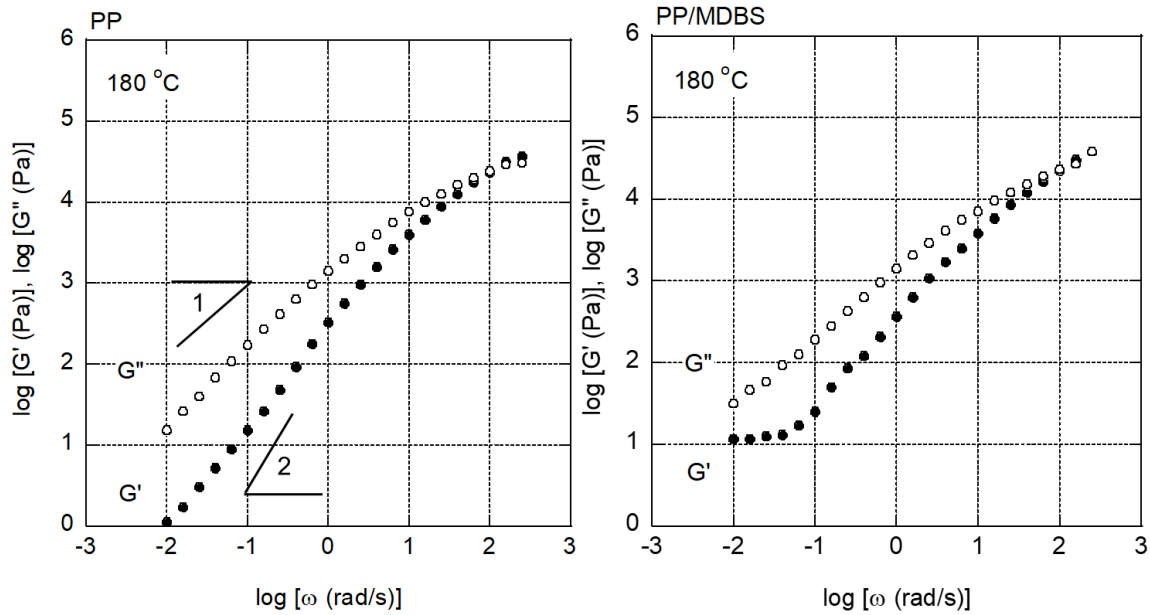


Figure 2.8. Angular frequency ω dependence of the shear storage modulus G' (closed symbols) and loss modulus G'' (open symbols) at 180 °C for PP (left) and PP/MDBS (right).

2.4.2 Thermal properties

Figure 2.9 presents the DSC cooling curves at a rate of 30 °C/min, illustrating the crystallization behavior in the absence of shear. Since the samples were cooled from 180 °C, the MDBS fibers did not melt in the PP. The DSC cooling curve for the PP/MDBS sample exhibited a crystallization peak at a high temperature compared to the PP sample, demonstrating that MDBS fibers act as nucleating agents. The crystallization peak temperature (T_c) and the onset temperature ($T_{\text{on-set}}$) are labeled in

the figure. For the PP/MDBS sample, the T_c was close to T_{on-set} , and the crystallization peak was notably sharp, indicating that the crystallization rate was markedly accelerated, even at high temperatures.

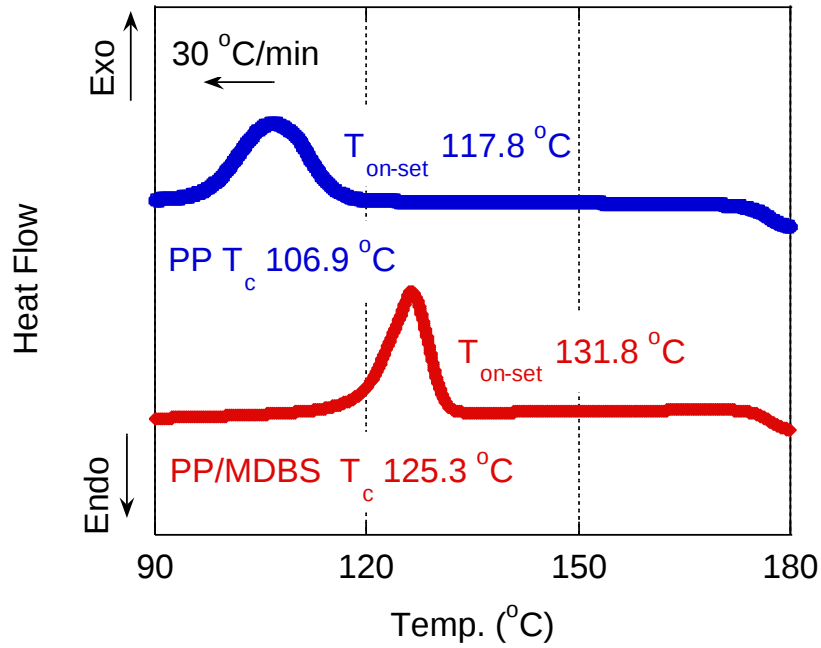


Figure 2.9. Differential scanning calorimeter (DSC) cooling curves from 180 °C at a cooling rate of 30 °C/min

The DSC heating process at 30 °C/min—i.e., melting temperature and heat of fusion ΔH_{f-s} of the samples obtained after cooling without shear. The melting temperature (T_m) values for PP and PP/MDBS samples were around 166 °C, a typical one for PP. The heat of fusion of PP and PP/MDBS were 88.1 and 97.1 J/g respectively.

The degree of crystallinity per unit of mass, χ , of PP, was calculated using the equation:

$$\chi = \frac{\Delta H_{f-s}}{\Delta H_{f-p}} \times 100 (\%) \quad (2-1),$$

where ΔH_{f-p} is the heat of fusion for a perfect crystal, with a value of 209 J/g [15]. The

degrees of crystallinity were as follows; 42.1% for PP and 48.7% for PP/MDBS, indicating MDBS greatly enhanced crystallinity.

2.4.3 Crystallization behavior

The crystallization behavior in the absence of shear was further analyzed at the same cooling rate using a polarizing optical microscope (POM) configured with crossed polarizers. The depolarized light intensity (DLI) during the cooling process represents the light transmittance shown in Figure 2.10. The DLI was determined using the following equation:

$$DLI(\%) = \frac{I_0 - I_X}{I_{//} - I_X} \times 100 \quad (2-2),$$

where I_X and $I_{//}$ are the light intensities without the sample under crossed and parallel polars, respectively. I_0 is the light intensities through the sample detected under crossed polars,

Crystallization started at around 118 and 130 °C for PP and PP/MDBS, respectively. Furthermore, PP/MDBS demonstrated a pronounced increase in crystallization within a limited temperature range, signifying an enhanced crystallization rate. These results agree with the DSC cooling curves illustrated in Figure 2.9.

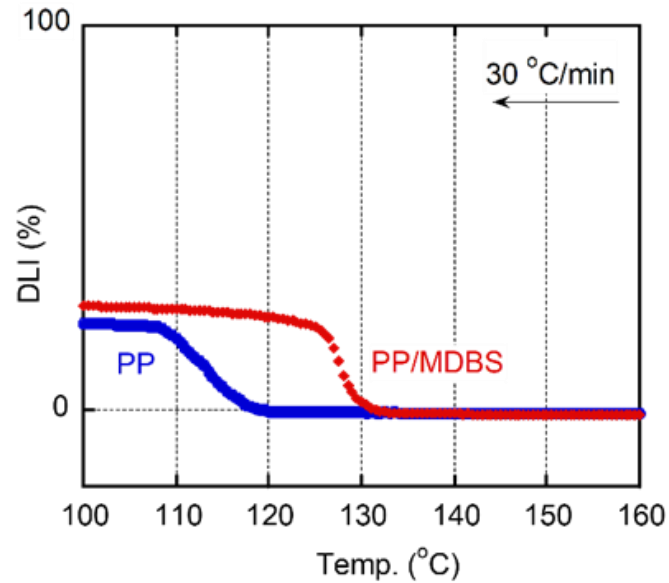


Figure 2.10. Growth curves of depolarized light intensity (DLI) at absence of shear during non-isothermal crystallization at 30 °C/min.

The morphological information during cooling is presented in Figure 2.11. In this investigation, crystallization from the quartz was not clearly observed. The figure illustrates that PP had a spherulite texture, without orientation. The dimensions of the spherulites were about 20–30 μm . In contrast, spherulite texture was not observed in the PP/MDBS sample.

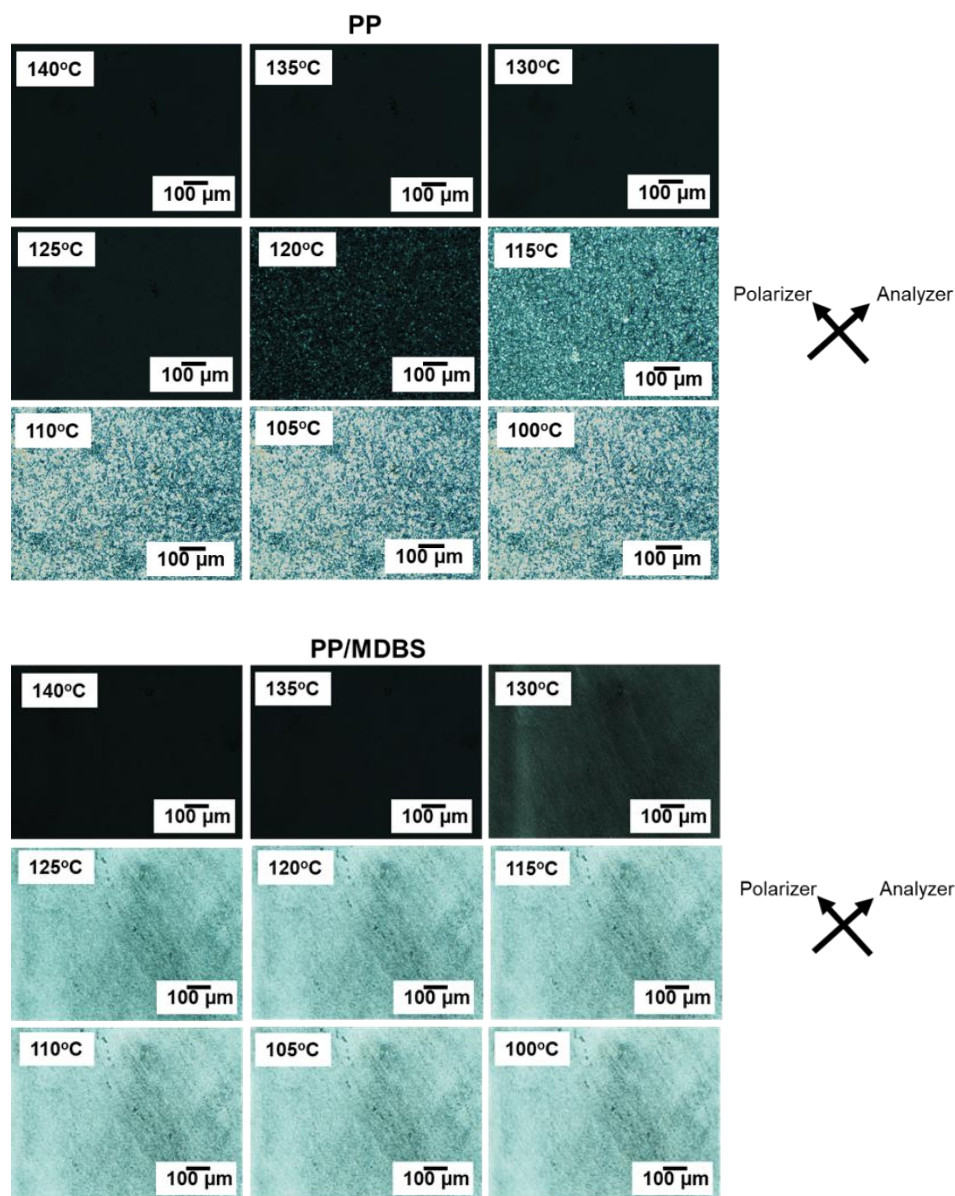


Figure 2.11. POM images of PP and PP/MDBS during the non-isothermal crystallization at absence of shear. The images were collected without a color filter.

The crystallization behavior with a shear history was evaluated at the same cooling rate as described above, using POM attached with a parallel-plate shear device. Figure 2.12 presents the light transmittance, represented by DLI, during the cooling process.

During exposure to shear from 180 to 160 °C, the light intensity in this temperature range remained close to zero, even at a shear rate of 100 s⁻¹. This indicates that the chain orientation induced by the shear was insufficient to produce significant optical retardation, suggesting that orientation birefringence in the molten state can be disregarded in this measurement.

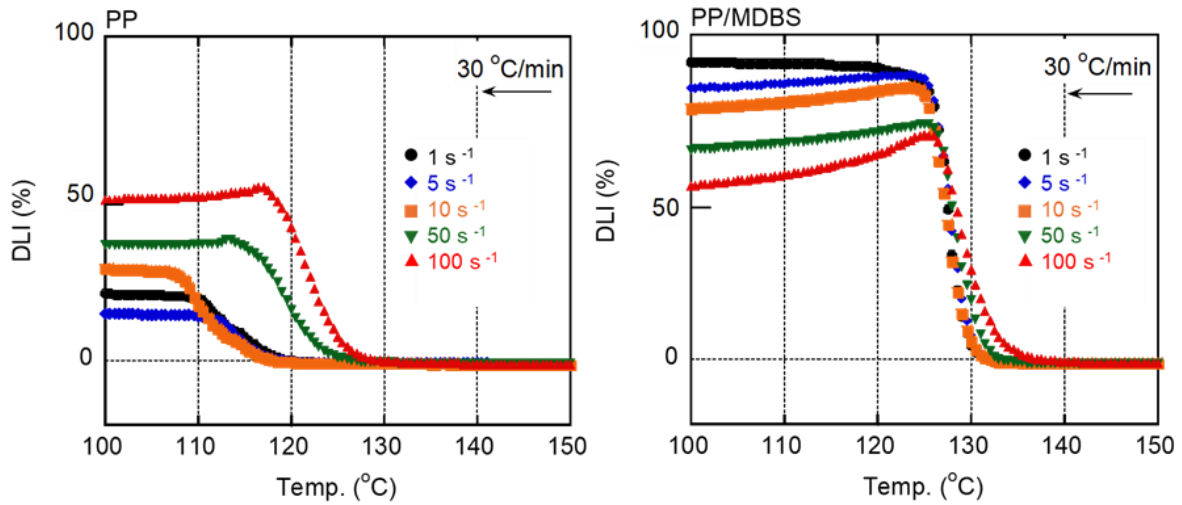
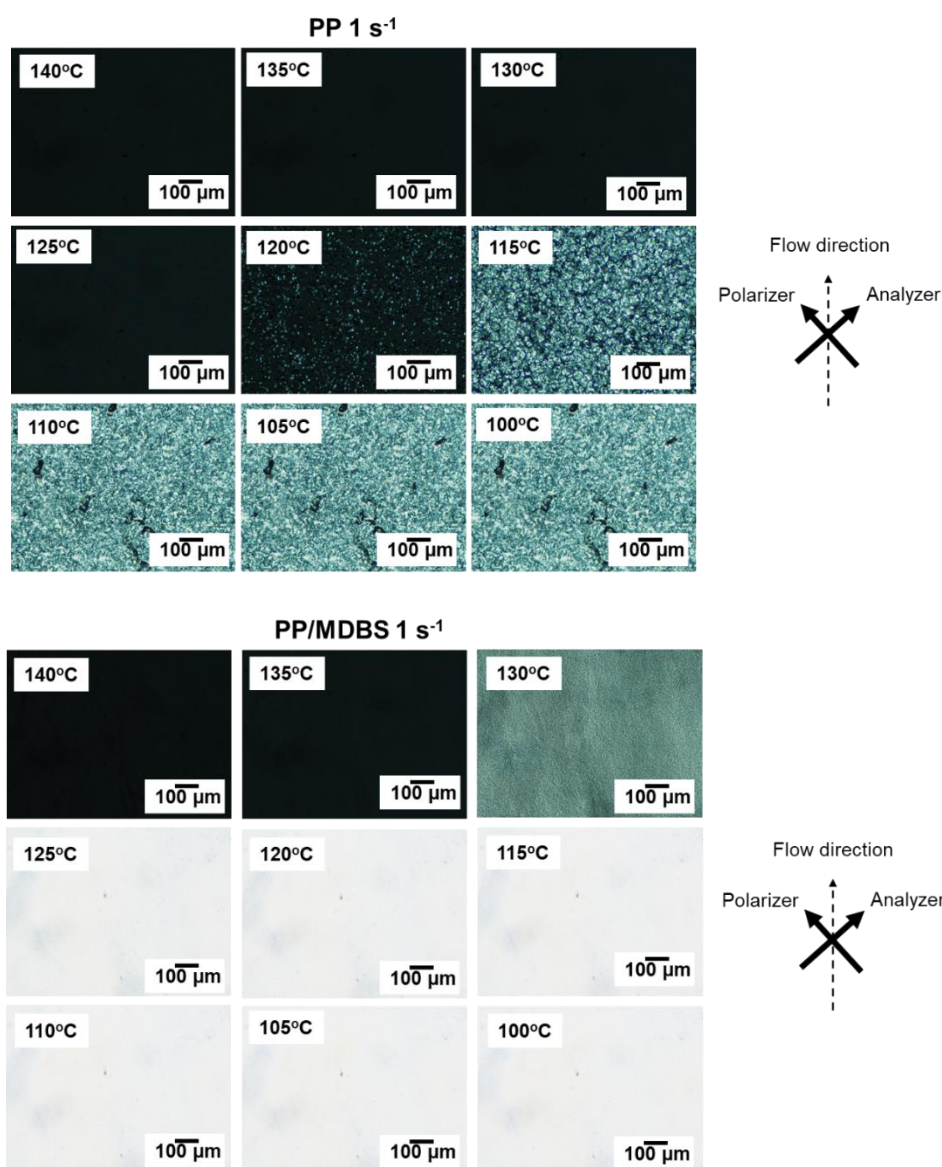
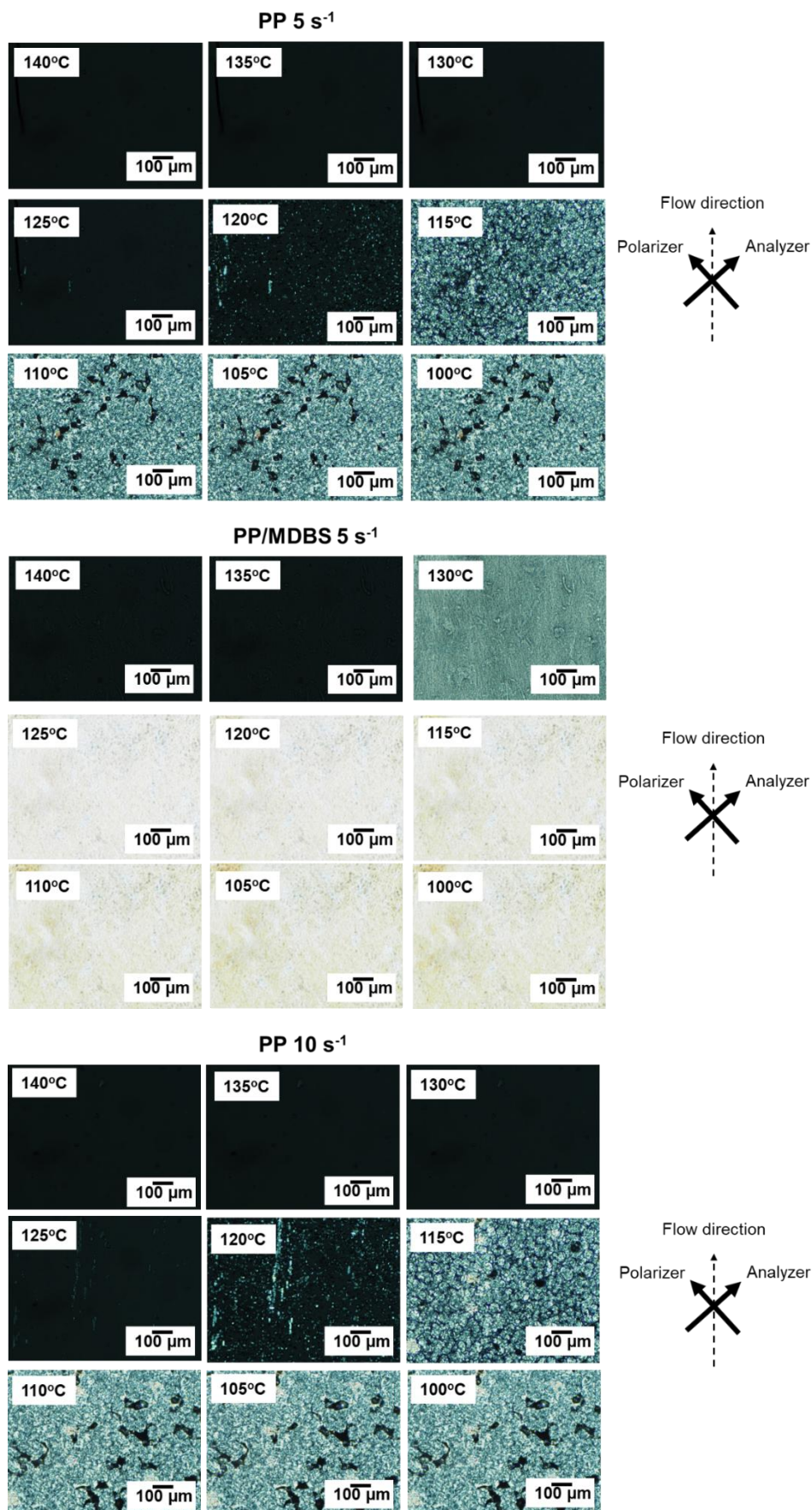


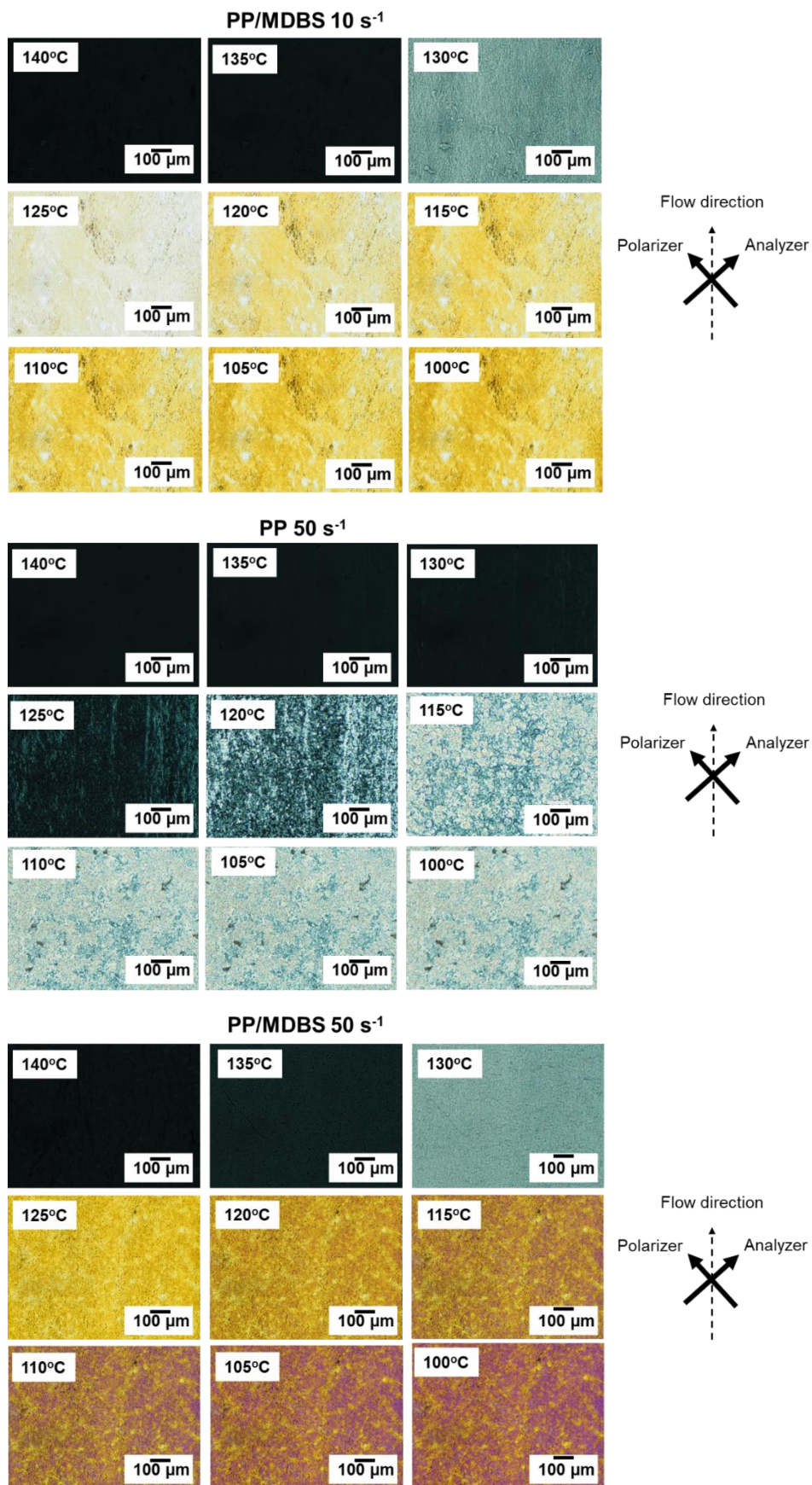
Figure 2.12. Growth curves of depolarized light intensity (DLI) during non-isothermal crystallization at 30 °C/min for PP (left) and PP/MDBS (right). Shear was applied from 180 to 160 °C at different shear rates.

The flow history greatly affected the crystallization behavior of pure PP. Crystallization occurred at temperatures that were over 50 s⁻¹, signifying the occurrence of flow-induced crystallization. Therefore, the Weissenberg number Wi_s is related with the Rouse time τ_R , given by eq. (1-1), must be larger than 1 for the high-molecular-weight fraction. Chain stretching under these conditions led to the formation of extended chain crystals, or "shish," which facilitated the rapid development of the shish-

kebab structure. The oriented structure was distinctly detected at 125 °C after shear exposure at 100 s⁻¹ for PP. While spherulite texture seems to be developed at lower temperatures in this sample. Although the DLI value started increasing at approximately 130 °C for PP with shear history at 100 s⁻¹, the shish formation must occur during shear flow from 180 to 160 °C. In contrast, at shear rates below 10 s⁻¹, spherulite texture without any orientation, indicating that the polymer chains were fully relaxed before crystallization.







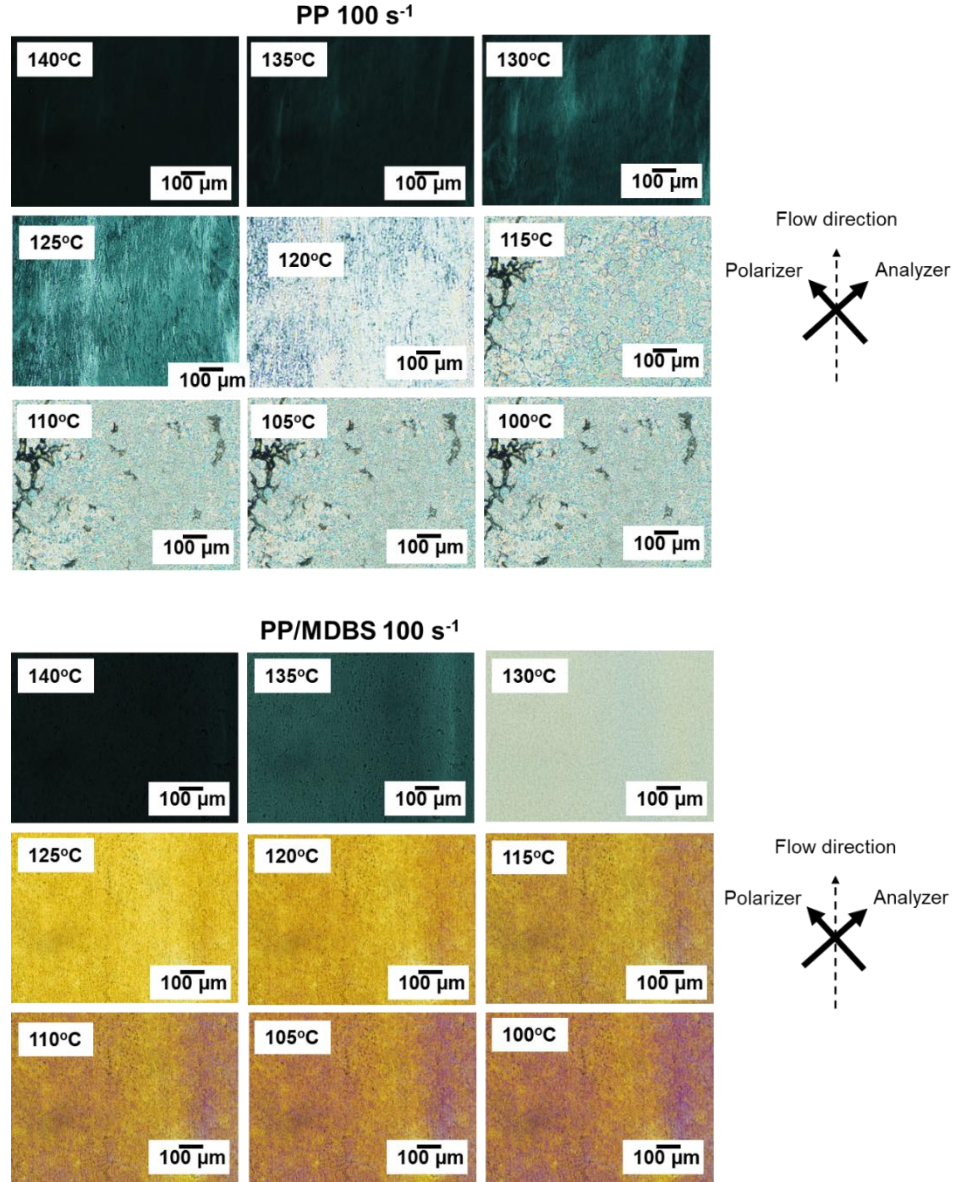


Figure 2.13. POM images of PP and PP/MDBS during non-isothermal crystallization at various shear rates. The images were examined without a color filter.

According to Hamad et al., τ_e of PP at 170°C is $1.5 \times 10^{-7} \text{ s}$ [7]. Because the M_e of PP has been reported to be 5250 [7], the critical molecular weight at a shear rate of 100 s^{-1} for $Wi_s > 1$ is calculated to be 1.4×10^6 . Furthermore, the result for PP illustrated in Figure 2.13 indicated that the light intensity following crystallization was affected by the applied shear rate. The shear-induced crystallization led to the formation of a

diagonally oriented optical axis, which generated significant retardation. However, the retardation did not exceed 350 nm, as indicated by the absence of distinct coloration in the POM image without the use of a color filter for PP, as shown in Figure 2.13. Moreover, when discussing DLI values, it is important to carefully consider the light scattering caused by spherulites, as it reduces light transmittance [16]. For PP, the orientated structure including a limited quantity of spherulites exhibited a high degree of light transmittance beyond 50 s⁻¹.

In PP/MDBS, crystallization occurred at high temperatures, and a highly oriented structure along the flow direction was observed even at a low shear rate (1 s⁻¹). This can be explained by the fact that MDBS fibers readily align with the flow direction under hydrodynamic forces, even at low shear rates. These fibers act as shish, enabling the development of a pseudo shish-kebab structure with high molecular orientation, a phenomenon previously observed with other fibrous materials [17,18]. Due to this characteristic, even the core region of injection-molded products containing MDBS exhibits significant molecular orientation, resulting in an increased modulus [12].

The birefringence Δn is giving by the following equation [19,20]:

$$\Delta n = \Gamma/d \quad (2-3),$$

where Γ is the retardation and d is the sample thickness.

Figure 2.13 shows a yellow color in PP/MDBS at 120 °C following the setting of a shear rate of 10 s⁻¹, indicating retardation of about 350 nm, as determined by the Michel-Levy interference chart [21]. The sample thickness is 100 μm, and the predicted birefringence is approximately 3.5 × 10⁻³. The intrinsic birefringence of PP is 0.04 [22], while the estimated orientation function is about 0.09. Retardation may also be

calculated using the DLI values when light scattering and absorption are negligible. Assuming that the light transmittance at the crossed polars absence of a sample—i.e., I_x —is 0, the value is given by the following equation [19,20,23]:

$$DLI \simeq \frac{I_0}{I_{//}} = \sin^2 \frac{\pi \Gamma}{\lambda_0} \quad (2-4),$$

where Γ is the retardation and λ_0 is the wavelength of the light (633 nm.)

According to Eq. (2-4), the DLI increased due to retardation increases when $\Gamma < 317$ nm, and then decreases when $317 < \Gamma < 633$ nm. As shown in the figure, DLI values for PP/MDBS decreased with an increasing shear rate. In addition, the DLI values after exposure to high shear exhibited a maximum and then decreased with cooling. These results are mainly attributed to significant retardation occurring beyond 317 nm. In fact, the POM image without the color filler at 120 °C following a shear rate of 100 s⁻¹ appeared orange, indicating a retardation is approximately 450 nm, resulting in an orientation function of 0.11. Furthermore, Eq. 2-4 produces a DLI of 62% with $\Gamma = 450$ nm, which closely resembles the DLI value recorded at 120 °C for PP/MDBS with a shear rate of 100 s⁻¹. Figure 2.14 presents optical microscope images taken after crystallization without the use of polarizers. Both samples underwent shear at a rate of 100 s⁻¹. It is evident that PP/MDBS exhibits a homogeneous texture compared to PP. Norris and Stein [24] identified three primary sources of light scattering in films made from crystalline polymers:

- (1) surface roughness, impurities, and voids
- (2) the presence of spherulitic morphology
- (3) differences in polarizability between crystalline aggregates

The factor (3) is markedly reduced when the correlation length of the crystalline aggregates is considerably longer/shorter than the wavelength of visible light. When a sorbitol derivative is incorporated into PP, the resulting film exhibits an extended correlation length without the development of spherulite texture [14], leading to the film becoming transparent. Therefore, MDBS is sometimes called a “clarifying agent” for PP.

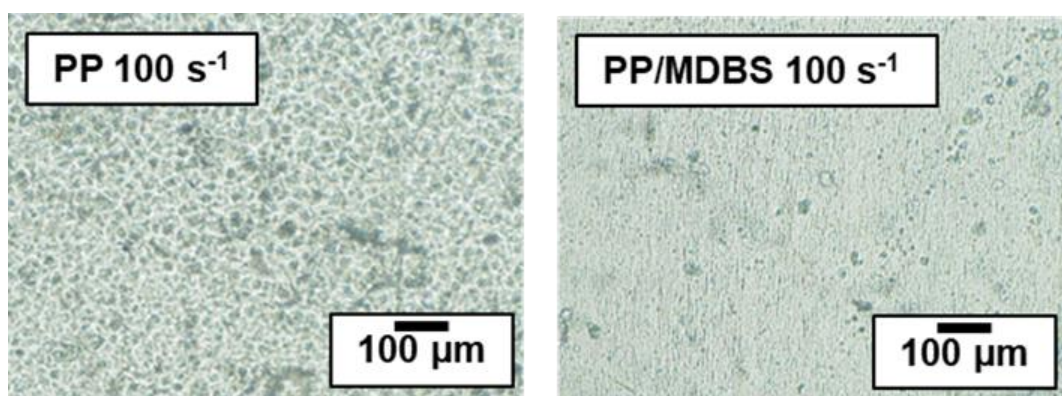


Figure 2.14. Optical microscope photographs after the crystallization without polarizers of PP (left) and PP/MDBS (right). The samples were sheared at 100 s⁻¹.

2.4.4 Molecular orientation

The sample was taken out from the parallel plates after cooling and evaluated orientation function using 2D-WAXD. X-ray measurements were performed in the window area as well as at two other positions (5 mm and 10 mm from the center) to examine the effect of shear rate. This was done because the shear rate increases proportionally with distance from the center. The setup is illustrated in Figure 2.15, along with an image of the film.

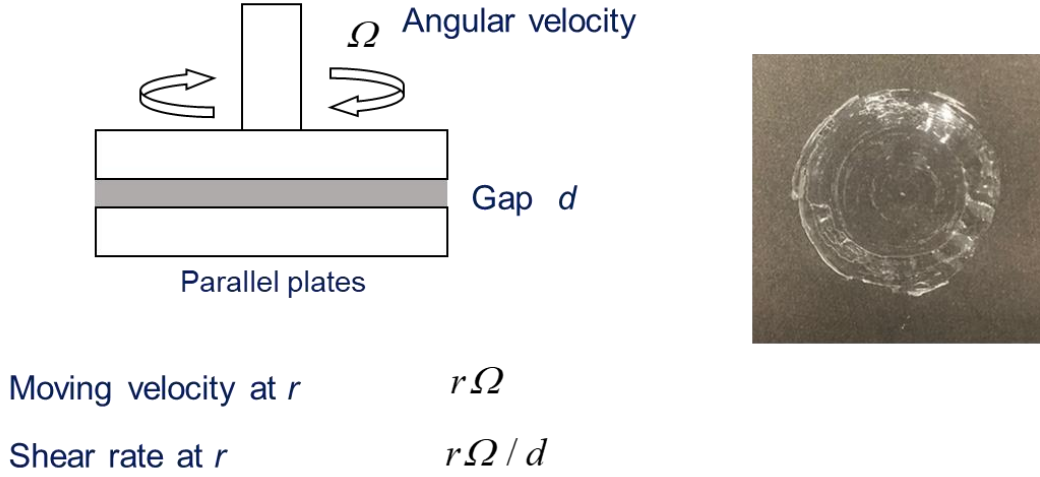


Figure 2.15. Parallel plate geometry and a sample film after POM measurement.

Figure 2.16 shows the 2θ profiles for samples exposed to a shear rate of 100 s^{-1} . The profiles exhibit four unique diffraction rings corresponding to the (110), (040), (130), and (111) planes of α -form crystals, with the values in parentheses denoting the Miller indices. Additionally, β -form crystals, which show strong intensity at 16.1° [2,25], were not detected for all samples. From the 2θ profiles, the degree of crystallinity, χ_c is calculated following the equation:

$$\chi_c = \frac{I_c}{I_c + I_a} \times 100 \quad (2-5),$$

The degree of crystallinity was measured at 58.9% for PP and 65.2% for PP/MDBS, demonstrating that the incorporation of MDBS significantly improved the crystallinity.

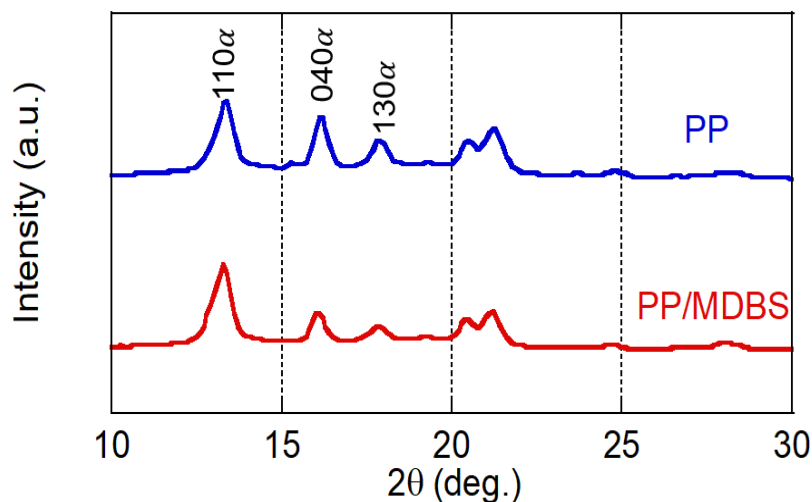
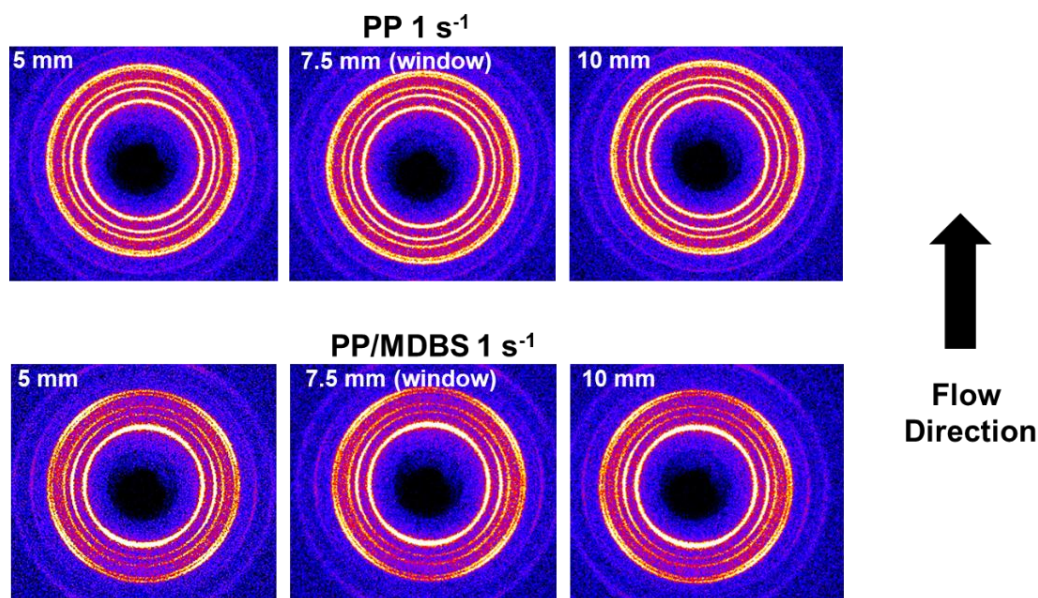
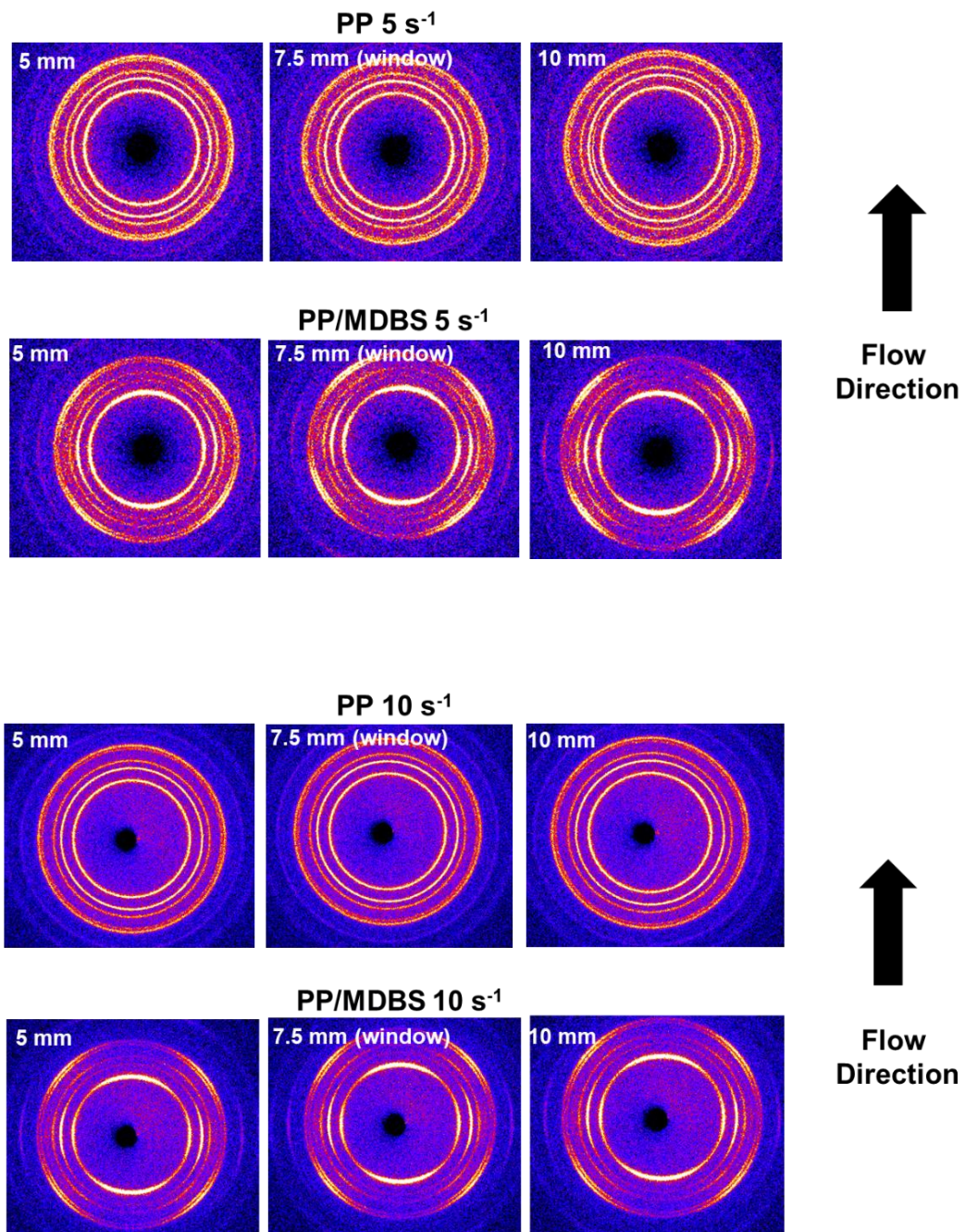


Figure 2.16. WAXD 2θ profiles of PP and PP/MDBS.

Figure 2.17 illustrates the 2D-WAXD patterns of the sample films. No orientation was observed for the PP sample. However, in the case of PP/MDBS, several distinct arcs were present, indicating that the addition of MDBS significantly enhanced chain orientation.





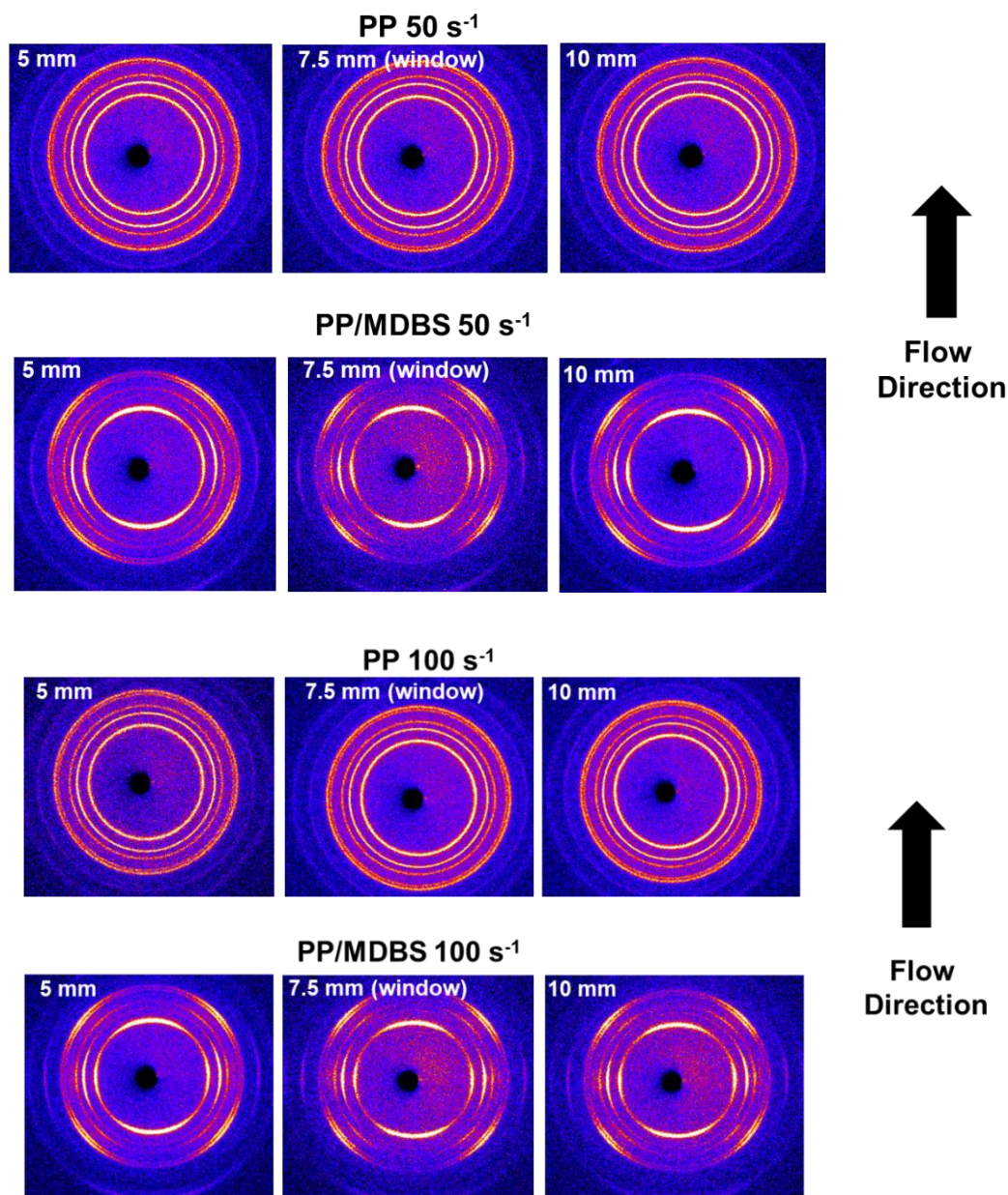


Figure 2.17. 2D-WAXD images of PP and PP/MDBS. The X-rays were directed at 5, 7.5 (the position of window), and 10 mm from the center of the sample films.

Figure 2.18 presents the 2D-SAXS patterns of the sample films subjected to a shear rate of 100 s^{-1} . As depicted, PP/MDBS displayed strong intensity along the meridian, indicating the well-developed formation of the shish-kebab structure. The long period for PP/MDBS was determined to be 17.8 nm.

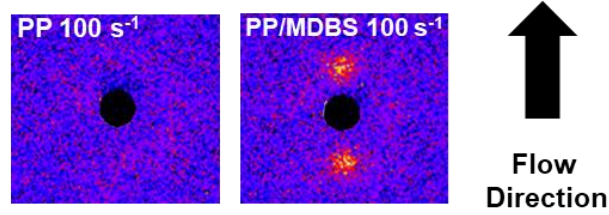


Figure 2.18. 2D-SAXS images of PP and PP/MDBS. The X-rays were directed at the window position relative to the sample films.

In the 2D-WAXD analysis, the orientation of the molecular chain is usually characterized by the calculation of peak at the half-height in the fitting curve, as follows:

$$H (\%) = \frac{180^\circ - W}{180^\circ} \times 100 \quad (2-6),$$

where W is the width of the peak at half height in the I/A (intensity/azimuth) curve obtained from 2D-WAXD.

Figure 2.19 illustrates the degree of orientation (%) of PP/MDBS. In the figure, data from the same film are represented by the same symbols. The horizontal axis indicates the actual shear rate at each position within the temperature range of 180 to 160 °C. The degree of orientation (%) increased with increasing the shear rate.

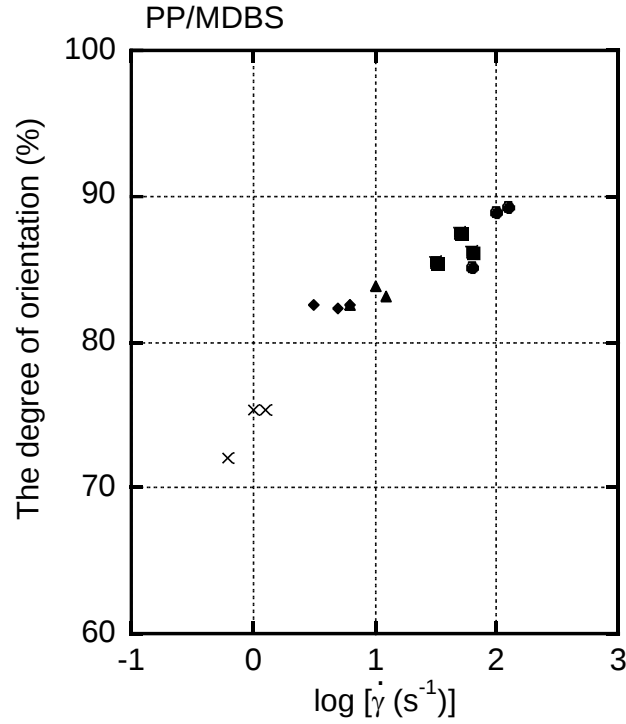


Figure 2.19. The degree of orientation (%) as a function of shear rate applied during cooling from 180 to 160 °C. The shear rates at the window area were 100 s⁻¹ (circles), 50 s⁻¹ (squares), 10 s⁻¹ (triangles), 5 s⁻¹ (diamonds), and 1 s⁻¹ (crosses).

Furthermore, the orientation function F_{WAXD} was quantitatively calculated using the (110) and (040) planes following the Wilchinky method as follows [26-29]:

$$F_{WAXD} = \frac{3\langle \cos^2 \phi \rangle - 1}{2} \quad (2-7),$$

$$\langle \cos^2 \phi \rangle = 1 - 1.080 \langle \cos^2 \phi_{110} \rangle - 0.090 \langle \cos^2 \phi_{040} \rangle \quad (2-8),$$

$$\langle \cos^2 \phi_{hkl} \rangle = \frac{\int_0^\pi I(\phi_{hkl}) \cos^2 \phi_{hkl} \sin \phi_{hkl} d\phi_{hkl}}{\int_0^\pi I(\phi_{hkl}) \sin \phi_{hkl} d\phi_{hkl}} \quad (2-9),$$

where φ is the angle between the normal of a given (hkl) crystal plane and the shear flow direction, ϕ is the angle between the flow direction and the PP chain, and I is the intensity.

The orientation function of the sample films is shown in Figure 2.20. For PP, the orientation function stayed close to zero at shear rates below 10 s^{-1} , suggesting that the PP chains were oriented randomly. This is consistent with the observation of spherulite texture without deformation, as illustrated in Figure 2.13. As the shear rate increased, the orientation function also rose. Compared to pure PP, PP/MDBS exhibited significantly higher orientation function values over the entire shear rate spectrum. These findings also align with the morphological observations.

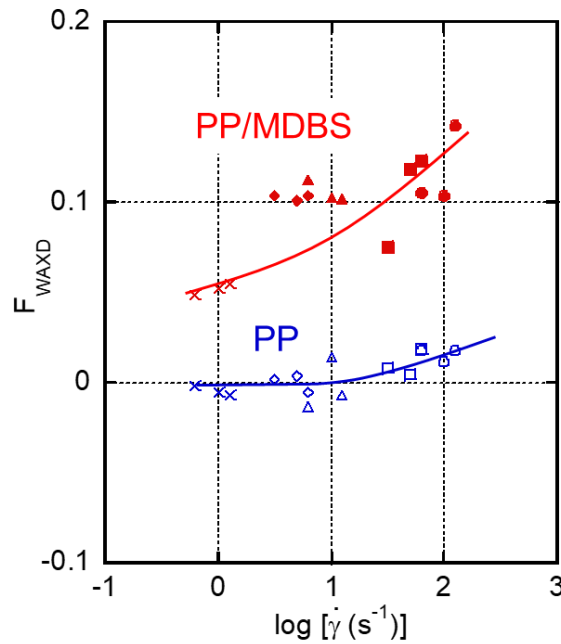


Figure 2.20. Orientation function F_{WAXD} as a function of shear rate applied during cooling from 180 to 160 °C. The shear rates at the window area were 100 s^{-1} (circles), 50 s^{-1} (squares), 10 s^{-1} (triangles), 5 s^{-1} (diamonds), and 1 s^{-1} (crosses).

The orientation function was evaluated by quantifying the IR dichroic ratio at 841 and 973 cm^{-1} using the sample films. These measurements were taken from a variety of positions. The absorption bands at 841 and 973 cm^{-1} are related to the crystalline and amorphous chain, respectively, with its transition moment aligned parallel to the molecular chain. Thus, the orientation function of crystalline and amorphous chains ($F_{IR, c}$, $F_{IR, a}$) can be calculated using the following equations [30]:

$$F_{IR} = \frac{2}{3\langle \cos^2 \alpha \rangle - 1} \times \frac{D-1}{D+2} \quad (2-10),$$

$$D = \frac{A_{//}}{A_{\perp}} \quad (2-11),$$

where α is the angle between the molecular chain axis and the transition moment of each molecular vibration. D is the IR dichroic ratio, where $A_{//}$ and $A_{\perp}$ are the IR absorbances parallel and perpendicular to the flow direction. It should be noted that the values of α of these IR bands are known to be 0° and 7.3° for 841 and 973 cm^{-1} , respectively [31,32].

The orientation function F_{IR} of the sample film is illustrated in Figure 2.21. In accordance with the results obtained by 2D-WAXD, $F_{IR, c}$ increased with the applied shear rate. The addition of MDBS significantly improved the values, even at a low shear rate. In the case of PP/MDBS, the slight reduction in orientation function at low shear rates is most likely attributable to a decrease in fiber orientation produced by the lower hydrodynamic force at these shear rates.

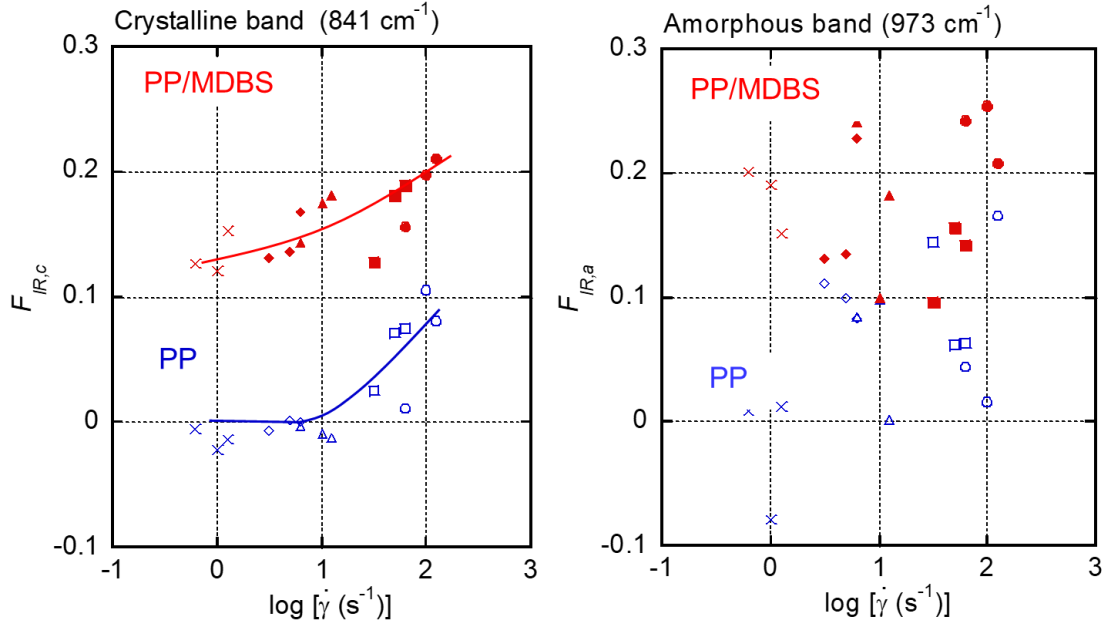


Figure 2.21. Orientation function $F_{IR,c}$ and $F_{IR,a}$, as a function of shear rate applied during cooling from 180 to 160 °C. The shear rates in the window area were 100 s⁻¹ (circles), 50 s⁻¹ (squares), 10 s⁻¹ (triangles), 5 s⁻¹ (diamonds), and 1 s⁻¹ (crosses).

2.4.5 Drawdown force

The draw force, defined as the force required to stretch an extruded strand, was measured and is presented in Figure 2.22. It was observed that the addition of the nucleating agent (MDBS) significantly increased the drawdown force, particularly at a draw ratio of 7.5 with a longer die length. This phenomenon can be attributed to several factors.

1. Because MDBS enhances crystallization, it reduces the molten part of an extruded stand. As a result, an actual elongational strain rate is enhanced by the MDBS addition providing a high elongational stress.

2. At a high draw ratio, drawdown force usually decreases because of the small cross-sectional area of an extruded strand. A thinner stand enhances crystallization

owing to rapid cooling. Therefore, the difference between PP and PP/MDBS is reduced at a high draw ratio.

3. The melt with a long relaxation time shows a high orientation which is pronounced using a long die length. As a result, the density of entanglement is reduced, and the chain orientation is enhanced to the flow direction.

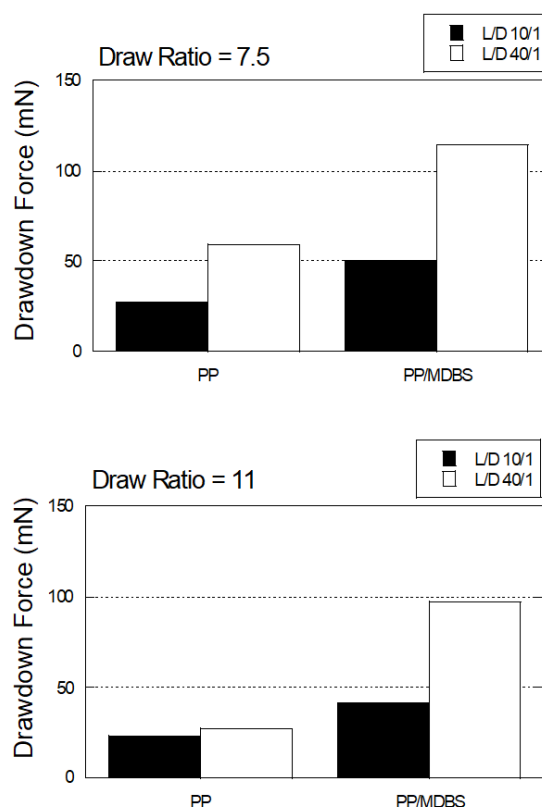


Figure 2.22. Drawdown force for PP and PP/MDBS measured by two types of dies having different lengths at two draw ratios. The extruded was carried out at 180 °C with a shear rate of 124 s⁻¹.

2.5 Conclusions

In this study, the crystallization behavior of PP containing a fibrous nucleating agent under shear history was examined using a polarized optical microscope equipped with a quartz parallel-plate shear device and a photo-detector. The findings revealed that the addition of the fibrous nucleating agent (MDBS), increased the crystallization temperature. In pure PP, no orientation was observed, and a spherulite texture remained even after shear rates below 50 s^{-1} were applied. In contrast, PP/MDBS exhibited a highly oriented structure to the flow direction, as demonstrated by POM, 2D-WAXD, and the IR dichroic ratio. This high degree of molecular orientation, contributing to an enhanced modulus, appears to originate from a pseudo shish-kebab structure, where the fibrous MDBS acts as shish and aligns with the flow direction. Moreover, crystallization from the oriented MDBS fibers markedly decreased light scattering, presumably owing to the extended correlation length and absence of spherulitic texture. Consequently, films including MDBS, fabricated by traditional processing under shear flow, have enhanced transparency.

References

- [1] Ed., Pasquini N, Polypropylene handbook 2nd ed. Hanser (2005)
- [2] Karger-Kocsis J, and Tamas B, Polypropylene handbook. Morphology, blends and composites. Springer Nature (2019)
- [3] Sugimoto M, Masubuchi, Takimoto J, and Koyama K. Melt rheology of polypropylene containing small amounts of high-molecular-weight chain. 2. uniaxial and biaxial extensional flow, *Macromolecules*, 34, 6056–6063 (2001)
- [4] Kida T, Kimura T, Eno A, Janchai K, Yamaguchi M, Otsuki Y, Kimura T, Mizukawa T, Murakami T, Hato K, and Okawa T, Effect of ultra-high-molecular-weight molecular chains on the morphology, crystallization, and mechanical properties of polypropylene, *Polymers*, 13, 4222 (2021)
- [5] Balzano L, Kukalyekar N, Rastogi S, Peters G W M, and Chadwick J.C. Crystallization and dissolution of flow-induced precursors, *Phys Rev Lett*, 100, 048302 (2008)
- [6] Mykhaylyk OO, Chambon P, Impradice C, Fairclough JPA, Terrill NJ, and Ryan AJ. Control of structural morphology in shear-induced crystallization of polymers, *Macromolecules*, 43, 2389-2405 (2010)
- [7] Hamad FG, Colby RH, and Milner ST. Onset of flow-induced crystallization kinetics of highly isotactic polypropylene, *Macromolecules*, 48, 3725-3738 (2015)

- [8] Wingstrand SL, Shen B, Kornfield JA, Mortensen K, Parisi D, Vlassopoulos D, and Hassager O. Rheological link between polymer melts with a high molecular weight tail and enhanced formation of shish-kebabs, *ACS Macro Lett*, 6, 1268-1273 (2017)
- [9] Zhang Q, Li L, Su F, Ji Y, Ali S, Zhao H, Meng L, and Li L. From molecular entanglement network to crystal-cross-linked network and crystal scaffold during film blowing of polyethylene: an in situ synchrotron radiation small- and wide-angle x-ray scattering study, *Macromolecules*, 51, 4350-4362 (2018)
- [10] Balzano L, Rastogi S, and Peters GWM. Flow induced crystallization in isotactic polypropylene-1,3:2,4-bis(3,4-dimethylbenzylidene)sorbitol blends: Implications on morphology of shear and phase separation, *Macromolecules*, 41, 399-408 (2008)
- [11] Phulkerd P, Nakabayashi T, Iwasaki S, and Yamaguchi M. Enhancement of drawdown force in polypropylene containing nucleating agent, *J Appl Polym Sci*, 136, 47295 (2018)
- [12] Iwasaki S, Inoue M, Takei Y, Nishikawa R, and Yamaguchi M. Modulus enhancement of polypropylene by sorbitol nucleating agent in flow field, *Polym Crystallization*, 4, e10170 (2021)
- [13] Iwasaki S, Uchiyama Y, Tenma M, and Yamaguchi M. Effect of neutralizer on transparency of nucleating agent-containing polypropylene, *Polymers*, 13, 680 (2021)

- [14] Tenma M, Mieda N, Takmatsu S, and Yamaguchi M. Structure and properties for transparent polypropylene containing sorbitol-based clarifier, *J Polym Sci B Polym Phys*, 46, 41-47 (2008)
- [15] Hai-Shan B, Stephen Z.D.C, and Bernhard W. Addendum to the thermal properties of polypropylene, *Makromol. Chem. Rapid Commun*, 9, 75–77 (1988)
- [16] Tenma M, and Yamaguchi M. Structure and properties of injection-molded polypropylene with sorbitol-based clarifier, *Polym Eng Sci*, 47,1441-1446 (2007)
- [17] Nishikawa R, and Yamaguchi M. Effect of carbon nanotube addition on structure and properties for extrudates of high-density polyethylene, *J Appl Polym Sci*, 136, 48010 (2019)
- [18] Nishikawa R, Aridome N, Ojima N, and Yamaguchi M. Structure and properties of fiber-reinforced polypropylene prepared by direct incorporation of aqueous solution of poly(vinyl alcohol). *Polymer*, 199, 122566 (2020)
- [19] Ward IW, Structure and properties of orientation polymer. Chapman & Hall (1975)
- [20] Born M, and Wolf E, Principles of optics, 7th ed, Cambridge (1990)
- [21] Nesse W.D, Introduction of optical mineralogy, 2nd ed, Oxford University Press (1991)
- [22] Masuko T, Tanaka H, and Okajima S. Studies on biaxial stretching of polypropylene film. IV. Overall orientation during one-step biaxial stretching and its application to the estimation of the principal refractive indices of isotactic polypropylene, *J Polym Sci A-2*, 8, 1565-1574 (1970)

- [23] Kato, T. A method to synthesize interference color chart with personal computer, J Geol Soc Japan, 107, 64-67 (2001)
- [24] Norris FH, and Stein RS. The scattering of light from thin polymer films. IV. Scattering from oriented polymers, J Polym Sci, 22, 87-115 (1958)
- [25] Yamaguchi M, Irie Y, Phulkard P, Hagihara H, Hirayama S, and Sasaki S, Plywood-like structure of injection-moulded polypropylene. Polymer, 51, 5983-5989 (2010)
- [26] Seemork J, Siriprumpoonthum M, Lee Y, Nobukawa S, and Yamaguchi M. Effect of die geometry on drawdown force of polypropylene at capillary extrusion, Adv Polym Technol, 34, 21477 (2015)
- [27] Wilchinsky ZW. Measurement of orientation in polypropylene film, J Appl Phys, 31, 1969-1972 (1960)
- [28] Tanaka M, and Young RJ. Molecular orientation distributions in uniaxially oriented poly(L-lactic acid) films determined by polarized Raman spectroscopy, Macromolecules, 39, 3312-3321 (2006)
- [29] Arvidson SA, Khan SA, and Gorga RE. Mesomorphic- α -monoclinic phase transition in isotactic polypropylene: a Study of processing effects on structure and mechanical properties, Macromolecules, 43, 2916-2924 (2010)
- [30] Parthasarthy G, Sevegney M, and Kannan RM. Rheoptical fourier transform infrared spectroscopy of the deformation behavior in quenched and slow-cooled isotactic polypropylene films, J Polym Sci B Polym Phys, 40, 2539-2551 (2002)

- [31] Bower D.I and Maddams,W.F. The Vibrational Spectroscopy of Polymers. Cambridge University Press (1992)
- [32] Nitta K.-H, Sawada T, Yoshida S, and Kawamura T. Three dimensional molecular orientation of isotactic polypropylene films under biaxial deformation at higher temperatures. *Polymer*,74, 30-37 (2015)

Chapter 3

Effect of low-density polyethylene addition on shear-induced crystallization of polypropylene

3.1 Introduction

Isotactic polypropylene (PP) is a main semi-crystalline polymer widely used in various applications [1,2]. Owing to its industrial significance, considerable research has focused on studying its blends. Additionally, the miscibility of ethylene/ α -olefin copolymers with PP has been extensively investigated, which are mixtures of nonpolar polymers [3–8]. According to them, the difference in local chain stiffness, e.g., Kuhn segment length and packing length, affected by the species and content of α -olefin, decides the miscibility. It was also clarified that a long-chain branch structure does not play a significant role in miscibility [9–11]. Commercially available polyethylene materials, such as high-density polyethylene (HDPE) and low-density polyethylene (LDPE), are known to be immiscible with PP because their α -olefin contents are too low. As a result, both PP/LDPE and PP/HDPE blends exhibit phase-separated structures. Naturally, the structure and properties of these blends have been extensively studied [11–15]. It is widely recognized that one of the main problems of a conventional PP is its limited melt elasticity, particularly the lack of strain hardening in its transient elongational viscosity. Consequently, significant research has focused on modifying the

rheological properties of PP. Various methods have been proposed, including the addition of a high-molecular-weight fraction [16,17], the incorporation of long-chain branched [18–20], and the introduction of a weak gel with segments that are miscible with PP [21]. These methods are known to enhance chain stretching during flow, which promotes flow-induced crystallization. For linear polymers, it is well established that applied flow can effectively accelerate crystal nucleation under specific conditions [22–33]. One critical factor is the specific work, defined as stress multiplied by strain, applied during the flow history; this value must exceed a critical threshold to facilitate the formation of extended-chain crystals. For instance, prompt crystallization is observed in a strand extruded through a long die [34]. Another key factor is the strain rate, particularly the Weissenberg number associated with the Rouse mode (Wi_R). This number must be greater than 1 [Eq. (3–1)] to induce flow-induced crystallization.

$$Wi_R \equiv \dot{\gamma}\tau_R > 1, \quad (3-1)$$

where $\dot{\gamma}$ is the strain rate and τ_R is the Rouse time. Therefore, the critical shear rate for the formation of extended-chain crystals, i.e., shish, $\dot{\gamma}_c$ is given by Eq. (3–2),

$$\dot{\gamma}_c = 1/\tau_R, \quad (3-2)$$

The Rouse time is known to be proportional to the square of molecular weight M and is often expressed by Eq. (3–3),

$$\tau_R = \tau_e (M / M_e)^2, \quad (3-3)$$

where τ_e is the equilibrium time between neighboring entanglements and is known to be 1.5×10^{-7} s for PP at 170 °C [25,35]. M_e is the average molecular weight between

entanglement couplings, which is known to be 5250 for PP [36].

Flow-induced crystallization significantly influences the crystalline morphology, often resulting in the formation of highly oriented shish-kebab structures, which contribute to an increased modulus. This technique is therefore important for enhancing the rigidity of plastic products. In the case of long-chain branched polymers and blends containing a weak gel, pronounced chain stretching between branch points or crosslink sites facilitates flow-induced crystallization [37–42], as well as strain hardening in the transient elongational viscosity. Such a phenomenon becomes less noticeable due to the so-called “shear modification” caused by a prolonged shear history [42].

A recent approach to introducing strain hardening involves the addition of a long-chain branched polymer, such as LDPE. Fujii et al. demonstrated that conventional PP exhibits strain hardening in transient elongational viscosity when LDPE is added, as illustrated in Figure 3.1[43]. In contrast, this effect was not observed with the addition of HDPE.

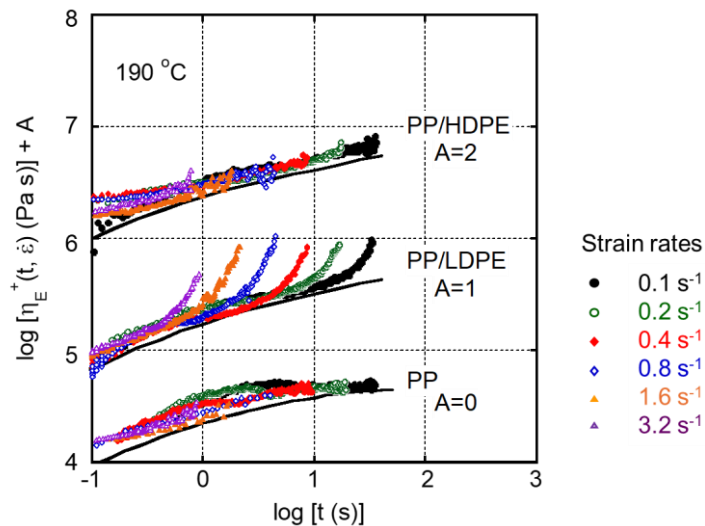


Figure 3.1. Transient elongational viscosity over time η_E^+ at various Hencky strain rates $\dot{\epsilon}$ at 190 °C for PP, PP/LDPE (70/30), and PP/HDPE (70/30) [43].

When the viscosity of LDPE is slightly lower than that of PP, the LDPE droplets dispersed within the continuous PP matrix deform in the flow direction, aligning with the PP. Eventually, however, fibrously deformed LDPE droplets exhibit strain hardening. Consequently, the degree of deformation in LDPE becomes significantly less than that in PP beyond a critical strain, at which point the elongational stress in LDPE equals that in PP. This situation is similar to a rigid fiber-dispersed system. According to the well-established slender body theory proposed by Batchelor [44], adding fibers greatly enhances elongational stress [45,46]. The experimental findings reported by Fujii et al. were well predicted by simulated values based on this mechanism [47]. Furthermore, this phenomenon has been observed in other systems, such as long-chain branched PP in linear low-density polyethylene [48] and ethylene-vinyl acetate copolymer in poly(lactic acid) [49], where both systems exhibited significant strain hardening in elongational viscosity, leading to improved processability. Notably, because the localized deformation is not obvious under shear flow, shear viscosity is barely affected by the addition of LDPE. However, in the present study, we unexpectedly discovered that shear flow, not elongational flow, induced the crystallization of PP/LDPE. This study focuses on the effect of LDPE on the shear-induced crystallization of PP, in comparison with PP/HDPE, as illustrated in Figure 3.1.

3.2 Experimental Procedure

3.2.1 Materials

The polymers used in this study were commercially available PP, LDPE, and HDPE. The properties of these polymer samples are summarized in Table 3.1. The size exclusion chromatography (SEC) profile for PP is illustrated in Figure 3.2. The structural characteristics and various non-linear viscoelastic behaviors of LDPE have been thoroughly discussed in previous works [20,50,51].

Table 3.1 Characteristics of the materials.

Materials	$M_w \times 10^{-4}$ (Da)	$M_n \times 10^{-4}$ (Da)	MFR (g / 10min)
PP	36	7.7	3.0 at 230 °C
LDPE	20	2.2	1.6 at 190 °C
HDPE	10	1.7	0.95 at 190 °C

PP/LDPE and PP/HDPE blends were produced using an internal mixer (Labo-Plastomill; Toyo Seiki Seisaku-sho, Ltd.) at a temperature of 190 °C. The screw rotation speed was set at 30 rpm, and mixing was carried out for 5 minutes. The weight fraction of LDPE and HDPE was 70/30 (w/w). Small quantities of thermal stabilizers were incorporated into the mixtures. Sheets with thicknesses of 100 μ m and 900 μ m were prepared using compression molding using a table-type test press (Tester Sangyo Co., Ltd.) at 190 °C under 10 MPa for 2 minutes, followed by quenching at 25 °C. The pure PP sheets with the same processing conditions were also prepared.

Furthermore, extrusion was conducted at different shear rates using a capillary rheometer (140 SAS-2002; Yasuda Seiki Seisakusyo, Ltd.). The temperature of the circular die and the reservoir was steady at 190°C. The die employed in the experiment had a length of 10 mm, a diameter of 1 mm, and an entrance angle of 2π . Neither Bagley nor Rabinowitsch corrections were applied to calculate the apparent shear stress and shear rate at the wall. The extruded strands were cooled at room temperature, which was 30 °C.

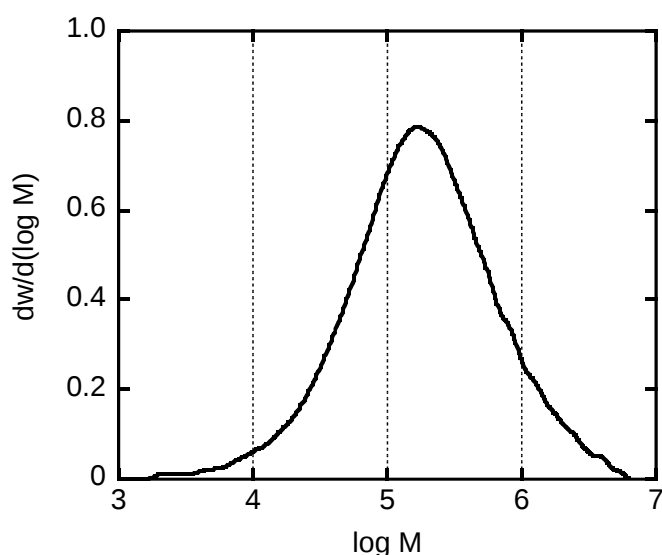


Figure 3.2 Size exclusion chromatography curve of PP

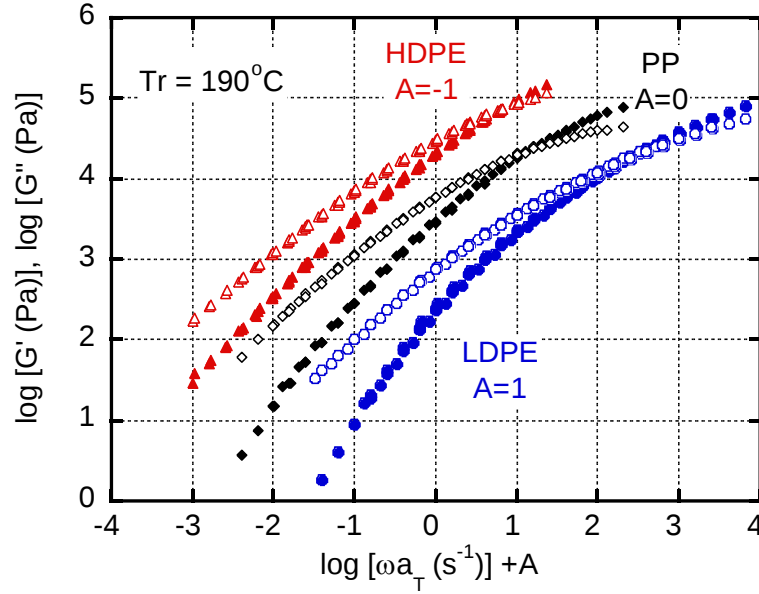


Figure 3.3. Master curves of the frequency dependence of oscillatory shear moduli such as storage modulus G' (closed symbols) and loss modulus G'' (open symbols) for PP (diamonds), LDPE (circles), and HDPE (triangles) at the reference temperature T_r of 190 °C. The horizontal axes were shifted for LDPE ($A = 1$), HDPE ($A = -1$) [43].

Table 3.2 Rheological terminal parameters at 190 °C.

Materials	η_0 (Pa s)	J_e^0 (Pa ⁻¹)	τ_w (s)	ω_x (s ⁻¹)
PP	18000	6.2×10^{-4}	11.1	0.082
LDPE	13000	5.9×10^{-4}	7.7	0.033
HDPE	16000	a	–	0.098

^aThe value cannot be determined.

3.2.2 Sample preparation

The obtained samples were molded into flat films (100 and 900 μm thick) using a compression-molding machine at 180 °C for 2 minutes.

3.3 Measurements

The frequency dependence of the oscillatory storage modulus G' and loss modulus G'' for both PP, PP/LDPE, and PP/HDPE was measured using a cone-and-plate rheometer (AR2000ex; TA Instruments, Inc.) at 190 °C under a nitrogen atmosphere. The cone used had a diameter of 25 mm, a cone angle of 4. The cone-and-plate rheometer was also used to measure the transient shear stress σ^+ and primary normal stress difference N_1^+ at 190 °C. The shear rates were 0.3, 1, and 3 s⁻¹. Each measurement was performed for 30 seconds. Furthermore, the steady values were collected from low to high shear rates at 170 and 190 °C.

The crystallization temperature was analyzed using a differential scanning calorimeter (DSC; model DSC8500, PerkinElmer Inc.). Approximately 10 mg of the sample was placed in an aluminum pan, heated to 200 °C for 5 minutes, and subsequently cooled to 25 °C at a cooling rate of 30 °C/min.

Crystallization behavior was examined using a polarizing optical microscope (POM) with a crossed-polarizer configuration. The microscope was equipped with a quartz parallel-plate shear stage, as discussed in Chapter 2. The experimental procedures related to temperature and shear conditions are shown in Figure 3.4. The sample film was heated to 170 °C to fully melt the film. After adjusting the gap to 100 μm, the sample were cooled to 130 °C to adjust the microscope. Subsequently, the sample was reheated at 190 °C for 5 minutes to ensure complete melting before the cooling process. The samples were then cooled at a constant rate of 30 °C/min from 190 °C. Shear was applied during the cooling process from 190 °C to 160 °C at various shear rates 0, 10, 30, and 50 s⁻¹ by rotating the bottom plate, the shear rate

was calculated at the center of the observation window. The depolarized light intensity (DLI), measured by a photo-detector through a band-pass filter of 633 nm, was calculated using the following equation:

$$DLI(\%) = \frac{I_0 - I_X}{I_{//} - I_X} \times 100, \quad (3-4)$$

where I_0 is the light intensity through the sample detected under crossed polars, and I_X and $I_{//}$ are the light intensities without the sample detected using crossed and parallel polars, respectively.

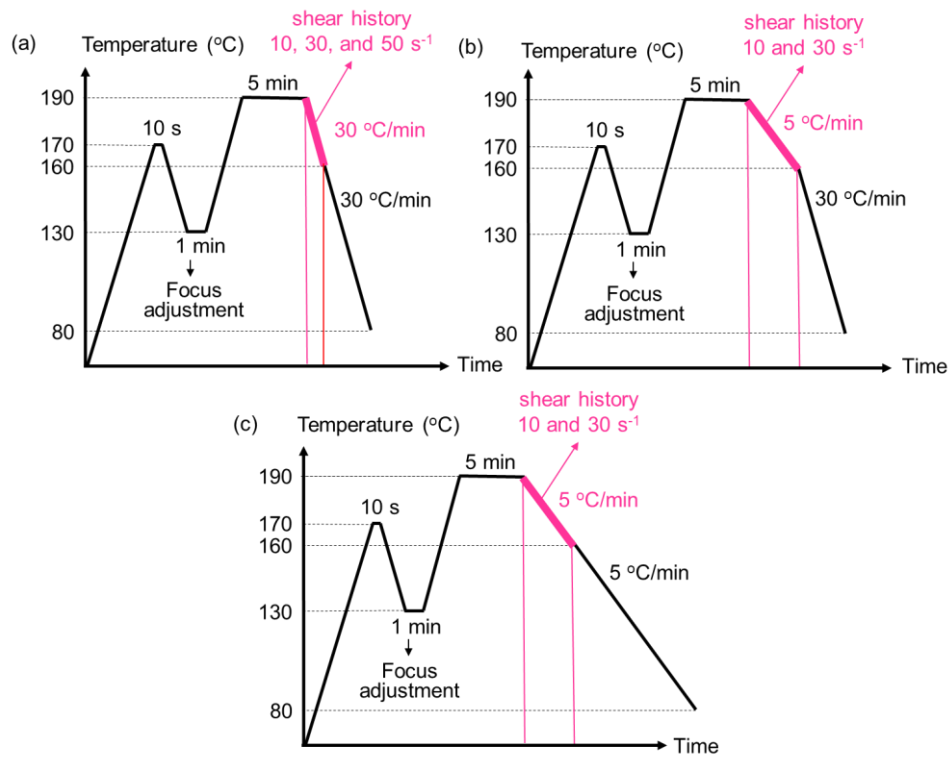


Figure 3.4. Experimental protocols of the temperature and shear protocol

The structure of sheets after the POM observation and stands extruded from capillary rheometer was characterized using a two-dimensional wide-angle X-ray

diffraction (2D-WAXD) (SmartLab; Rigaku.). The films were irradiated with a graphite-monochromatized Cu K α radiation beam, operated at 45 kV and 200 mA. The X-ray exposure time was set for 30 minutes with a beam spot diameter of 1.5 mm. The molecular chain orientation was evaluated by its azimuthal distribution.

3.4 Results and Discussion

3.4.1 Rheological properties

The linear viscoelastic properties of the polymers, i.e., master curves of the shear storage modulus G' and the loss modulus G'' as a function of angular frequency ω , are shown in Figure 3.3 [43]. The rheological parameters in the terminal region at 190 °C, such as zero-shear viscosity η_0 , steady-state shear compliance J_e^0 , and weight-average relaxation time τ_w , are summarized in Table 3.2 with the inverse of angular frequency at which both moduli are identical, i.e., $G' = G''$, as ω_x^{-1} . Moreover, the transient elongational viscosities of the samples are shown in Figure 3.1.

Figure 3.5 illustrates the dependence of the oscillatory shear moduli specifically the storage modulus G' and loss modulus G'' on angular frequency ω at 190 °C of pure PP and blends containing 30 wt.% of LDPE and HDPE. As seen in the low-frequency region, the G' values of PP/LDPE and PP/HDPE were higher than those of pure PP. This may be attributed to the long-time relaxation mechanism associated with the interfacial tension between the continuous PP phase and the dispersed polyethylene droplets, as explained by the emulsion model [52]. In the present study, a sea-island phase-separated structure was clearly discernable with an average diameter of 2 μm for both PP/LDPE and PP/HDPE [43].

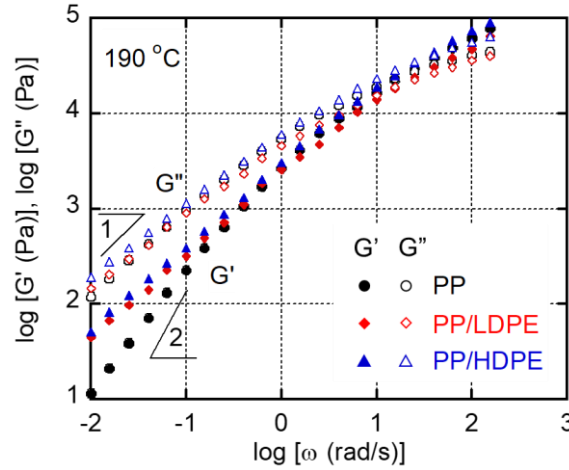


Figure 3.5. Angular frequency ω dependence of (closed symbols) the shear storage modulus G' and (open symbols) the loss modulus G'' at 190 °C for (circles) PP, (diamonds) PP/LDPE (70/30), and (triangles) PP/HDPE (70/30).

Growth curves of shear stress σ^+ and primary normal stress difference N_1^+ during the transient shear are shown in Figure 3.6. The measurements were carried out at various shear rates at 190 °C. Although the overshooting of transient shear stress was detected at 1 and 3 s^{-1} in all samples, there was no discernible difference among the samples.

Figure 3.7 shows the shear rate $\dot{\gamma}$ dependences of the shear stress σ and the primary normal stress difference N_1 during steady-state shear flow at 170 and 190 °C. Both σ and N_1 increased with increasing $\dot{\gamma}$ in PP, PP/LDPE, and PP/HDPE. The σ values were similar in all samples, as suggested by the transient measurement. However, in the low $\dot{\gamma}$ region, the N_1 values of PP/LDPE and PP/HDPE were slightly higher than those of PP. This must have originated from interfacial tension as described in the Doi-Ohta theory [53].

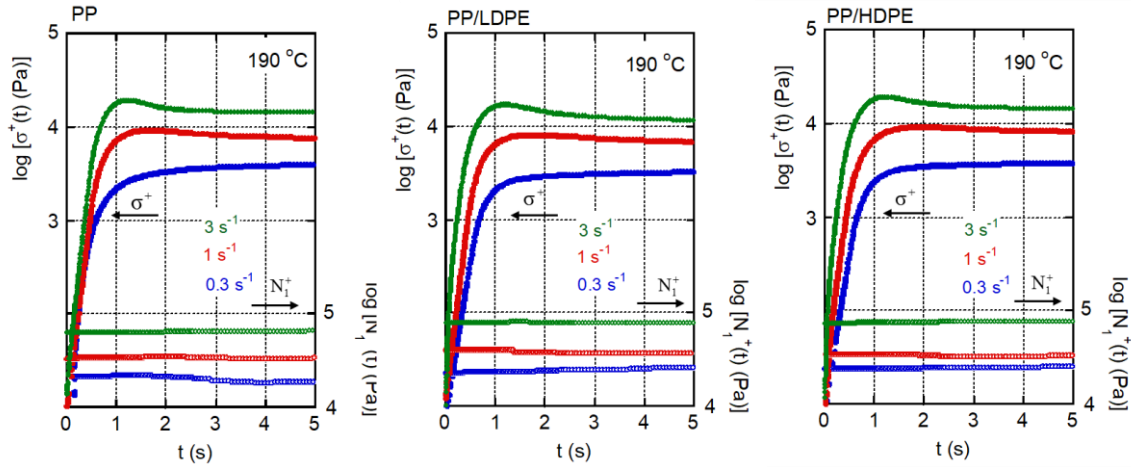


Figure 3.6. Growth curves of (closed symbols) shear stress σ^+ and (open symbols) primary normal stress difference N_1^+ at (circles) 0.3 s^{-1} , (diamonds) 1 s^{-1} , and (triangles) 3 s^{-1} for (left) PP, (center) PP/LDPE (70/30), and (right) PP/HDPE (70/30) at 190 °C.

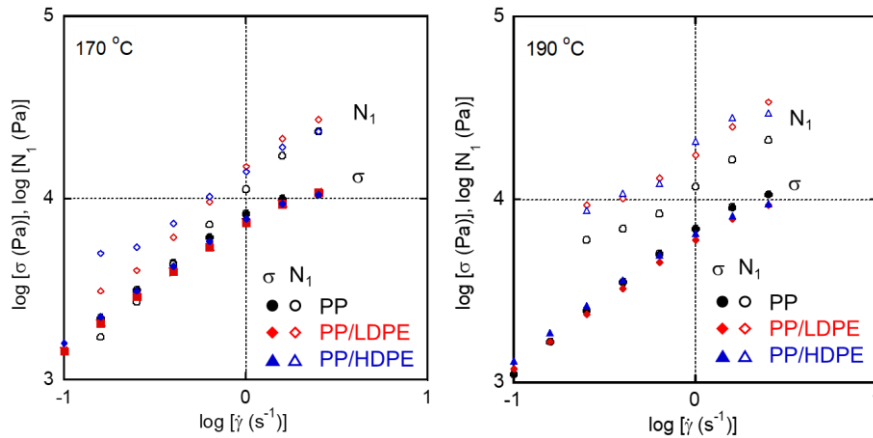


Figure 3.7. Steady-state (closed symbols) shear stress σ and (open symbols) primary normal stress difference N_1 as a function of the shear rate $\dot{\gamma}$ for (circles) PP, (diamonds) PP/LDPE (70/30), and (triangles) PP/HDPE (70/30) at (left) 170 °C and (right) 190 °C.

3.4.2 Thermal properties

DSC heating and cooling curves are shown in Figure 3.8. The heating and cooling rates were 30 °C/min. The PP/LDPE and PP/HDPE samples each produced two heating curve peaks, which were ascribed to the melting of each polymer. Moreover, the crystallization temperature, which is defined as the peak temperature of the heat flow, was almost the same (106-107 °C) for pure PP and PP/LDPE. The on-set crystallization temperature was approximately 115 °C for both samples. At a cooling rate of 30 °C/min, moreover, the crystallization temperature of HDPE (111.2 °C) was slightly higher than that of PP. Therefore, PP/HDPE was crystallized at a slightly higher temperature (110.6 °C) than PP (107.4 °C) and PP/LDPE (106.0 °C). The HDPE crystals acted as nuclei for PP crystallization at this cooling rate, which was previously reported [54].

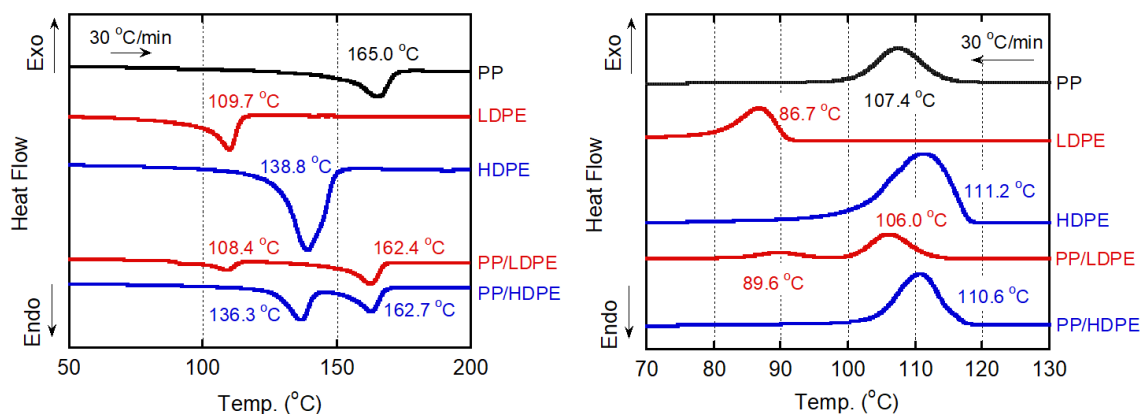


Figure 3.8. Differential scanning calorimetry DSC (left) heating and (right) cooling at 30 °C/min for PP, LDPE, HDPE, PP/LDPE (70/30), and PP/HDPE (70/30).

3.4.3 Crystallization behavior

The crystallization behavior in the absence of shear was further analyzed at the same cooling rate at which the DSC measurements were performed, i.e., 30°C/min using a polarizing optical microscope (POM) configured with crossed polarizers. As shown in Figure 3.9, the DLI values increased at approximately 113-115 °C for both pure PP se and PP/LDPE. However, the PP/HDPE shown the crystallization at a slightly higher temperature than the other samples. These were in quantitative agreement with the DSC results. The morphology observed during cooling is also evident in the figure and demonstrates that all the samples had a spherulite texture without any orientation. Although the image was unclear, the average size of the spherulites in PP and PP/LDPE was approximately 20-30 μm . In contrast, the PP/HDPE sample had a fine texture compared with the other samples. This must be attributed to the nucleating effect of HDPE on PP crystallization as mentioned above [54].

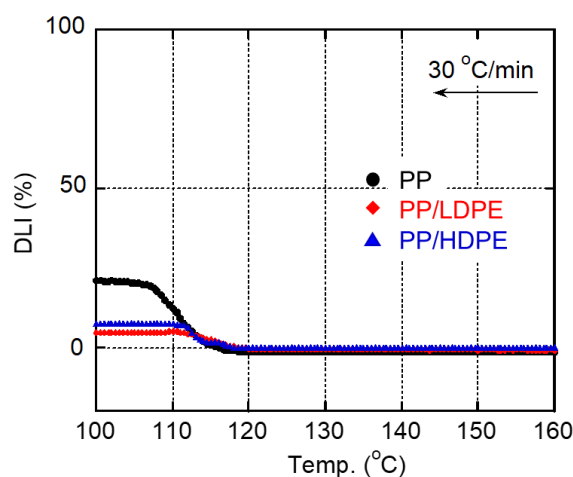


Figure 3.9. Growth curves of depolarized light intensity (DLI) at absence of shear during non-isothermal crystallization at 30 °C/min.

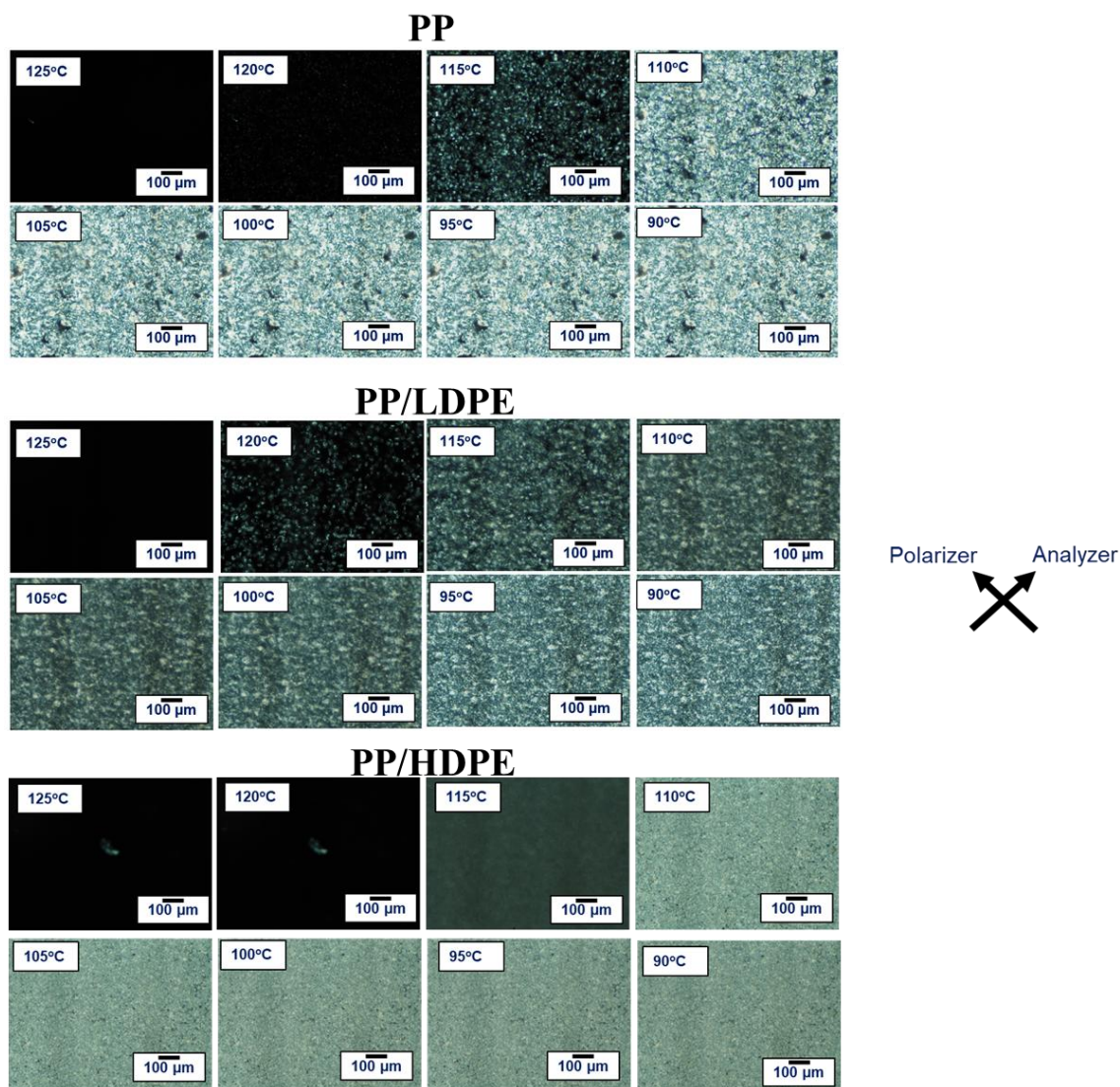


Figure 3.10. POM images of PP, PP/LDPE (70/30), and PP/HDPE (70/30) during non-isothermal crystallization at absence of shear. The images were collected without a color filter.

The crystallization behavior with shear history was evaluated from 190 to 160 °C at a cooling rate of 30 °C/min. For such experiments, edge fracture must be considered as originally suggested by Mykhylak et al. [25], since edge fracture perturbs shear-induced crystallization. Parisi et al. recently revealed that the onset shear rate of edge fracture is determined by the zero-shear viscosity and the measurement geometry [55].

Therefore, first, we checked the sample sheets after the crystallization as shown in Figure 3.11. In the experiments, edge fracture was not detected at least in the window area for all samples at any shear rates.

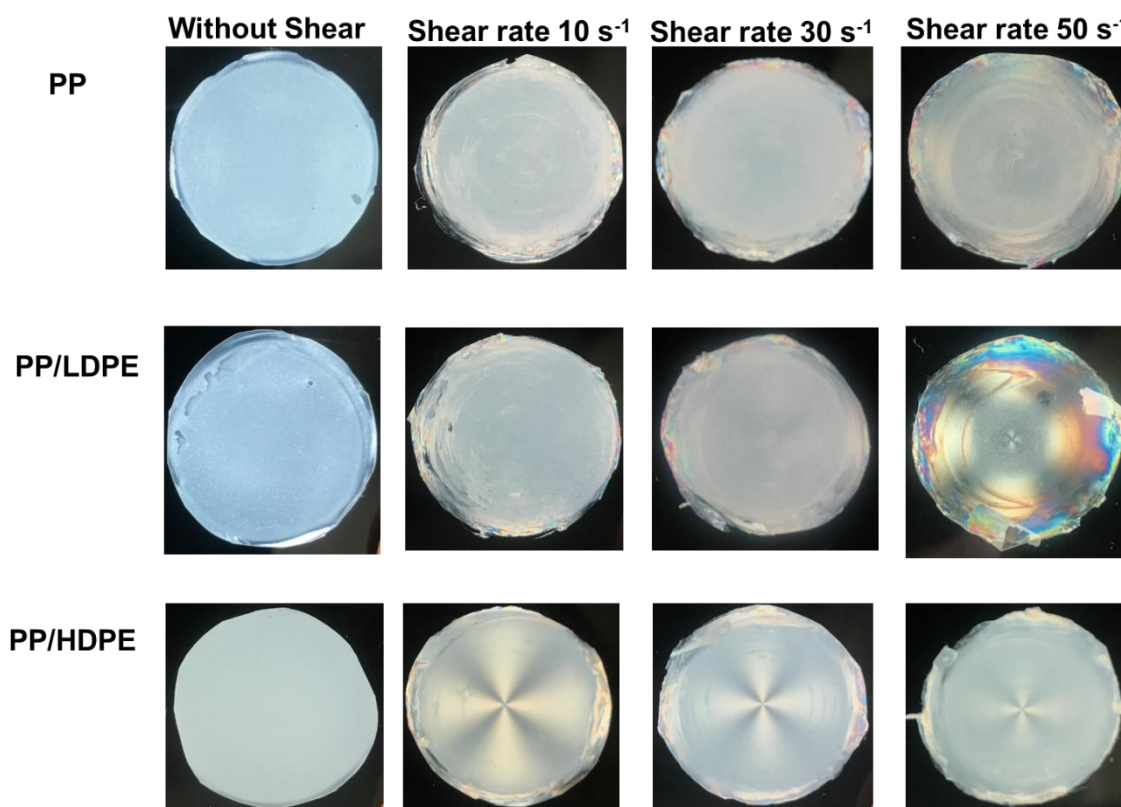


Figure 3.11. Sample sheets under crossed polars after the POM observation.

The DLI values during cooling are shown in Figure 3.12. The shear history markedly influenced the crystallization of all the samples. In pure PP, shear-induced crystallization was obvious beyond 30 s⁻¹. It should be noted that PP/LDPE crystallized at higher temperatures than the pure PP and PP/HDPE, demonstrating that shear-induced crystallization was greatly accelerated by the addition of LDPE. Figure 3.14 shows the onset crystallization temperature ($T_{\text{on-set}}$) of PP after shear flow. Apparently,

crystallization occurred at higher temperatures in PP/LDPE than in pure PP or PP/HDPE, which obvious at 30 and 50 s^{-1} . At 10 s^{-1} , T_{on-set} was the same as those without shear history. Furthermore, the addition of HDPE barely affected the shear-induced crystallization of PP.

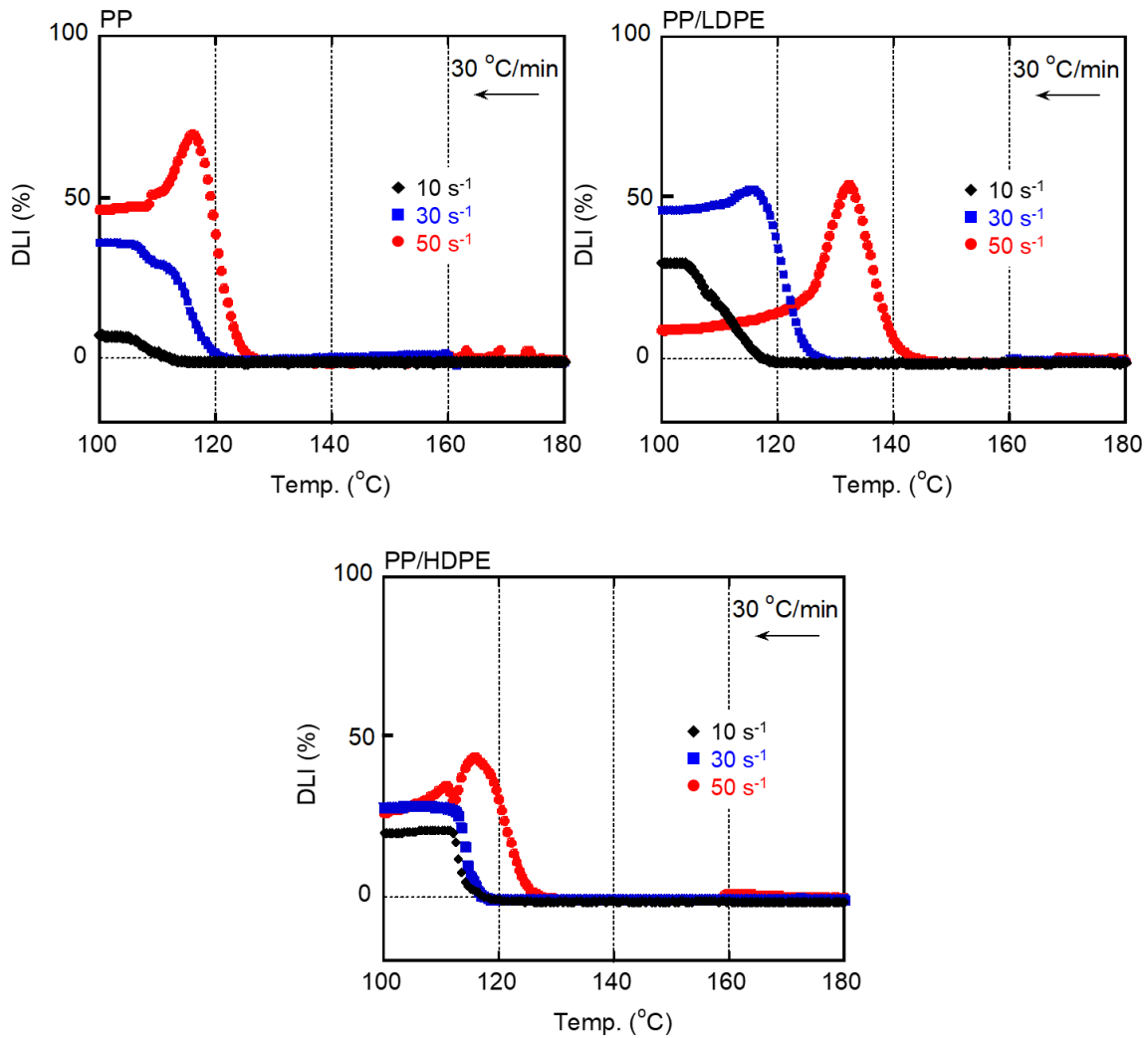
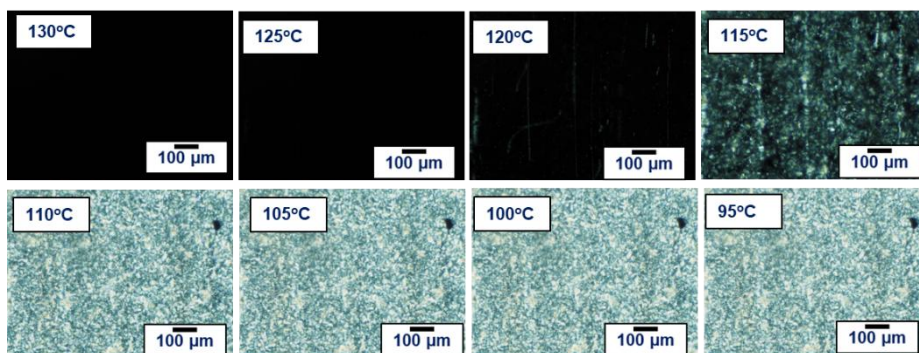
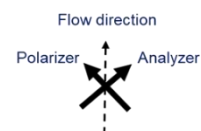
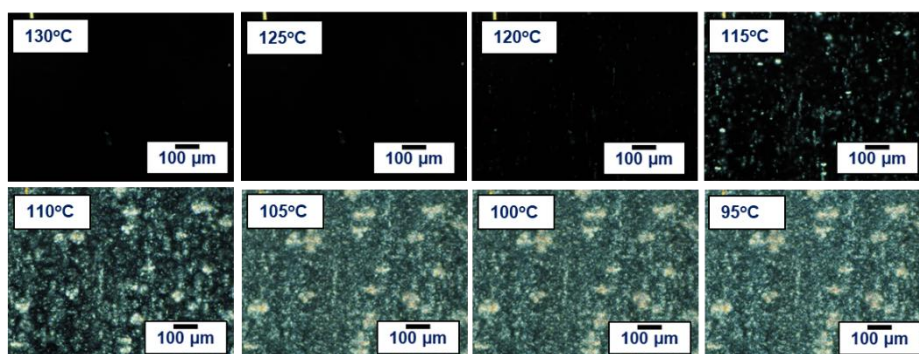


Figure 3.12. Growth curves of depolarized light intensity (DLI) during non-isothermal crystallization at 30 °C/min for PP, PP/LDPE (70/30), and PP/HDPE (70/30). Shear was applied from 190 to 160 °C at various shear rates.

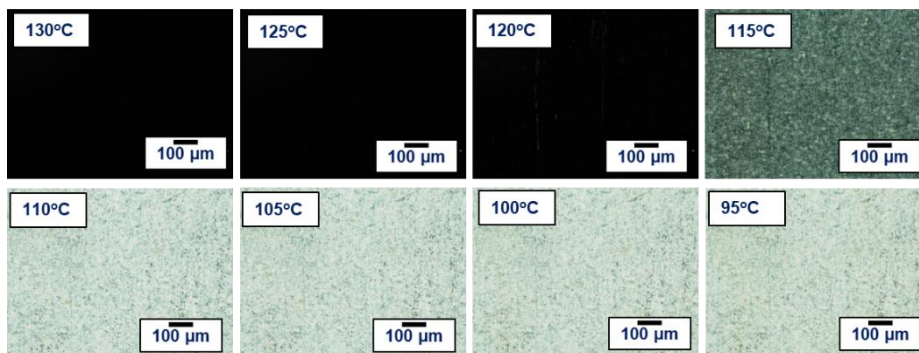
PP at 10 s^{-1}



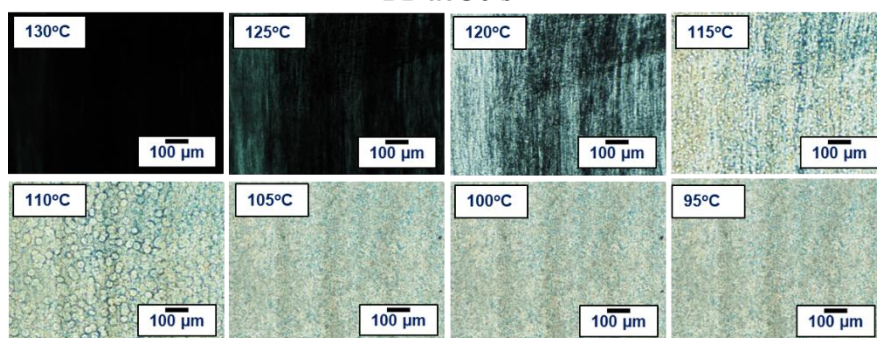
PP/LDPE at 10 s^{-1}



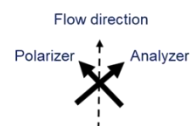
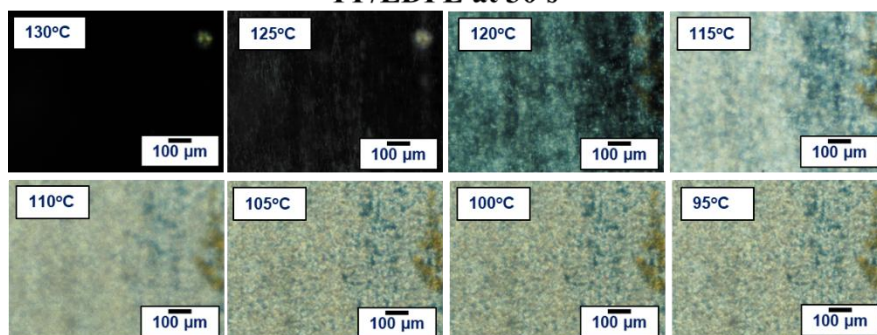
PP/HDPE at 10 s^{-1}



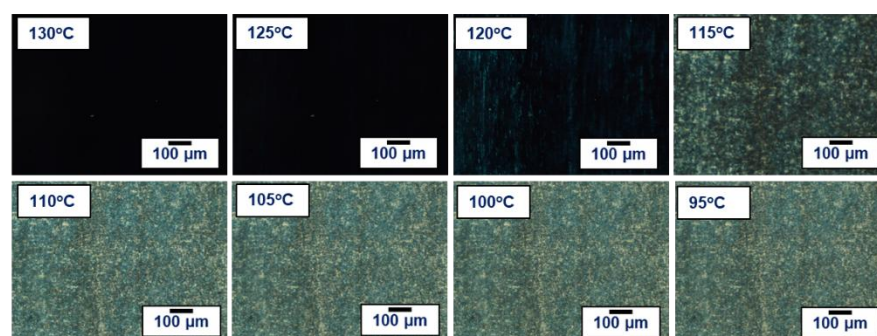
PP at 30 s⁻¹



PP/LDPE at 30 s⁻¹



PP/HDPE at 30 s⁻¹



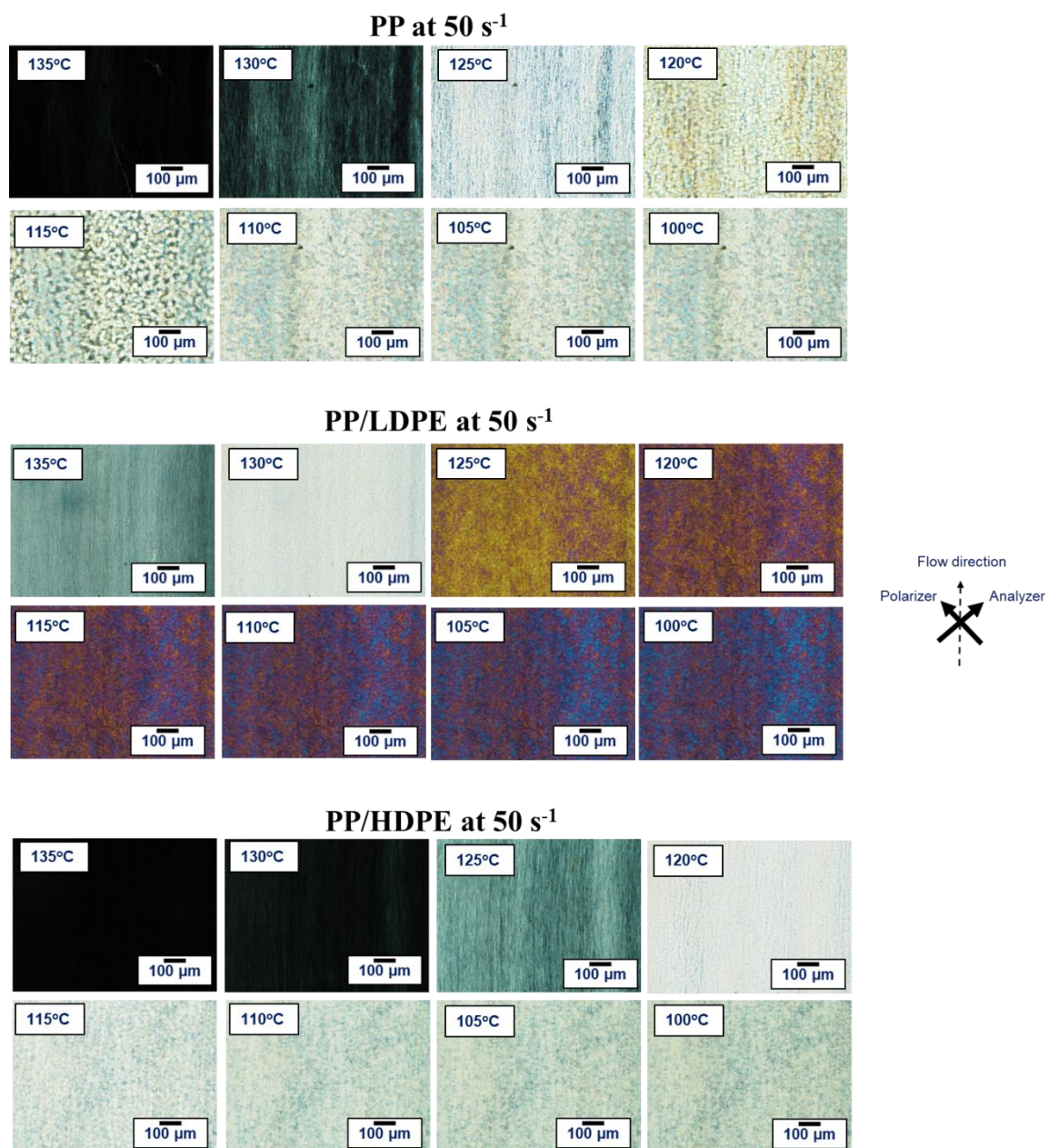


Figure 3.13. POM images of PP, PP/LDPE (70/30), and PP/HDPE (70/30) during non-isothermal crystallization at various shear rates. The images were observed without a color filter.

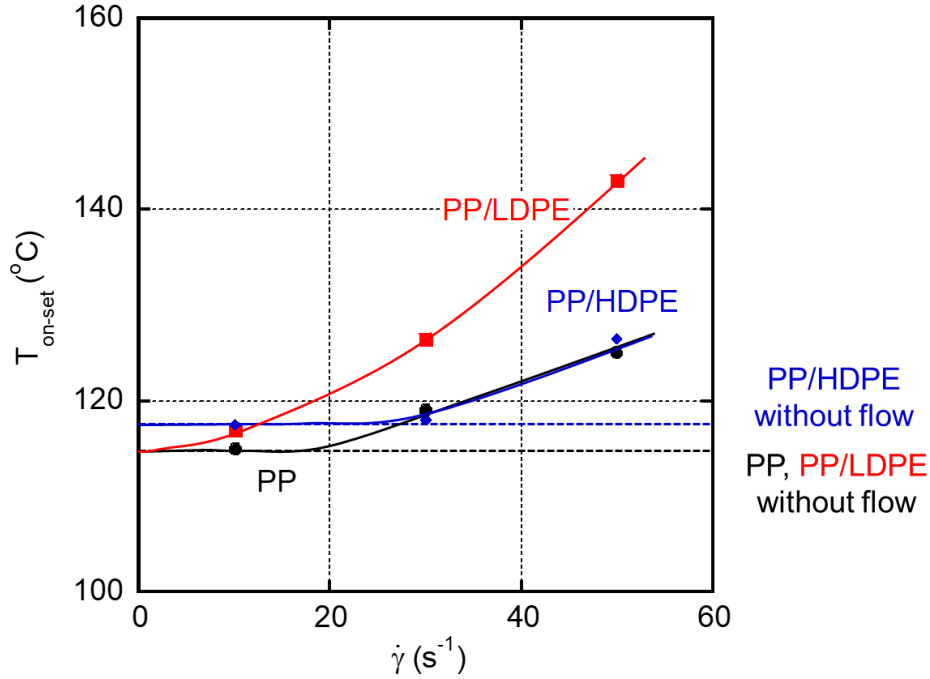


Figure 3.14. On-set crystallization temperature (T_{on-set}) at various shear rates (10, 30, and $50 s^{-1}$) of PP, PP/LDPE (70/30), and PP/HDPE (70/30) at a cooling rate of $30 s^{-1}$.

The dotted lines represent T_{on-set} under quiescent condition.

3.4.4 Molecular orientation

After cooling, the samples were removed from the machine to evaluate the molecular chain orientation. The 2D-WAXD patterns of pure PP, PP/LDPE, and PP/HDPE obtained at a cooling rate of $30 ^{\circ}C/min$ and a shear rate of 0, 10, 30, and $50 s^{-1}$ are shown in Figure 3.15. No orientation was detected in PP. In contrast, several distinct arcs were detected in PP/LDPE, demonstrating that the addition of LDPE had a significant effect on the chain orientation of PP.

Figure 3.16 also shows the azimuthal angle distributions of the (040) and (110) diffraction planes of PP, PP/LDPE, and PP/HDPE at a shear rate of $50 s^{-1}$. As shown in

the figure, only the PP/LDPE sample produced sharp peaks on the equator, i.e., 90° and 270° , for the (040) diffraction plane. In the case of the (110) plane, double peaks were detected on each polar beside the peak on the equator. These were ascribed to the tangential daughter lamellae grown from the original parent lamellae that developed perpendicular to the flow direction [56]. Therefore, the azimuthal distribution of the (110) plane also indicated the well-developed extended chain crystal in the PP/LDPE sheet. These results demonstrated that adding LDPE at an optimized shear rate enhanced the molecular chain orientation.

The crystalline texture of the samples with an applied shear history was also examined. At a shear rate of 10 s^{-1} , spherulite texture without any orientation was observed in all the samples. For pure PP, the oriented structure along the flow direction was observed beyond 10 s^{-1} at $120\text{ }^\circ\text{C}$. However, the spherulite texture was developed at low temperatures, demonstrating that the polymer chains in the molten state were completely relaxed. This is in accordance with a previous study on flow-induced PP crystallization [57]. As shown in Figure 3.13, a highly oriented structure without spherulite texture was detected in PP/LDPE, i.e., the sample had a high on-set temperature after applying shear flow at 50 s^{-1} . In the POM images obtained without a color filter, red/purple color was detected in PP/LDPE at $100\text{ }^\circ\text{C}$, indicating that retardation was approximately 550 nm based on the polarization color chart [58]. Therefore, the orientation function was approximately 0.14, assuming the intrinsic birefringence of PP is 0.04 [59].

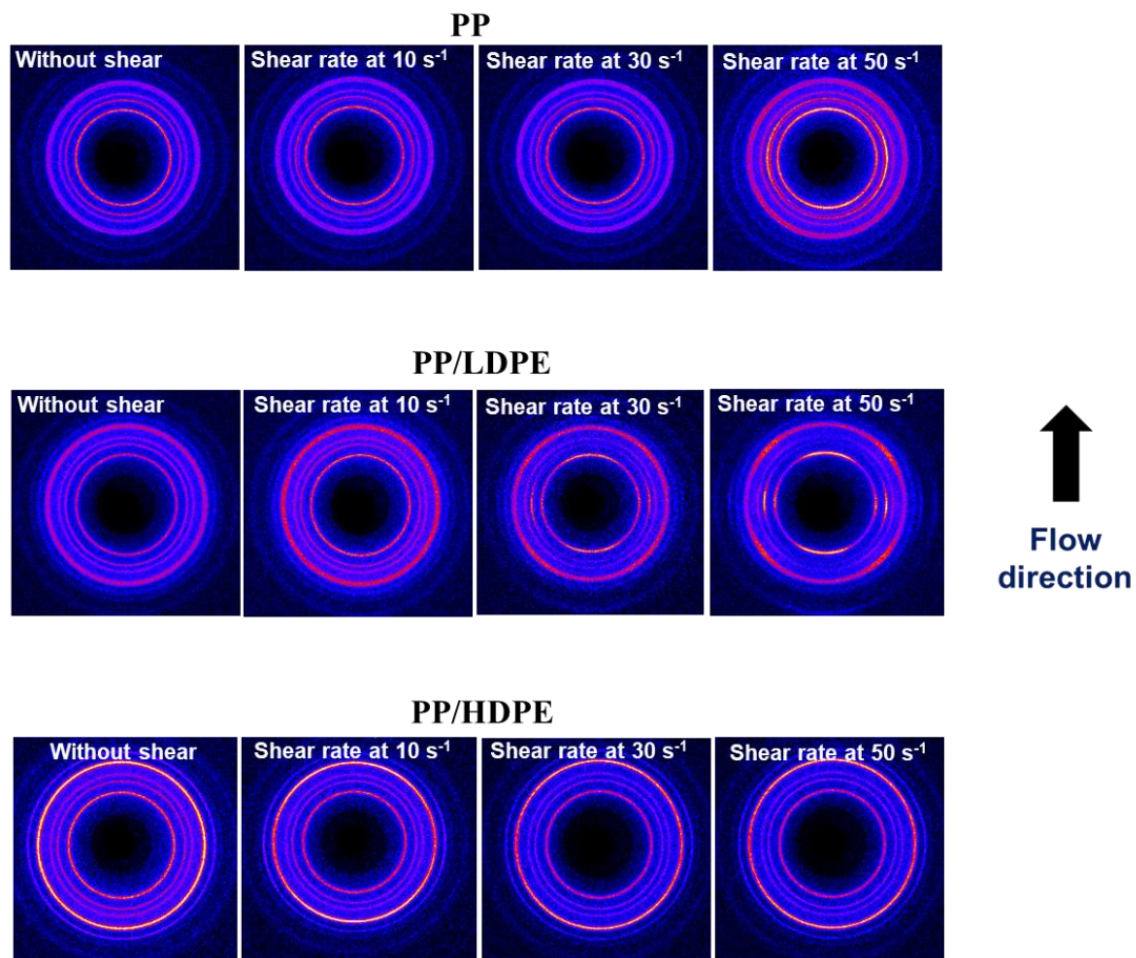


Figure 3.15. 2D-WAXD images of PP, PP/LDPE (70/30), and PP/HDPE (70/30).

The X-rays were directed at 7.5 mm (window position).

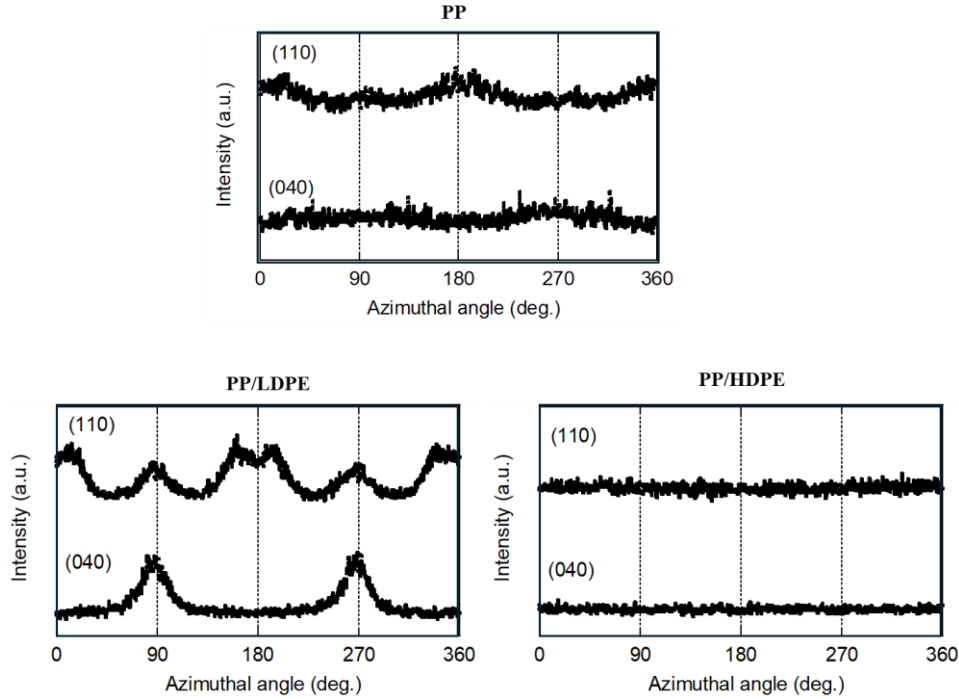


Figure 3.16. Azimuthal angle distribution of the (110) and (040) planes of α -form PP crystal for PP, PP/LDPE (70/30), and PP/HDPE (70/30). The samples with shear history at 50 s^{-1} from 190 to 160 $^{\circ}\text{C}$ are cooled at 30 $^{\circ}\text{C}/\text{min}$.

As mentioned in the introduction, the present sample, PP/LDPE, exhibited strain-hardening behavior in the transient elongational viscosity. This can be attributed to the significant deformation of the continuous PP phase, which is located between elongated LDPE droplets that undergo viscous enhancement, leading to strain hardening. This situation must accelerate flow-induced crystallization under elongation flow. However, under shear flow, no strain hardening was observed during transient shear, as illustrated in Figure 3.6. Additionally, the steady-state shear stress and normal stress difference for the PP/LDPE blend were not significantly different from those of pure PP or the PP/HDPE blend at constant temperatures of 170 $^{\circ}\text{C}$ and 190 $^{\circ}\text{C}$, as shown in Figure 3.7.

In this study, however, crystallization behavior was evaluated during cooling rather than at constant temperatures. Such a situation must increase Wi_R , i.e., dimensionless shear rate [60], with decreasing temperature. Since the Rouse relaxation time τ_R follows the Arrhenius-type equation [Eq. (3–5)], Wi_R increased exponentially under a fixed cooling rate.

$$\tau_R \propto \exp\left(\frac{\Delta E}{RT}\right), \quad (3-5)$$

where ΔE is the flow activation energy in the Arrhenius plot and R is the gas constant.

This is a similar situation to exponential shear [61–63], which is also called “strong shear.” Assuming that ΔE is 40 kJ/mol, τ_R at 160 °C is almost twice that at 190 °C for PP. As a result, Wi_R becomes twice even at a constant shear rate.

Under exponential shear flow, i.e., exponential increase in shear strain, shear stress increases rapidly with time for LDPE. This indicates that LDPE exhibits strain hardening in transient shear stress, although HDPE hardly shows. This strain hardening under an exponential increase in the shear rate, i.e., Wi_R , could be the origin of the marked shear-induced crystallization of PP/LDPE. In contrast, for PP/HDPE, excessive deformation is not observed because the deformation of the HDPE dispersion aligns with that of the PP matrix. Consequently, shear-induced crystallization is not enhanced.

To confirm this hypothesis, we intend to carry out experiments on shear-induced crystallization at a slow cooling rate. A slow cooling rate must decrease the increasing rate of Wi_R . In the present experiment, the samples were exposed to shear at 10 and 30 s^{-1} while cooling from 190 to 160 °C at a rate of 5 °C/min. After the cessation of shear flow at 160 °C, they were cooled at 30 °C/min. As illustrated in Figure 3.17, no

differences in $T_{\text{on-set}}$ were detected for PP, PP/LDPE, or PP/HDPE. The results demonstrated that the cooling rate during shear has a critical impact on flow-induced crystallization.

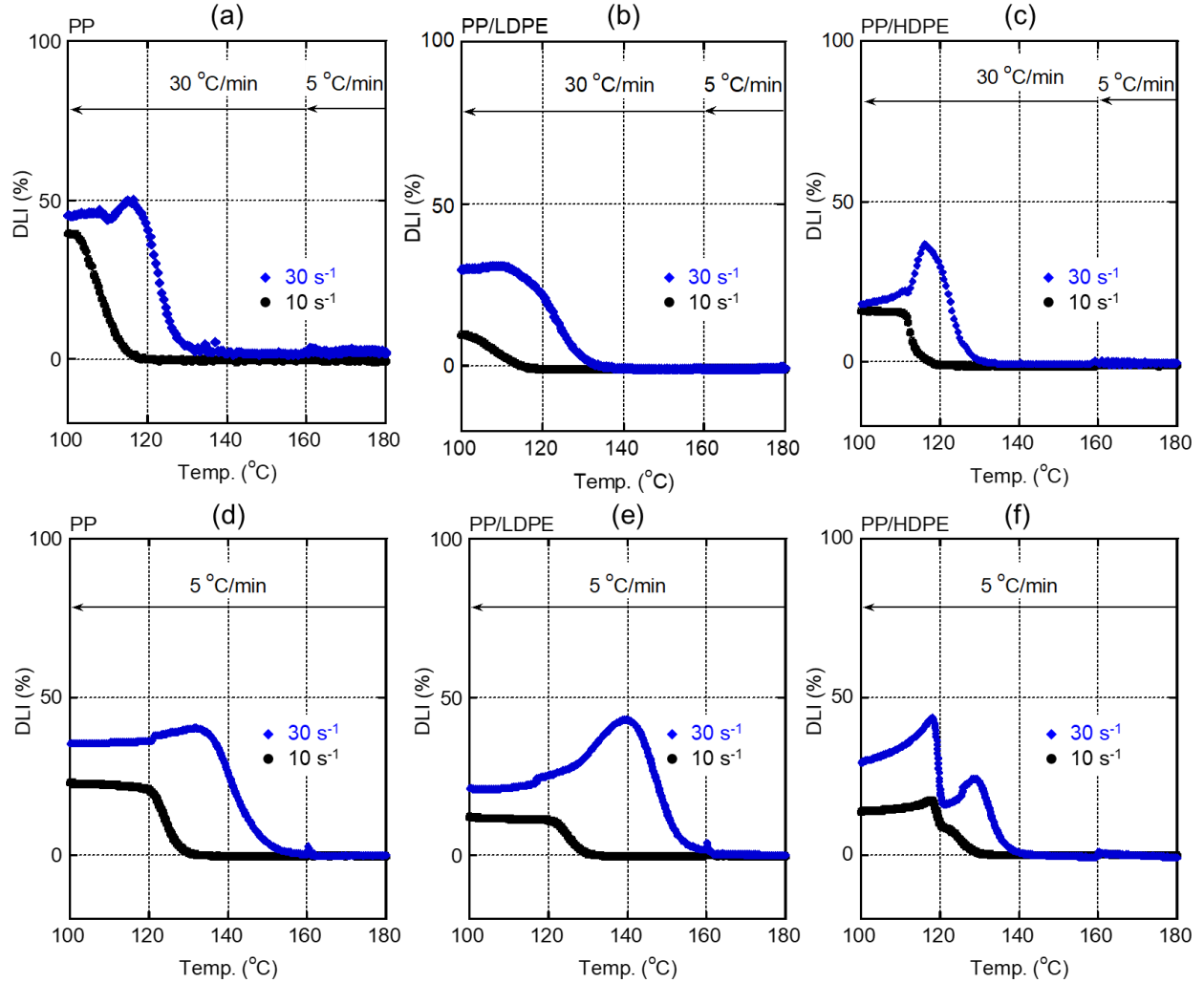


Figure 3.17. Growth curves of DLI values for (a) and (d) PP, (b) and (e) PP/LDPE (70/30), and (c) and (f) PP/HDPE (70/30). The shear history at 10 and 30 s⁻¹ is applied from 190 to 160 °C during non-isothermal crystallization at 5 °C/min. After the cessation of shear flow, the samples are cooled at (a) – (c) 30 °C/min and (d) – (f) 5 °C/min.

The experimental results obtained by cooling in the parallel-plate geometry should be applicable to actual extrusion processing because solidification occurs during cooling, not at a constant temperature after passing the die exit. To extend the applicability of these findings, additional experiments were conducted using capillary extrusion with the same sample materials. Figure 3.18 presents the steady-state shear viscosities at the wall (η_w) plotted against the shear rate at the wall ($\dot{\gamma}_w$), which align with the complex shear viscosity values. The flow curves for all samples, including PP/LDPE, were found to be nearly identical. After having a contraction flow at the die entry, the samples were extruded and cooled in the air. Although gross melt fracture was observed at a shear rate of 1000 s^{-1} for PP, no evidence of shark-skin failure was detected for any of the samples within the experimental range. Given that the ambient temperature was maintained at $30 \text{ }^{\circ}\text{C}$ using circulating air, the cooling rate remained consistent across all samples extruded at the same shear rate [64]. While the strand diameter increased with higher shear rates, no significant variation in diameter was observed among the different samples as shown in Figure 3.19. Molecular orientation was evaluated using 2D-WAXD profiles of the collected strands. Figure 3.20 illustrates the azimuthal angle distributions for the (040) plane of α -form PP crystals. It is important to note that the shear rates indicated in the figure represent the values on wall. As the X-ray beam passed through the entire strand, the data obtained reflect the average molecular orientation, including the strand center.

It was evident that the PP/LDPE strands exhibited a high degree of chain orientation in the flow direction. In contrast, the incorporation of HDPE did not enhance chain orientation. These findings indicate that the addition of LDPE significantly

accelerated the flow-induced crystallization of PP, even during the extrusion process.

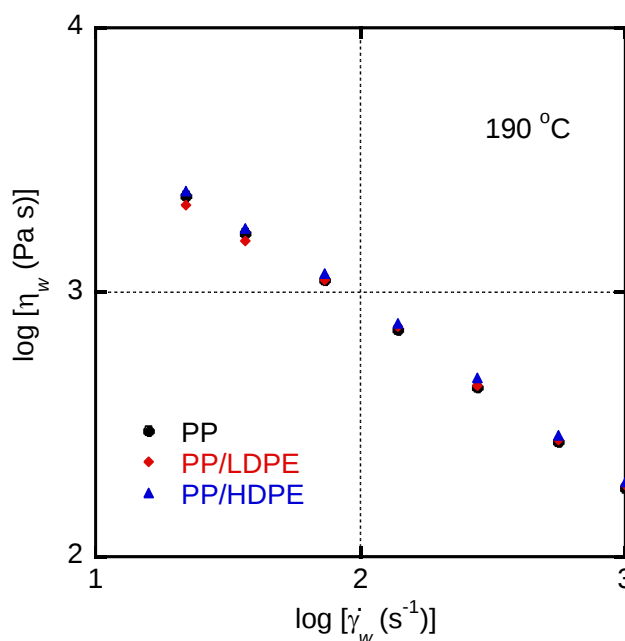


Figure 3.18. Steady-state shear viscosity η_w evaluated by the capillary rheometer as a function of shear rate $\dot{\gamma}_w$ at 190 °C. (circles) PP, (diamonds) PP/ LDPE (70/30), and (triangles) PP/HDPE (70/30).

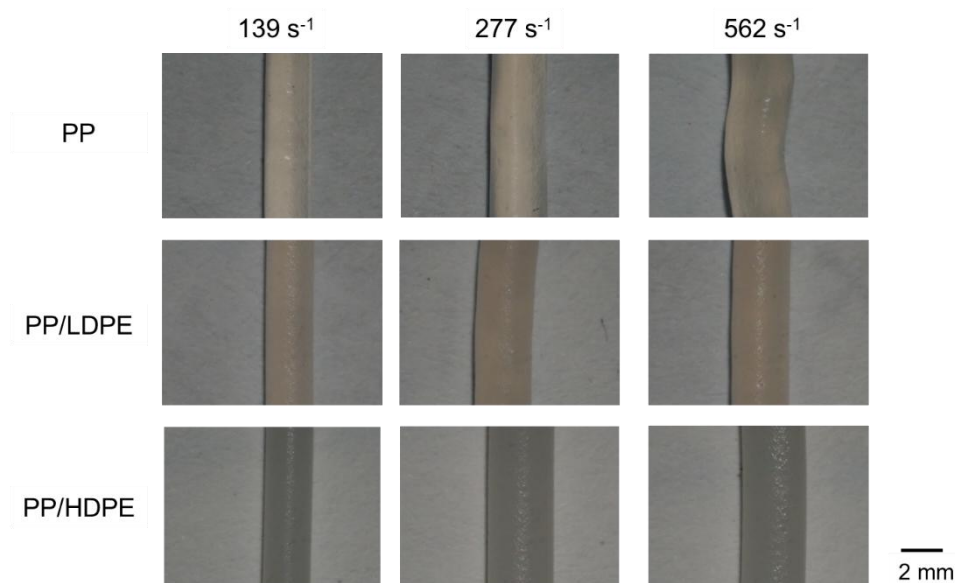


Figure 3.19. The strand pictures of PP, PP/LDPE (70/30), and PP/HDPE (70/30).

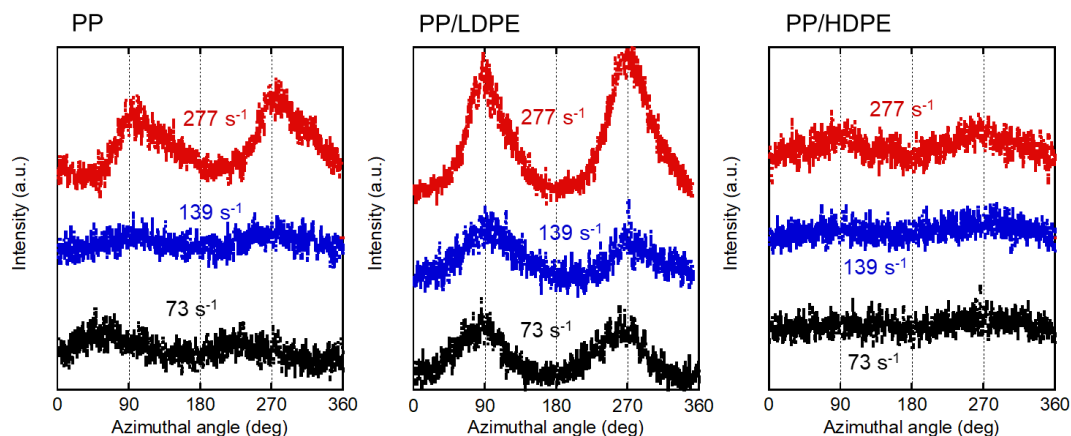


Figure 3.20. Azimuthal angle distribution of the (040) plane of α -form PP crystal for stands extruded from the rheometer at (top) 277 s^{-1} , (middle) 139 s^{-1} , and (bottom) 73 s^{-1} for PP, PP/LDPE (70/30), and PP/HDPE (70/30).

3.5 Conclusions

In this study, the effect of LDPE addition on the shear-induced crystallization of PP was examined and compared to the effect of HDPE addition. A polarized optical microscope attached with a quartz parallel-plate shear device was employed to obtain the necessary measurements. While the addition of LDPE did not significantly influence shear stress or normal stress difference, the blend exhibited shear-induced crystallization at higher temperatures compared to both pure PP and the PP/HDPE blend. During cooling at a constant rate, the Weissenberg number, which represents the dimensionless shear rate associated with the Rouse relaxation time, increased exponentially. This situation must markedly increase the stress of LDPE. As a result, excessive deformation occurred within the PP matrix, leading to a high actual strain rate. Therefore, the sample containing LDPE had a high level of molecular orientation to the flow direction.

References

- [1] Ed., Pasquini N, Polypropylene handbook 2nd ed. Hanser (2005)
- [2] Karger-Kocsis J, and Tamas B, Polypropylene handbook. Morphology, blends and composites. Springer Nature (2019)
- [3] Yamaguchi M, Miyata H, and K Nitta. Compatibility of binary blends of polypropylene with ethylene- α -olefin copolymer, J Appl Polym Sci, 62, 87–97 (1996)
- [4] Weimann P A, Jones T D, Hillmyer M A, Bates F S, Londono J D, Wignall Y G D, and Almdal K. Phase behavior of isotactic polypropylene poly(ethylene/ethylene) random copolymer blends, Macromolecules, 30, 3650–3657 (1997)
- [5] Montes P, Rafiq Y A, and Hill M J. A study of blends of isotactic polypropylene with high density polyethylene by transmission electron microscopy, Polymer, 39, 6669–6672 (1998)
- [6] Yamaguchi M and Miyata H. Influence of stereoregularity of polypropylene on miscibility with ethylene-1-hexene copolymer, Macromolecules, 32, 5911–5916 (1999)
- [7] Mäder D, Thomann Y, Suhm J, and Mülhaupt R. Influence of comonomer incorporation on morphology and thermal and mechanical properties of blends based upon isotactic metallocene–polypropylene and random ethene/1-butene copolymers, J Appl Polym Sci, 74, 838–848 (1999)

- [8] Lohse D. J. The influence of chemical structure on polyolefin melt rheology and miscibility, *J Macromol Sci, Part C: Polym Rev*, 45, 289–308 (2005)
- [9] Alamo R G, Londono J D, Mandelkern L, Stehling F, and Wignall G D. Phase behavior of blends of linear and branched polyethylenes in the molten and solid states by small-angle neutron scattering, *Macromolecules*, 27, 411–417 (1994)
- [10] Fredrickson G H and Liu A J. Design of miscible polyolefin copolymer blends, *J Polym Sci, Part B: Polym Phys*, 33, 1203–1212 (1995)
- [11] Yamaguchi M. Effect of molecular structure in branched polyethylene on adhesion properties with polypropylene, *J Appl Polym Sci*, 70, 457–463 (1998)
- [12] Robertson R E and Paul D R. Stress-strain behavior of polyolefin blends, *J Appl Polym Sci*, 17, 2579–2595 (1973)
- [13] Rizzo G and Spadaro G. Mechanical properties of low density polyethylene-isotactic polypropylene blends I. Effect of mixing time, *Eur Polym J*, 24, 303–306 (1988)
- [14] Liang J Z, Tang C Y, and Man H C. Flow and mechanical properties of polypropylene/low density polyethylene blends, *J. Mater Process Technol*, 66, 158–164 (1997)
- [15] Dong L S, Olley R H, and Bassett D C. On morphology and the competition between crystallization and phase separation in polypropylene-polyethylene blends, *J Mater Sci*, 33, 4043–4048 (1998)

- [16] Sugimoto M, Masubuchi Y, Takimoto J, and Koyama K. Melt rheology of polypropylene containing small amounts of high-molecular-weight chain. 2.: uniaxial and biaxial extensional flow, *Macromolecules*, 34, 6056–6063 (2001)
- [17] Kida T, Kimura T, Eno A, Janchai K, Yamaguchi M, Otsuki Y, Kimura T, Mizukawa T, Murakami T, Hato K, and Okawa T. Effect of ultra-high-molecular-weight molecular chains on the morphology, crystallization, and mechanical properties of polypropylene, *Polymers*, 13, 4222 (2021)
- [18] Hingmann R and Marczinke B. L. Shear and elongational flow properties of polypropylene melt, *J Rheol*, 38, 573–587 (1994)
- [19] Auhl D, Stange J, Münstedt H, Krause B, Voigt D, Lederer A, Lappan U, and Lunkwitz K. Long-chain branched polypropylenes by electron beam irradiation and their rheological properties, *Macromolecules*, 37 9465–9472 (2004)
- [20] Yamaguchi M and Wagner M H. Impact of processing history on rheological properties for branched polypropylene, *Polymer*, 47, 3629–3635 (2006)
- [21] Yamaguchi M and Miyata H. Strain hardening behavior in elongational viscosity for binary blends of linear polymer and crosslinked polymer, *Polym J*, 32, 164–170 (2000)
- [22] Thomas A. S, Carl R D, Richard M L, L Jonathan, David W A, Noel G H, and Richard J S. Self-organization and polyolefin nucleation efficacy of 1,3:2,4-di-p-methylbenzylidene sorbitol, *J Polym Sci Part B: Polym Phys*, 35, 2617–2628 (1997)

- [23] Ogino Y, Fukushima H, Matsuba G, Takahashi N, Nishida K, and Kanaya T J P. Effects of high molecular weight component on crystallization of polyethylene under shear flow, *Polymer*, 47, 5669–5677 (2006)
- [24] Balzano L, Kukalyekar N, Rastogi S, Peters G W M and Chadwick J C. Crystallization and dissolution of flow-induced precursors, *Phys Rev Lett*, 100, 048302 (2008)
- [25] Mykhaylyk, O. O., P. Chambon, C. Impradice, J. P. A. Fairclough, N. J. Terrill, and A. J. Ryan. Control of structural morphology in shear-induced crystallization of polymers, *Macromolecules*, 43, 2389–2405 (2010)
- [26] Hamad F G, Colby R H, and Milner S T. Onset of flow-induced crystallization kinetics of highly isotactic polypropylene, *Macromolecules*, 48, 3725–3738 (2015)
- [27] Jordan A M, Kim K, Soetrisno D, Hannah J, Bates F S, Jaffer S A, Lhost O, and Macosko C. Role of crystallization on polyolefin interfaces: An improved outlook for polyolefin blends, *Macromolecules*, 51, 2506–2516 (2018)
- [28] Ruan C. Skin-core-skin structure of polymer crystallization investigated by multiscale simulation, *Materials*, 11, 610 (2018)
- [29] Zhang Q, Li L, Su F, Ji Y, Ali S, Zhao H, Meng L, and Li L. From molecular entanglement network to crystal-cross-linked network and crystal scaffold during film blowing of polyethylene: An in situ synchrotron radiation small- and wide-angle x-ray scattering study, *Macromolecules*, 51, 4350–4362 (2018)

- [30] Nazari B, Tran H, Beauregard B, Flynn-Hepford M, Harrell D, Milner S T, and Colby R H. Two distinct morphologies for semicrystalline isotactic polypropylene crystallized after shear flow, *Macromolecules*, 51, 4750–4761 (2018)
- [31] Speranza V, Liparoti S, Volpe V, Titomanlio G, and Pantani R. Modelling of morphology development towards spherulites and shish–kebabs: Application to isothermal flow-induced crystallization experiments on isotactic polypropylene, *Polymer*, 196, 122459 (2020)
- [32] Nie C., F. Peng, R. Cao, K. Cui, J. Sheng, W. Chen, and L. Li. Recent progress in flow-induced polymer crystallization, *J Polym Sci*, 60, 3149–3175 (2022)
- [33] Nie Y, Zhao Y, Matsuba G, and Hu W. Shish-kebab crystallites initiated by shear fracture in bulk polymers: 2. Crystallization on shearing, *Polymer*, 274, 125909 (2023)
- [34] Seemork J, Siriprumpoonthum M, Lee Y, Nobukawa S, and Yamaguchi M. Effect of die geometry on drawdown force of polypropylene at capillary extrusion, *Adv Polym Technol*, 34, 21477 (2015)
- [35] Dealy J, Read M D J, and Larson R G, *Structure and Rheology of Molten Polymers* 2nd ed. Hanser (2005)
- [36] Fetters L, Lohse J D J, and Graessley W W. Chain dimensions and entanglement spacings in dense macromolecular systems, *J Polym Sci, Part B: Polym Phys*, 37, 1023–1033 (1999)

- [37] Agarwal P K, Somani R H, Weng W, Mehta A, Yang L, Ran S, Liu L, and Hsiao B S. Shear-induced crystallization in novel long chain branched polypropylenes by in situ rheo-SAXS and-WAXD, *Macromolecules*, 36, 5226–5235 (2003)
- [38] Fernandez-Ballester L, Thurman D W, Zhou W, and Kornfield J A. Effect of long chains on the threshold stresses for flow-induced crystallization in iPP: Shish kebabs vs sausages, *Macromolecules*, 45, 6557–6570 (2012)
- [39] Zhou D, Yang S, Lei J, Hsiao B S, and Li Z. Role of stably entangled chain network density in shish-kebab formation in polyethylene under an intense flow field, *Macromolecules*, 48, 6652–6661 (2015)
- [40] Wingstrand S L, Drongelen M, Mortensen K, Graham R S, Huang Q, and Hassager O. Influence of extensional stress overshoot on crystallization of LDPE, *Macromolecules*, 50, 1134–1140 (2017)
- [41] Wingstrand S L, Shen B, Kornfield J A, Mortensen K, Parisi D, Vlassopoulos D, and Hassager O. Rheological link between polymer melts with a high molecular weight tail and enhanced formation of shish-kebabs, *ACS Macro Lett*, 6, 1268–1273 (2017)
- [42] Drabek J, K Janchai, Kida T, Yamaguchi M, and Zatloukal M. Effect of pre-shear on flow-induced crystallization of branched polypropylene, *AIP Conf Proc*, 2997, 020005 (2023)
- [43] Fujii Y, Nishikawa R, Phulkerd P, and Yamaguchi M. Modifying the rheological properties of polypropylene under elongational flow by adding polyethylene, *J Rheol*, 63, 11–18 (2019)

- [44] Batchelor G K. The stress generated in a non-dilute suspension of elongated particles by pure straining motion, *J Fluid Mech*, 46, 813–829 (1971)
- [45] Mewis J, and Metzner A B. The rheological properties of suspensions of fibers in newtonian fluids subjected to extensional deformations, *J Fluid Mech*, 62, 593–600 (1974)
- [46] Laun H M. Orientation effects and rheology of short glass fiber reinforced thermoplastics, *Colloid Polym Sci*, 262, 257–269 (1984)
- [47] Otsuki Y, Fujii Y, Sasaki H, Phulkerd P, and Yamaguchi M. Experimental and numerical study on transient elongational viscosity for PP/LDPE blends, *Polym J*, 52, 529–538 (2020)
- [48] Yamaguchi M, Fujii Y, and Phulkerd P. Rheological properties of polyolefin blends containing long-chain branched polypropylene as dispersed phase, *J Soc Rheol Jpn*, 48, 109–112 (2020)
- [49] Kugimoto D, Kouda S, and Yamaguchi M. Environment, modification of poly (lactic acid) rheological properties using ethylene–vinyl acetate copolymer, *J Polym Environ*, 29, 121–129 (2021)
- [50] Yamaguchi M, and Gogos C G. Quantitative relation between shear history and rheological properties of LDPE, *Adv Polym Technol* 20, 261–269 (2001)
- [51] Yamaguchi M, and Takahashi M. Rheological properties of low-density polyethylenes produced by tubular and vessel processes, *Polymer*, 42, 8663–8670 (2001)
- [52] Palierne J F. Linear rheology of viscoelastic emulsions with interfacial tension, *Rheol Acta*, 29, 204–214 (1990)

- [53] Doi M, and Ohta T. Dynamics and rheology of complex interfaces. I, *J Chem Phys*, 95, 1242–1248 (1991)
- [54] Carmeli E, Kandioller G, Gahleitner M, Müller A J, Tranchida D, and Cavallo D. Continuous cooling curve diagrams of isotactic polypropylene/polyethylene blends: Mutual nucleating effects under fast cooling conditions, *Macromolecules*, 54, 4834–4846 (2021)
- [55] Parisi D, Han A, Seo J, and Colby R H. Rheological response of entangled isotactic polypropylene melts in strong shear flows: Edge fracture, flow curves, and normal stress, *J. Rheol*, 65, 605–616 (2021)
- [56] Fukuda Y, Kida T, and Yamaguchi M. Mechanical properties of isotactic polypropylene with nodular and spherulite morphologies, *Polym Eng Sci*, 63, 4043–4050 (2023)
- [57] Janchai K, Kida T, Inoue T, Iwasaki S, and Yamaguchi M. Crystallization behavior of isotactic polypropylene containing a fibrous nucleating agent in a flow field, *Polym J*, 54, 367–375 (2022)
- [58] Nesse W D, *Introduction of optical mineralogy* 2nd ed, Oxford (1991)
- [59] Masuko T, Tanaka H, and Okajima S. Studies on biaxial stretching of polypropylene film. IV. Overall orientation during one-step biaxial stretching and its application to the estimation of the principal refractive indices of isotactic polypropylene, *J Polym Sci, A-2* 8, 1565–1574 (1970)
- [60] Neergaard J, Park K, Venerus D C, Schieber J D. Exponential shear flow of linear, entangled polymeric liquids, *J Rheol*, 44, 1043–1054 (2000)
- [61] Zülle B, Linster J, Meissner J, and Hürlimann H P. Deformation hardening and

thinning in both elongation and shear of a low density polyethylene melt, J Rheol, 31, 583–598 (1987)

[62] S Doshi, and Dealy J M. Exponential shear: A strong flow, J Rheol, 31, 563–582 (1987)

[63] Liu G, Sun H, Rangou S, Ntetsikas K, Avgeropoulos A, and Wang S. Studying the origin of strain hardening: Basic difference between extension and shear, J Rheo, 57, 89–104 (2013)

[64] Seemork J, Sako T, Mohd Amran A M, and Yamaguchi M. Rheological response under nonisothermal stretching for immiscible blends of isotactic polypropylene and acrylate polymers, J Rheol, 61, 1–11 (2017)

Chapter 4

Appropriate processing condition to enhance crystallization rate for poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)

4.1 Introduction

Plastic is an extraordinary synthetic material due to its strength, durability, and lightweight combination, making it a more efficient alternative to other materials. Additionally, the properties of plastic can be customized by modifying the synthesis process or incorporating various additives, making it useful in a wide range of industries and our daily lives [1,2]. Despite its advantages, improper disposal of plastic can lead to a waste crisis with severe negative impacts on both the environment and living things. Proper waste management and developing environmentally friendly plastics are essential for resolving this issue. Consequently, bioplastics and alternative materials with enhanced degradability have been developed [3,4].

4.1.1 Bio-based plastics

Bio-based plastics are now being developed to replace conventional plastics in several applications. Their specific applications typically determine the design of these materials. Poly(3-hydroxybutyrate) (PHB) is a highly appealing bio-based plastic, as it is derived from renewable resources and readily biodegrades into carbon dioxide and

water, even in marine environments [5–9]. However, PHB is prone to significant thermal degradation due to six-membered ring ester decomposition at the high temperatures needed for processing [10,11]. While the degradation rate and its effects on processability have been quantitatively predicted, the material's poor processability remains a notable concern [12,13]. As a result, extensive research was undertaken to incorporate alternative monomer species that could reduce the melting point of the polymer, facilitating processing at lower temperatures [14,15]. One example of a commercially successful copolymer developed from this approach is poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx). PHBHHx has already been utilized in a range of applications, including shopping bags, cutlery, straws, and food packaging [16,17]. To broaden its potential uses, enhancing the crystallization rate of PHBHHx is crucial to shorten cycle times and/or boost production rates [18–22]. Therefore, for actual processing operations, this study investigated the crystallization behavior of PHBHHx under different thermal and shear histories. Several studies have been performed on the crystallization behavior of PHB and its copolymers. These studies indicate that PHB typically forms an orthorhombic structure, known as the α -form, when cooled using standard methods [23]. Its equilibrium melting point T_m^0 is around 200 °C [24]. Since the linear crystallization growth rate reaches its peak between T_m^0 and the glass transition temperature T_g , which is around 10 °C [25], the optimal temperature for enhancing crystallization is roughly 105 °C [26], a conclusion supported by experimental findings [27]. In general, PHB and its copolymers tend to form relatively large spherulites due to the slow nucleation process. Therefore, a variety of materials have been utilized to increase nucleation, including talc, boron nitride,

hydroxyapatite, carbon nanotubes, terbium oxide, uracil, thymine, orotic acid, benzoic acid, as well as behenamide, its derivatives, and diethyl 4,5,10,11-tetraoxo-3,6,9,12-tetraazatetradecane-1,14-dioate [28].

Additionally, shear-induced crystallization has been investigated. The formation of shish structures is recognized because of chain stretching during flow [20,29–33]. Consequently, the high-molecular-weight fraction, which has a long characteristic time for chain stretching—known as the Rouse relaxation time—plays a critical role in the initial phase of flow-induced crystallization, although PHB and its copolymers produced by microbes usually have narrow molecular weight distribution. Therefore, Fujita et al. [34] introduced high-molecular-weight PHB through solution mixing to promote shish formation and verified that the shish-kebab structure was enhanced. However, on an industrial scale, it is challenging to evenly incorporate a small amount of high-molecular-weight PHB. Another common method to improve crystallization rates involves adding a homopolymer to a copolymer. In the case of PHBHHx, however, the use of PHB as a homopolymer leads to significant thermal degradation issues.

4.2 Experimental Procedure

4.2.1 Material

The PHBHHx used in this study was produced by Kaneka Corp., Japan, containing 5.4 mol% of 3-hydroxyhexanoate. Differential scanning calorimetry (DSC) measurements, performed at a heating rate of 10 °C/min, showed that the melting point of the sample pellets was 147 °C during the first heating cycle. Table 4.1 presents the average molecular weights obtained through gel permeation chromatography (GPC). Additionally, multi-angle light scattering coupled with GPC was employed to determine the absolute molecular weight, yielding a Q factor of 0.457.

Table 4.1 Average molecular weights of the PHBHHx sample.

Materials	M_n (Da)	M_w (Da)	M_z (Da)	M_{z+1} (Da)
PHBHHx	89,000	179,000	284,000	389,000

4.2.2 Sample preparation

The PHBHHx pellets were dried in a vacuum oven for 3 hours at 80 °C prior to the melting process. The dried material was then molded into flat films, with thicknesses of 300 μ m, using a compression molding machine at 180 °C for 2 minutes.

4.3 Measurements

The frequency dependence of the oscillatory shear modulus was measured using a cone-and-plate rheometer (AR2000ex; TA Instruments, Inc.) at temperatures of 150, 160, 170, and 180 °C. The cone-and-plate rheometer used had a diameter of 25 mm and a 4° angle.

The thermal properties were evaluated using a differential scanning calorimeter (DSC; model DSC8500, PerkinElmer Inc.). A film sample weighing approximately 3 mg was placed in an aluminum pan. The sample was kept at 170 and 180 °C for 5 minutes and then cooled at a rate of 10 °C/min.

The crystallization behavior was analyzed using a polarized optical microscope (POM) in a crossed-polarizer configuration equipped with a quartz parallel-plate shear stage, as discussed in Chapter 2. The gap between plates was 300 μm. Shear was applied during both isothermal and cooling at shear rates of 10 and 50 s⁻¹ at the window area. Figure 4.1 shows the experimental protocols for temperature and shear. The depolarized light intensity (DLI) value was determined using the following relation:

$$DLI(\%) = \frac{I_0 - I_X}{I_{//} - I_X} \times 100, \quad (4-1)$$

where I_0 is the light intensity passing through a sample under crossed polars, and I_X and $I_{//}$ are the light intensities without a sample under crossed and parallel polars, respectively.

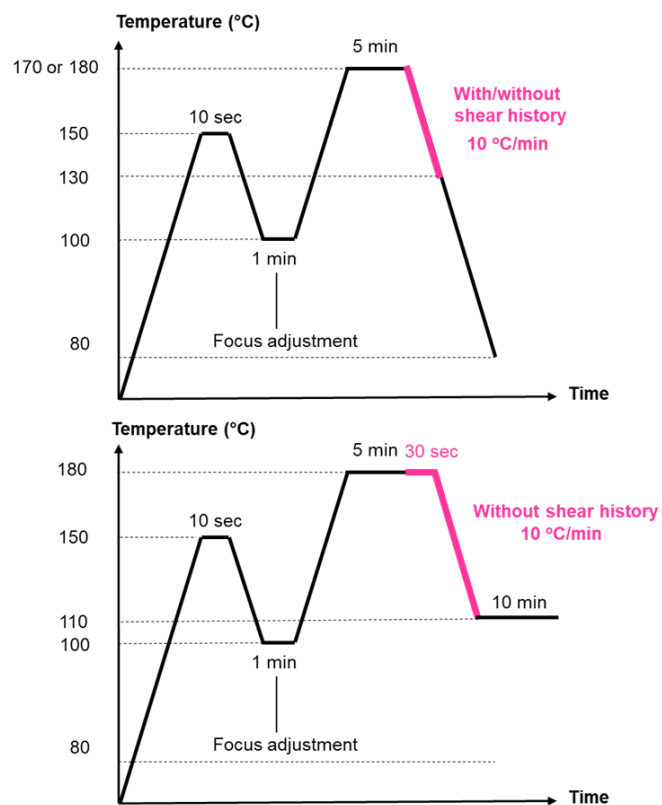


Figure 4.1. Experimental protocols of the temperature and shear at cooling process (top) and isothermal process (bottom)

4.4 Results and Discussion

4.4.1 Rheological properties

Figure 4.2 presents the master curves of the angular frequency (ω) dependence of the oscillatory shear moduli, i.e., the storage modulus (G') and the loss modulus (G''), at 160 °C (the reference temperature T_r).

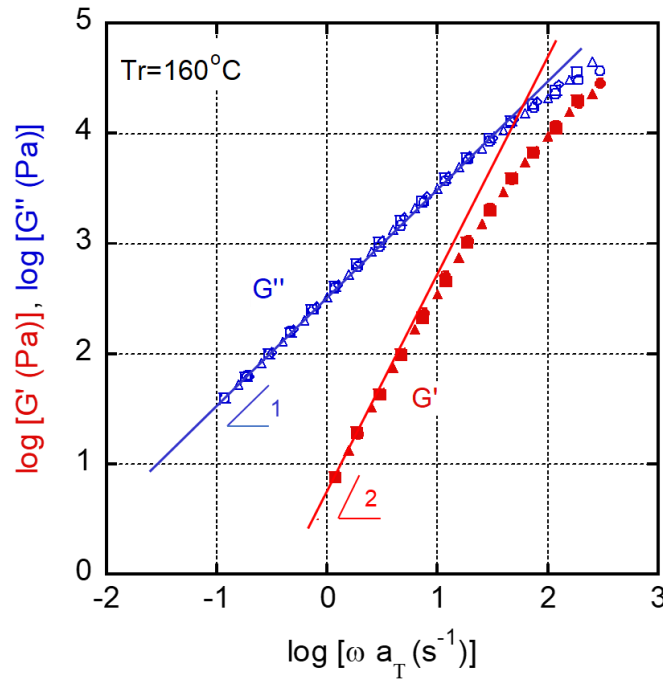


Figure 4.2. Master curves of the frequency dependencies of the shear storage modulus (G') and the loss modulus (G'') at the reference temperature T_r was 160 °C.

Both G' and G'' steadily decreased with decreasing angular frequency. In the low-frequency region, the slopes of G' and G'' curves were 1 and 2, respectively, which are typical viscoelastic behaviors of a polymer melt [35]. As a result, the rheological parameters in the terminal zone, such as the zero-shear viscosity η_0 , steady-state shear compliance J_e^0 , and weight-average relaxation time τ_w , defined in Eqs. [(4-2)– (4-4)],

were calculated and found to be $\eta_0 = 3.2 \times 10^2 \text{ Pa s}$, $J_e^0 = 4.0 \times 10^{-5} \text{ Pa}^{-1}$, and $\tau_w = 1.2 \times 10^{-2} \text{ s}$ at the reference temperature of 160 °C.

$$\eta_0 = \lim_{\omega \rightarrow 0} \frac{G''}{\omega}, \quad (4-2)$$

$$J_e^0 = \lim_{\omega \rightarrow 0} \frac{G'}{G''^2}, \quad (4-3)$$

$$\tau_w \equiv \frac{\int \tau^2 H(\tau) d \ln \tau}{\int \tau H(\tau) d \ln \tau} = \eta_0 J_e^0, \quad (4-4)$$

where $H(\tau)$ is the relaxation spectrum.

The τ_w value was also confirmed in Figure 4.2. The inverse of the angular frequency at the cross point of the two straight lines was $1.3 \times 10^{-2} \text{ s}$. As is well known, J_e^0 is strongly affected by the molecular weight distribution. According to Eq. (4-5), which was reported by Mills [36], the J_e^0 value of monodispersed PHBHHx, i.e., J_e^{00} , was calculated to be $7.2 \times 10^{-6} \text{ Pa}^{-1}$.

$$J_e^0 = J_e^{00} \left(\frac{M_z}{M_w} \right)^{3.7} \quad (4-5)$$

Using the relationship between J_e^{00} and entanglement compliance J_N^0 , the rubbery plateau modulus G_N^0 , was estimated from Eq. (4-6), [37,38] and calculated to be $3.5 \times 10^5 \text{ Pa}$. Previous researchers have evaluated the G_N^0 value for PHB and its copolymers. Liao et al. [39] reported it to be $2.43\text{--}3.05 \times 10^5 \text{ Pa}$ using PHBHHx samples with 3-hydroxyhexanoate content of 3.8–10.0 mol%. Ebrahimi et al. [40] evaluated a PHB homopolymer and found that its G_N^0 is $2.4 \times 10^5 \text{ Pa}$. According to Eq. (4-7), these data give the M_e values as 9400–14500. Using the data obtained in the present study, G_N^0 was

calculated to be 3.5×10^5 Pa, which is slightly higher than in previous reports, presumably owing to an experimental error in the molecular weight distribution. Only a tiny difference in the high molecular weight fraction, i.e., M_z , produces a large difference in J_e^{00} . Moreover, J_e^0 may contain some experimental errors.

$$G_N^0 = \frac{1}{J_N^0} = \frac{2.5}{J_e^{00}} \quad (4-6)$$

$$M_e = \frac{\rho RT}{G_N^0} \quad (4-7)$$

The horizontal shift factors a_T in Figure 4.2 provided the flow activation energy E_a from the Arrhenius plot Eq. [(4-8)], which was calculated to be 36.9 kJ/mol. The value corresponds to those reported previously [39,41,42].

$$a_T = A \exp\left(\frac{E_a}{RT}\right) \quad (4-8)$$

4.4.2 Crystallization behaviors

Figure 4.3 shows DSC cooling curves at a cooling rate of 10 °C/min. For the sample was cooled from 170 °C, the onset temperature of crystallization around 103 °C and the peak temperature T_c was 93.7 °C. However, no crystallization peak was detected the sample was cooled from 180 °C. This suggests that any remaining crystals were completely melted when the sample was heated up to 180 °C. In other words, a small number of crystals are present at 170 °C, serving as nucleation sites for the molten samples.

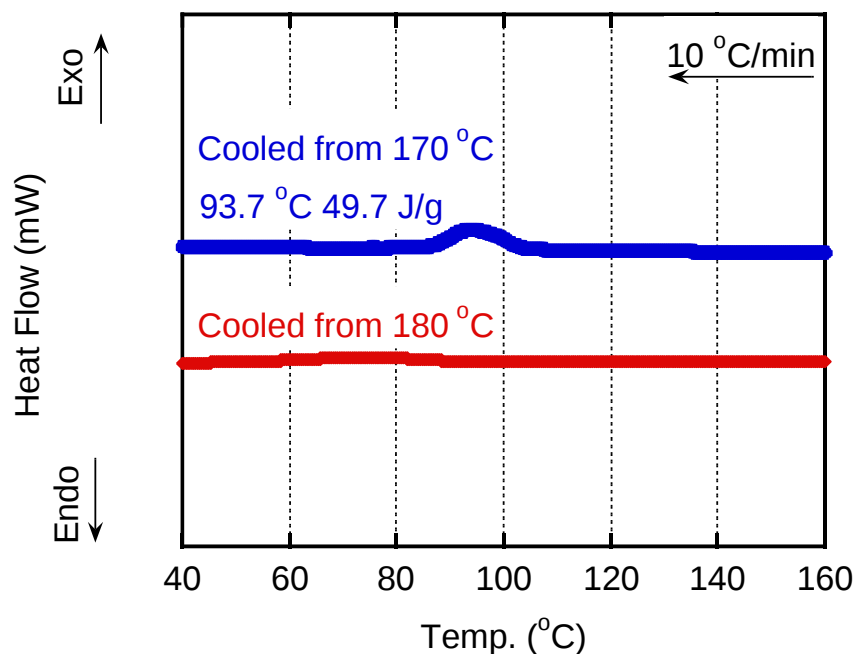


Figure 4.3. DSC cooling curves obtained at rate of 10 °C/min. The samples were cooled from 170 and 180 °C.

Crystallization behavior was examined using a POM under a cross-polar configuration, during a cooling rate of 10 °C/min. Figure 4.4 presents growth curve of depolarized light intensity (DLI) during cooling from 170 °C and 180 °C. The sample cooled from 170 °C, the DLI value was around 103 °C, closely aligning with the DSC results. In contrast, during cooling from 180 °C, the DLI showed a slight increase at 75 °C. The absence of an exothermic peak or shoulder at 75 °C in the DSC curve indicates that POM is more sensitive in detecting the initial stages of crystallization. The drop in DLI values after reaching a peak in the cooling curve from 170 °C must be attributed to the increase in the light scattering from spherulites.

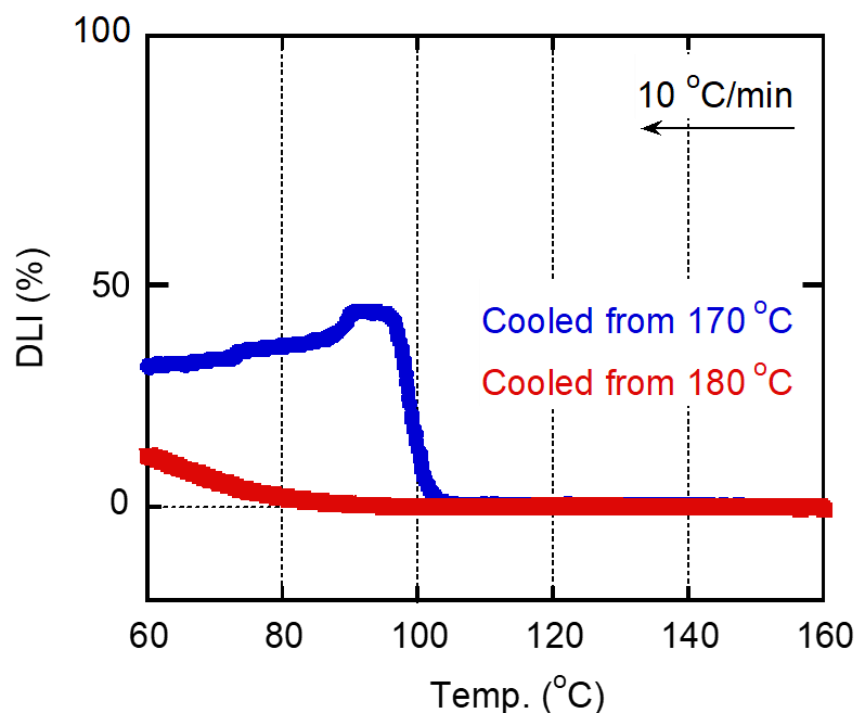
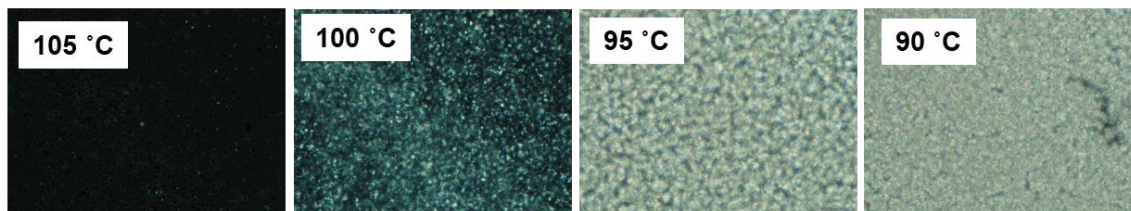


Figure 4.4. Growth curves of depolarized light intensity (DLI) during non-isothermal crystallization at 10 °C/min. The sample had no shear history.

POM images during cooling are shown in Figure 4.5. It's important to note that the POM images do not consistently align with the DLI value due to the camera's automated selection of shutter speed to ensure image clarity. Therefore, when the DLI was low, the shutter speed was slowed to prevent the image from appearing too dark. Regardless of the initial heating temperature (170 °C or 180 °C), spherulite textures were observed without any orientation. However, the number of spherulites varied significantly, with a greater number detected when cooling from 170 °C. This was expected, as the unmolten crystals at 170 °C acted as nuclei. Additionally, these unmolten crystals hardly affected the linear viscoelastic properties because the rheological terminal region was clearly detected, even at 160 °C, as shown in Figure 4.2. This indicates that the crystals existed as solid particles without interacting with

polymer chains in the molten state. If the crystals formed a fringed micelle or network structure, a longer relaxation mechanism would be observed.

Cooling from 170 °C



Cooling from 180 °C

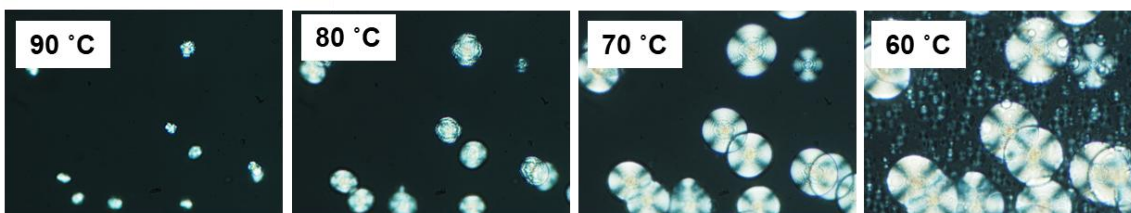


Figure 4.5. POM images were obtained using crossed polars during non-isothermal crystallization at 10 °C/min from 170 °C (top) and 180 °C (bottom) in the absent of shear.

Figure 4.6 presents the DLI curves obtained during cooling. The samples were exposed to shear from 170 °C or 180 °C to 130 °C. For the sample cooled from 170 °C, the crystallization temperature was not affected by the shear history, indicating that the remaining crystal residues were the primary factor in the crystallization process. However, in the case of sample cooling from 180 °C with applying shear at 50 s⁻¹, crystallization occurred at a higher temperature, suggesting the occurrence of shear-induced crystallization. This implies that the critical shear rate for shish formation between 10 and 50 s⁻¹.

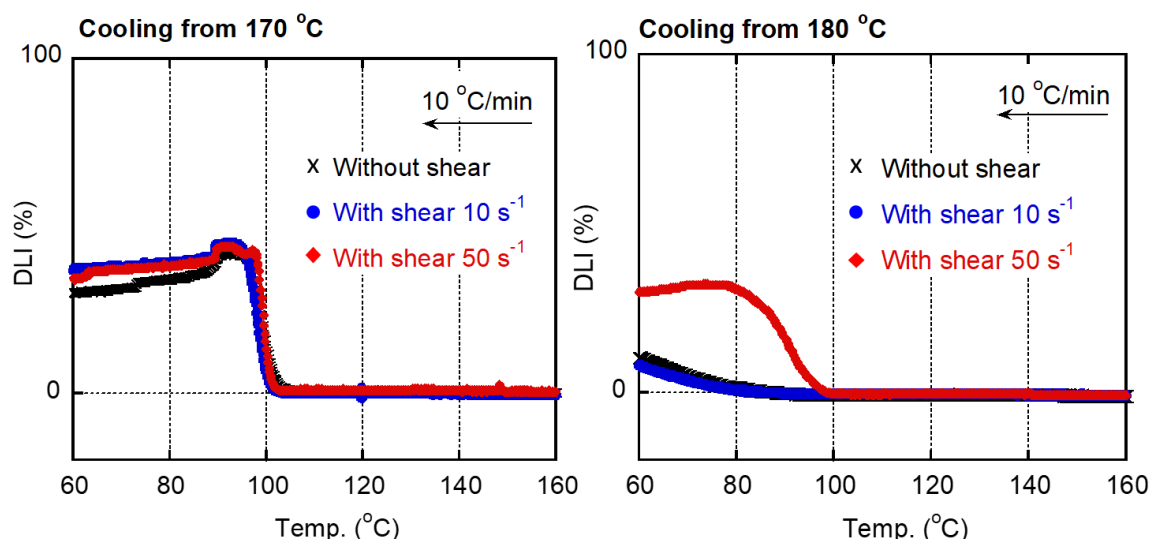


Figure 4.6. Growth curves of depolarized light intensity (DLI) with/without applied shear history during non-isothermal crystallization at 10 °C/min. The shear history was applied from 170 °C (left) and 180 °C (right) to 130 °C at 10 and 50 s⁻¹.

Figures 4.7 and 4.8. are shown the POM images. The morphologies shown in Figure 4.7 were almost similar to the top images in Figure 4.5. As expected, because the applied shear did not affect the crystallization kinetics, crystallization occurred quickly due to the presence of unmolten crystals. When the sample was cooled from 180 °C, however, the crystallization behavior changed significantly. As seen in Figure 4.8, the POM images after applying shear at 10 s⁻¹ resembled those without any shear history (Figure 4.5, bottom). After applying shear at 50 s⁻¹, the number of spherulites increased significantly, as revealed in the previous report [10,18]. However, the applied shear flow did not affect the shape of the spherulites. This suggests that the chain orientation induced by shear was fully relaxed before the lateral growth of the crystals.

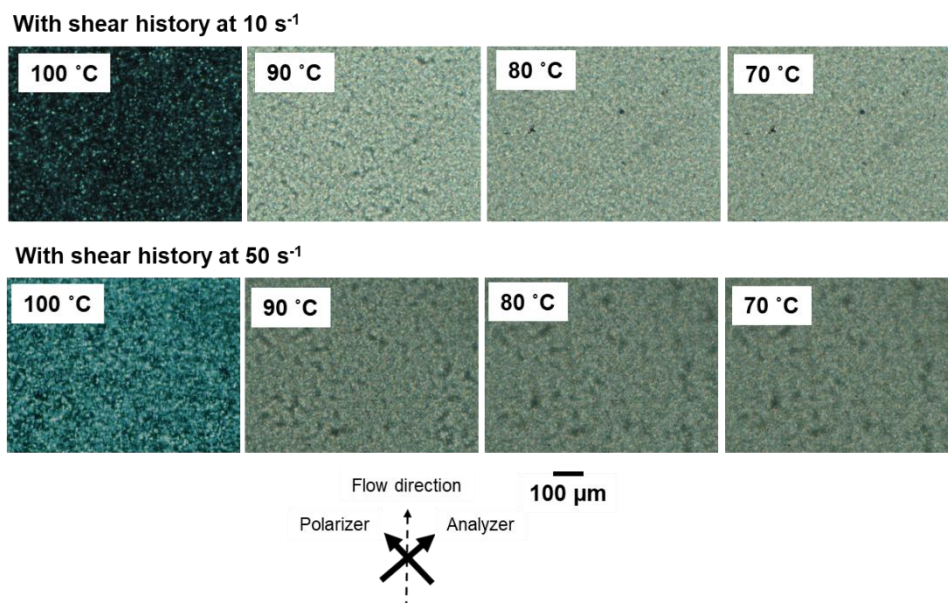


Figure 4.7. POM images were obtained using crossed polars during non-isothermal crystallization at a rate of $10 \text{ }^{\circ}\text{C}/\text{min}$. The shear history was applied from 170 to $130 \text{ }^{\circ}\text{C}$ at shear rates of 10 and 50 s^{-1} .

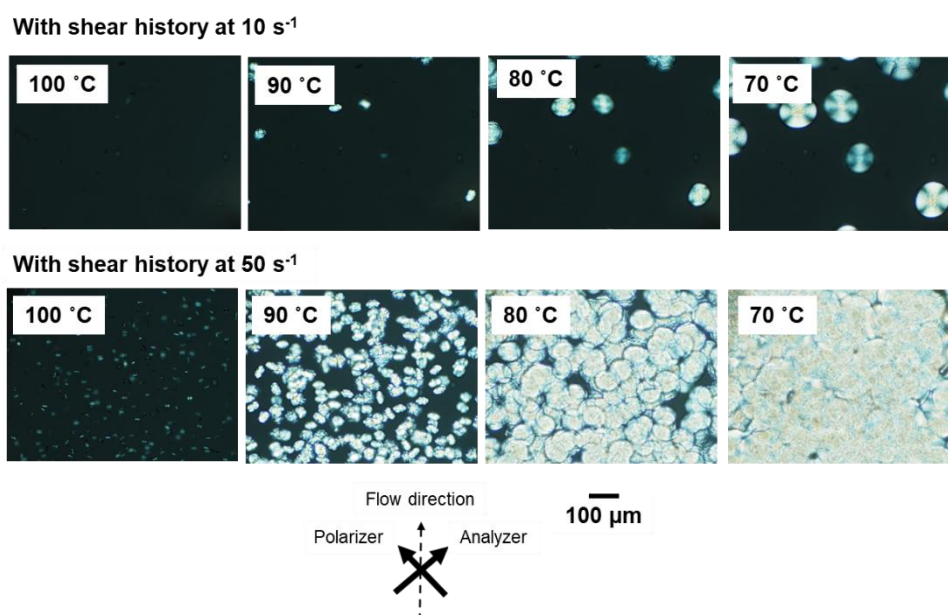


Figure 4.8. POM images were obtained using crossed polars during non-isothermal crystallization at $10 \text{ }^{\circ}\text{C}/\text{min}$. The shear history was applied from 180 to $130 \text{ }^{\circ}\text{C}$ at shear rates of 10 and 50 s^{-1} .

Figures 4.9 and 4.10 illustrate the isothermal crystallization behaviors at 110 °C. The samples were cooled to 110 °C, just prior to the isothermal process, while subjected to shear flows of 1, 10, and 50 s⁻¹. Shear flow significantly impacted the crystallization rate. Specifically, shear flows of 10 and 50 s⁻¹ notably shortened the crystallization induction period, reducing it to 180 seconds for 10 s⁻¹ and 150 seconds for 50 s⁻¹. As shown in Figure 4.10, the applied shear flow did not result in the formation of a shish-kebab structure but instead increased the number of crystal nuclei. Additionally, it is worth noting that after shear at 50 s⁻¹, many spherulites were aligned in rows along the flow direction. This anomalous structure suggests the presence of extended chain crystals, indicating that shish formation likely occurred during flow. However, it was not directly observed through POM analysis, possibly because the diameter of the shish structures was too small to be detected [29, 31–34]. Subsequently, a part of the shish sporadically served as nucleation site for spherulites. Since the shish aligned with the flow direction, i.e., vertical direction, the spherulites formed in vertical rows in the sample subjected to shear at 50 s⁻¹. The POM images further showed that the spherulites did not orient or deform along the flow direction, indicating that their lateral growth occurred uniformly in all directions. This finding suggests that even extended chain crystals do not act as effective nucleating agents to induce transcrystallization in PHBHHx. Although the reason why spherulite structures formed instead of a kebab structure remains unclear, the crystalline form of the shish may differ from that of folded chain crystals.

The weight-average relaxation time τ_w at 110 °C was estimated using the flow activation energy E_a , and was found to be 0.040 s. Consequently, the Weissenberg number, related to reptation motion [32], given by Eq. (4–9), became larger than 1 at 50 s⁻¹. This suggests the potential for anisotropic crystal growth during the initial phase of crystallization. However, due to the slow linear growth rate of PHBHHx, most of the molten polymer chains lost their orientation prior to crystallization, leading to the formation of typical spherulites.

$$Wi_{rep} \equiv \tau_{rep} \dot{\gamma} \quad (4-9)$$

Furthermore, the Weissenberg number related to the Rouse mode, defined in Eq. (4–10), must be larger than 1 at 10 s⁻¹ because the number of crystals increased markedly.

$$Wi_R \equiv \tau_R \dot{\gamma} \quad (4-10)$$

The Rouse relaxation time is determined by the molecular weight as follows:

$$\tau_R = \tau_e \left(\frac{M}{M_e} \right)^2 \quad (4-11)$$

where τ_e is the Rouse relaxation time of a chain segment between neighboring entanglement points and is reported to be 3×10^{-4} s for PHB [33]. Assuming that the M_e is 10,700, the molecular weight needed for shish formation at a shear rate of 10 s⁻¹ must be greater than 195,000. That is higher than the M_{z+1} of the present sample, which is 183,000 (the absolute molecular weight). This is expected because a tiny amount of a high-molecular-weight fraction, e.g., 0.1% [43], is sufficient for shish formation.

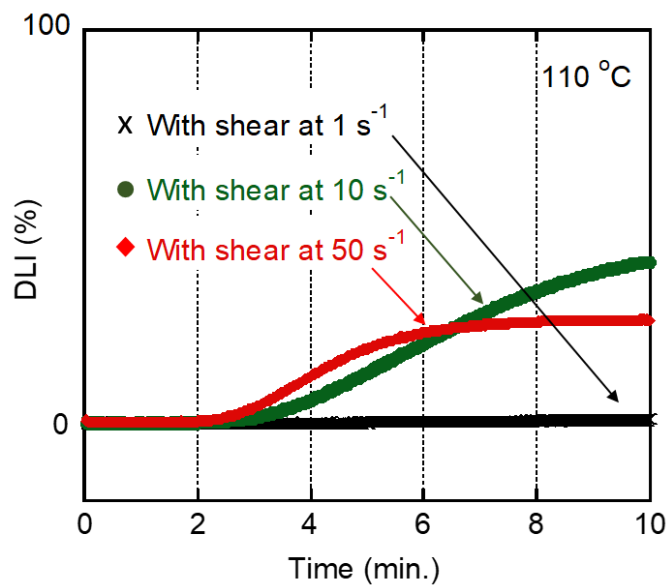


Figure 4.9. Growth curves of depolarized light intensity (DLI) during the isothermal crystallization with applied shear history during cooling at 10 °C/min. The shear history was applied from 180 to 110 °C at various shear rate, then held at 110 °C for 10 min.

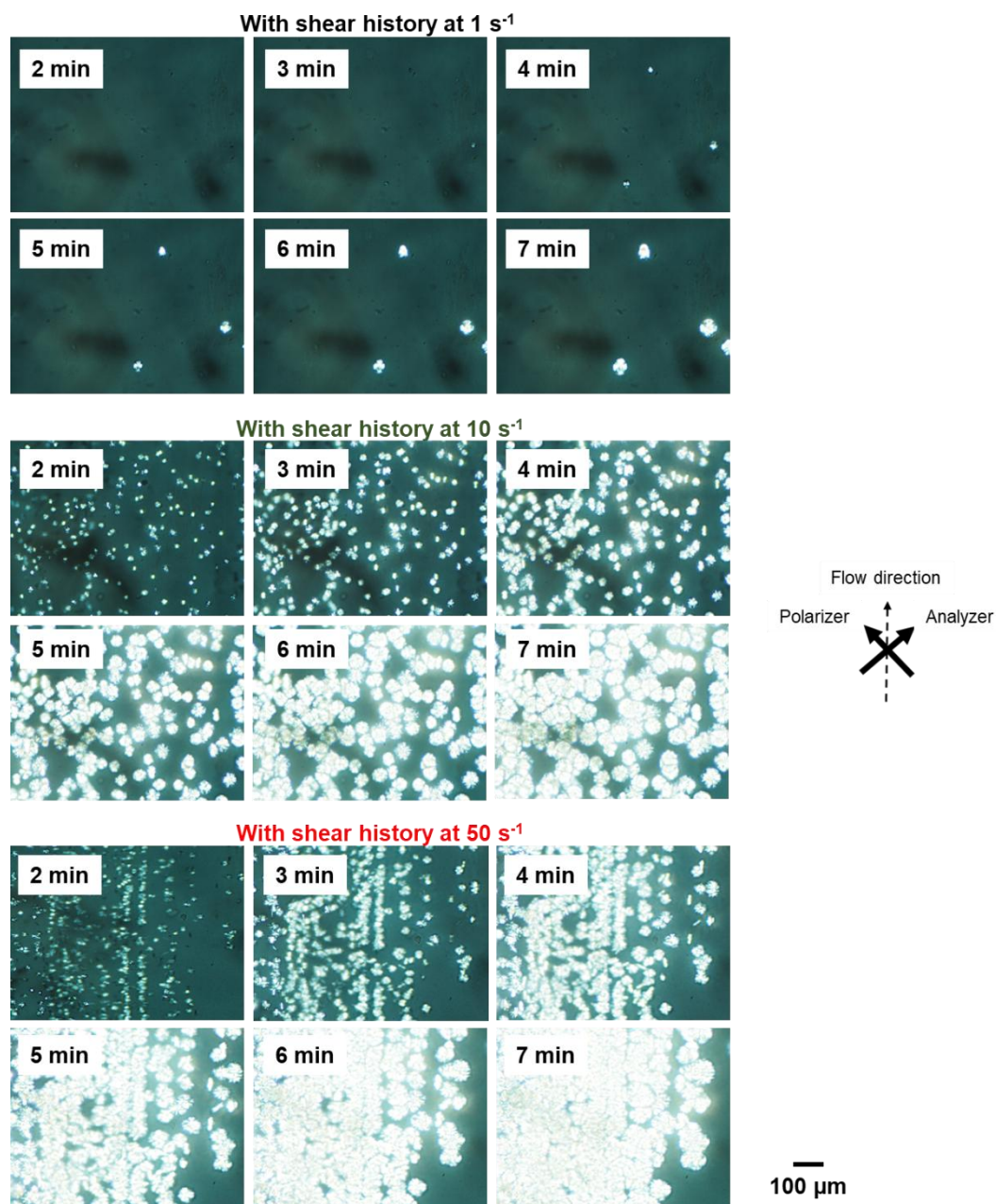


Figure 4.10. POM images of the morphology during the isothermal crystallization with applied shear history during cooling at 10 °C/min. The shear history was applied from 180 to 110 °C at various shear rates, then held at 110 °C for 10 min.

4.5 Conclusions

The crystallization behavior of PHBHHx was examined considering actual processing conditions. The melting temperature before to cooling significantly influences the crystallization rate. Heating a sample at or above 180 °C is not recommended, as it causes all crystal parts to melt, leading to slow nucleation. Melting at 170 °C retains some unmolten crystals without affecting the rheological characteristics. These unmolten crystals act as nucleating agents, significantly speeding up the crystallization process. This suggests that unmolten crystals can persist even without introducing additional PHBHHx with lower hydroxyhexanoate content, providing valuable insights for enhancing crystallization rates, particularly during secondary processes like thermoforming, injection-blow molding, and hot-stretching. When these unmolten crystals are exposed to high temperatures and subsequently melted, a strong shear flow is applied, where the Weissenberg number related to the Rouse mode exceeds unity and encourages shish formation. However, an oriented crystal structure such as shish kebab is largely absent after the cessation of flow. In the present study, instead of the formation of an oriented crystal structure, several spherulites appeared in a row-oriented with the flow direction. This unique structure results from the sporadic growth of spherulites on the extended chain crystals.

References

- [1] Brydson J A, *Plastics materials*. Elsevier, (1999)
- [2] Gilbert M, *Brydson's plastics materials*. William Andrew, (2016)
- [3] Chanprateep S. Current trends in biodegradable polyhydroxyalkanoates. *JBB*, 110, 621-632 (2010)
- [4] Bastioli C. *Handbook of biodegradable polymers*. Walter de Gruyter GmbH & Co KG, Boston (2020)
- [5] Sharma M, *Biodegradable polymers: materials and their structures*. CRC Press, (2021)
- [6] Mergaert J, Anderson C, Wouters A, and Swings J. Microbial degradation of poly (3-hydroxybutyrate) and poly (3-hydroxybutyrate-co-3-hydroxyvalerate) in compost, *J Environ Polym Degrad*, 2, 177-183 (1994)
- [7] Iwata T, Doi Y, Nakayama S, Sasatsuki and H, Teramachi S. Structure and enzymatic degradation of poly(3-hydroxybutyrate) copolymer single crystals with an extracellular PHB depolymerase from *Alcaligenes faecalis* T1, *Macromolecules*, 25, 169-176 (1999)
- [8] Sanyal P, Samaddar P, and Paul A. Degradation of Poly (3-hydroxybutyrate) and Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) by some soil *Aspergillus* spp, *J Environ Polym Degrad*, 14, 257-263 (2006)

- [9] Sangkharak K, Paichid N, Yunu T, and Prasertsan P. Novel polyhydroxyalkanoate-based biocomposites obtained by solution casting and their application for bacteria removal and domestic wastewater purification, *J Environ Polym Degrad*, 28, 1893-1900 (2020)
- [10] Grassie N, Murray E, and Holmes P. The thermal degradation of poly $-(d)\text{-}\beta\text{-hydroxybutyric acid}$): Part 1 Identification and quantitative analysis of products, *Polymer Degradation and Stability*, 6, 47-61 (1984)
- [11] Kunioka M, and Doi Y. Thermal degradation of microbial copolyesters: poly (3-hydroxybutyrate-co-3-hydroxyvalerate) and poly (3-hydroxybutyrate-co-4-hydroxybutyrate), *Macromolecules*, 23, 1933-1936 (1990)
- [12] Daly P A, Bruce D A, Melik D H, and Harrison G M. Thermal degradation kinetics of poly (3-hydroxybutyrate-co-3-hydroxyhexanoate), *J Appl Polym Sci*, 98, 66-74 (2005)
- [13] Yamaguchi M and Arakawa K. Effect of thermal degradation on rheological properties for poly (3-hydroxybutyrate), *Eur Polym J*, 42,1479-1486 (2006)
- [14] Abe H and Doi Y. Molecular and material design of biodegradable polyhydroxyalkanoates (PHAs), *Biopolymers Online: Biology Chemistry Biotechnology Applications*, 3, (2005)
- [15] Arakawa K, Yokohara T, and Yamaguchi M. Enhancement of melt elasticity for poly(3-hydroxybutyrate-co-3-hydroxyvalerate) by addition of weak gel, *J Appl Polym Sci*, 107, 1320-1324 (2007)

- [16] Lambert S and Wagner M. Environmental performance of bio-based and biodegradable plastics: the road ahead, *Chem Soc Rev*, 46, 6855-6871 (2017)
- [17] Kumar V, Sehgal R, and Gupta R. Blends and composites of polyhydroxyalkanoates (PHAs) and their applications, *Eur Polym J*, 161, 110824 (2021)
- [18] Yamaguchi M and Arakawa K. Control of structural mechanical properties for binary blends of poly(3-hydroxybutyrate) and cellulose-derivative, *J Appl Polym Sci*, 103, 3447-3452 (2007)
- [19] Balzano L, Kukalyekar N, Rastogi S, Peters G W, and Chadwick J C. Crystallization and dissolution of flow-induced precursors, *PRL*, 100, 048302 (2008)
- [20] Mykhaylyk OO, Chambon P, Impradice C, Fairclough JPA, Terrill N J, Ryan A J. Control of structural morphology in shear-induced crystallization of polymers, *Macromolecules*, 43, 2389-2405, (2010)
- [21] Duangphet S, Szegda D, Song J, and Tarverdi K. The effect of chain extender on poly (3-hydroxybutyrate-co-3-hydroxyvalerate): Thermal degradation, crystallization, and rheological behaviors, *J Environ Polym Degrad*, 22, 1-8 (2014)
- [22] Nie C, Peng F, Cao R, Cui K, Sheng J, Chen W, and Li L. Recent progress in flow-induced polymer crystallization, *J Polym Sci*, 60, 3149-3175 (2022)

- [23] Yokouchi M, Chatani Y, Tadokoro H, Teranishi K, and Tani H. Structural studies of polyesters: 5. Molecular and crystal structures of optically active and racemic poly (β -hydroxybutyrate), *Polymer*, 14, 267-272 (1973)
- [24] Barham P J, Keller A, Otun E L, and Holmes P A. Crystallization and morphology of a bacterial thermoplastic: poly-3-hydroxybutyrate, *J Mater Sci*, 19, 2781-2794 (1984)
- [25] Okui N. Relationships between melting temperature, maximum crystallization temperature and glass transition temperature, *Polymer*, 31, 92-94 (1990)
- [26] Reiter G and Sommer J U. Polymer crystallization: observations, concepts and interpretations. Springer Science & Business Media, (2003)
- [27] Iannace S, Ambrosio L, Huang S, and Nicolais L. Poly (3-hydroxybutyrate)-co-(3-hydroxyvalerate)/poly-L-lactide blends: Thermal and mechanical properties, *J Appl Polym Sci*, 54, 1525-1535 (1994)
- [28] Wypych G. Handbook of nucleating agents. ChemTec Publishing, (2016)
- [29] De G P. Coil-stretch transition of dilute flexible polymers under ultrahigh velocity gradients, *J Chem Phys*, 60, 5030 (1974)
- [30] Housmans J W, Steenbakkers R J, Roozmond P C, Peters G W, and Meijer H E. Saturation of pointlike nuclei and the transition to oriented structures in flow-induced crystallization of isotactic polypropylene, *Macromolecules*, 42, 5728-5740 (2009)

- [31] Watanabe K, Okada K, Toda A, Yamazaki S, Taniguchi T, Koyama K, Yamada K, and Hikosaka M. Acceleration mechanism of growth rates under shear flow due to the oriented melt The novel morphology of spiral crystal (Spiralite), *Macromolecules*, 39, 1515-1524 (2006)
- [32] Van MJ, Peters GW, and Hütter M. Towards a rheological classification of flow induced crystallization experiments of polymer melts, *Rheol Acta*, 44, 119-134 (2004)
- [33] Ebrahimi T, Taghipour H, Griebel D, Mehrkhodavandi P, Hatzikiriakos S G, and Van R E. Binary blends of entangled star and linear poly (hydroxybutyrate): Effect of constraint release and dynamic tube dilation, *Macromolecules*, 50, 2535-2546 (2017)
- [35] Yamaguchi M. Manufacturing of high performance biomass-based polyesters by rheological approach, *Handbook of composites from renewable materials, design and manufacturing*, 2, 25 (2017)
- [36] Mills N. Elasticity of polydimethylsiloxane melts, *Nature*, 219, 1249-1250 (1968)
- [37] Sawada T, Qiao X, and Watanabe H. Rheology of entangled polymeric liquids: current molecular pictures and problems, *Journal of the Society of Rheology*, 3, 1-14 (2003)
- [38] Auhl, D Ramirez J, Likhtman A E, Chambon P, and Fernyhough C. Linear and nonlinear shear flow behavior of monodisperse polyisoprene melts with a large range of molecular weights, *J Rheol*, 52, 801-835 (2008)

- [39] Liao Q, Noda I, and Frank CW. Melt viscoelasticity of biodegradable poly (3-hydroxybutyrate-co-3-hydroxyhexanoate) copolymers, *Polymer*, 50, 6139-6148 (2009)
- [40] Ebrahimi T, Aluthge DC, Hatzikiriakos SG, and Mehrkhodavandi P. Highly active chiral zinc catalysts for immortal polymerization of β -butyrolactone form melt processable syndio-rich poly (hydroxybutyrate), *Macromolecules*, 49, 8812-8824 (2016)
- [41] Harrison G M and Melik D H. Application of degradation kinetics to the rheology of poly (hydroxyalkanoates), *J Appl Polym Sci*, 102, 1794-1802 (2006)
- [42] Xu P, Yang W, Ni D, Yu M, Du M, Dong W, Chen M, and Ma P. Rheology determined critical conditions for shear-induced crystallization of biosynthesized polyhydroxyalkanoates, *Int J Biol Macromol*, 147, 1301-1308 (2020)
- [43] Hamad F G, Colby R H, and Milner S T. Onset of flow-induced crystallization kinetics of highly isotactic polypropylene, *Macromolecules*, 48, 3725-3738 (2015)

Chapter 5

General conclusion

My research proposed new ideas for enhancing the crystallization of polymer materials with a flow history. In each chapter, a novel method to be employed in the industry was proposed as follows.

Chapter 2 Effect of fibrous nucleating agent on shear-induced crystallization of polypropylene

The effect of a fibrous nucleating agent on the crystallization of PP under flow field was studied. The fibrous nucleating agent, MDBS, significantly increased the crystallization temperature and thus accelerated the whole crystallization rate. Without MDBS, the crystallization of PP was only enhanced after exposure to high shear rates. Moreover, no molecular orientation was observed, but the spherulite texture at lower shear rates. In the PP/MDBS system, a strong molecular orientation in the flow direction was detected, even at low shear rates. This is attributed to the formation of a pseudo shish-kebab structure. Thus, the combination of a fibrous nucleating agent and shear flow not only significantly increases the crystallization temperature and accelerates the crystallization rate but also changes the crystalline morphology from a spherulite texture to a highly oriented shish-kebab structure, leading to enhanced rigidity.

Chapter 3 Effect of low-density polyethylene addition on shear-induced crystallization of polypropylene

The effect of the LDPE addition on PP crystallization under shear flow was studied. The addition of LDPE enhanced the PP crystallization greatly only after shear history. In other words, shear-induced crystallization was significantly accelerated by the LDPE addition. As a result, the molecular orientation of PP significantly increased, which is responsible for high modulus. This technique must be available in the industry without any difficulty.

Chapter 4 Appropriate processing condition to enhance crystallization rate for poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)

The crystallization rate of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx) having various thermal and shear histories was studied. The melt temperature before cooling process was significant because a small amount of unmolten crystals could remain at a specific temperature at which the materials showed flowability. These unmolten crystals acted as nucleating agents and accelerated the crystallization rate. Furthermore, the shear history greatly enhanced the crystallization rate and the number of spherulites. The spherulites were aligned in a row to the flow direction. This unique structure must be the result of sporadic spherulite growths on extended chain crystals.

Future Scope

Accelerated crystallization can reduce the cycle time in the production and enhance molecular chain orientation resulting in high modulus. Based on recent research on flow-induced crystallization, crystallization can be accelerated by the addition of a high molecular weight fraction or exposure to a high shear rate. The results obtained in this thesis, such as the effects of the shape of a nucleating agent, external forces, i.e., shear flow, and long-chain branched polymers, will be helpful for future design considerations. A fibrous nucleating agent significantly enhanced the crystallization temperature and accelerated the crystallization rate. In the case of combining a nucleating agent with shear flow, the transformation of crystal form was greatly enhanced, shifting from a spherulite texture to an anisotropic, highly oriented shish-kebab structure. Furthermore, even in an immiscible blend system, the addition of a long chain branched polymer also enhanced the flow-induced crystallization and gave a highly oriented structure to the flow direction, which resulted in high modulus. This research also studies bio-based plastics that are biodegradable even in marine environments, focusing on optimizing processing conditions to enhance the crystallization rate.

At most polymer processing operations, such as injection molding, film blowing, and film casting, a molten polymer is exposed to shear flow. Therefore, the crystallization behavior of a crystalline polymer during/after flow is significantly important. Depending on the conditions including temperature, shear rate, and residence time, the growing structures varied from spherulite to orientation structures such as row-

nucleated and shish-kebab structures. As known, precise morphology control is essential to the properties of final products. Shear flow influences crystallization, which significantly enhances the crystallization rate and generates orientated crystallites.

Therefore, this research is very interesting and valuable because it aims to find the feasibility of enhancing the product's performance. This has advantages not only for academic research but also for designing the controlling processing conditions in the industry. Currently, I am mainly conducting research on polypropylene (PP), polyethylene (PE), and bio-based plastics, i.e., poly(hydroxyhexanoate) (PHBHHx). Since the methods must be independent of the polymer species, they can be applied to other crystalline polymers.

Achievements

Publications

- [1] **Janchai, K.;** Kida, T.; Inoue, T.; Iwasaki, S.; Yamaguchi, M. Crystallization behavior of isotactic polypropylene containing a fibrous nucleating agent in a flow field. *Polymer Journal* 2022, 54 (3), 367-375.
- [2] **Janchai, K.;** Kida, T.; Yamaguchi, M.; Sunagawa, T.; Okura, T. Optimum processing conditions for the maximum crystallization rate of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate). *Scientific Reports*, 2023, 13(1), 497.
- [3] **Janchai, K.;** Kida, T.; Inoue, T.; Iwasaki, S.; Yamaguchi, M. Role of nucleating agent on molecular orientation of polypropylene crystallized under flow field. *Novel Trends in Rheology IX* 2023, 2997, 040002.
- [4] **Janchai, K.;** 井上貴博; 岩崎祥平; 木田拓充; 山口政之, ポリプロピレンのせん断誘起結晶化に及ぼす繊維状結晶核剤の影響. *成形加工* 2023, 35(9), 318-323.
- [5] **Janchai, K.;** Yamaguchi, M. Shear-induced crystallization of polypropylene/low-density polyethylene blend. *Journal of Rheology* 2024, 68(1), 59–69. **FEATURED ARTICLE**

Other publications

- [1] **Janchai, K.**; Boonmahitthisud, A.; Chaiwuttinan, P.; Chuayjuljit, S.; Hongrattanavichit, I. Property improvement of recycled nylon 6 by thermoplastic poly(ether-ester) elastomer and wollastonite, *Materials Science Forum* 2022, 1053, 47–51.
- [2] Kida, T.; Kimura, T.; Eno, A.; **Janchai, K.**; Yamaguchi, M.; Otsuki, Y.; Kimura, T.; Mizukawa, T.; Murakami, T.; Hato, K.; Okawa, T. Effect of ultra-high-molecular-weight molecular chains on the morphology, crystallization, and mechanical properties of polypropylene, *Polymers* 2021, 13, 4222.
- [3] Nishikawa, R.; Eno, A.; **Janchai, K.**; Kida, T.; Aridome, N.; Miyamoto, A.; Yamaguchi, M. Crystallinity enhancement of extruded polypropylene containing poly(vinyl alcohol) fibers prepared in situ, *Polymer* 2022, 254, 125043.
- [4] Kida, T.; **Janchai, K.**; Tokumitsu, K.; Yamaguchi, M. Flow-induced crystallization behavior of high-density polyethylene evaluated by Rheo-Raman spectroscopic system. *Polymer Journal* 2023, 55, 1141–1150.
- [5] Drabek, J.; **Janchai, K.**; Kida, T.; Yamaguchi, M.; Zatloukal M. Effect of pre-shear on flow-induced crystallization of branched polypropylene. *Novel Trends in Rheology IX* 2023, 2997, 020005.
- [6] Kitabatake, S.; **Janchai, K.**; Yamaguchi, M. Pronounced shear-induced crystallization of polypropylene by addition of poly(methyl methacrylate). *Polymer* 2024, 307, 127260.

- [7] Fukuda, Y.; **Janchai, K.**; Sunagawa, T.; Yamaguchi, M. Anomalous Mechanical Response of Stretched Film of Poly(3-Hydroxybutyrate-co-3-Hydroxyhexanoate). *J. Environ. Polym. Degrad.* 2024, 1-11.

International Conferences

- [1] **Janchai, K.**; Boonmahitthisud, A.; Chaiwuttinan, P.; Chuayjuljit, S.; Hongrattanavichit, I. Property improvement of recycled nylon 6 by thermoplastic poly(ether-ester) elastomer and wollastonite. The Conference on the 6th International Conference on Materials Technology and Applications, October 2021, (Oral).
- [2] **Janchai, K.**; Kimura, T.; Kida, T.; Yamaguchi, M. Effect of shear flow on the structure and properties of polypropylene film, International Chemistry Conference, June 2022, Virtual, (Poster) **BEST POSTER AWARD.**
- [3] **Janchai, K.**; Kida, T.; Yamaguchi, M.; Sunagawa, T.; Okura, T. Crystallization behavior of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) under shear flow. ANTEC® 2023, Denver, CO, USA, March 2023, (Poster).
- [4] **Janchai, K.**; Kida, T.; Yamaguchi, M. Role of nucleating agent on molecular orientation of polypropylene crystallized under flow field. Novel trends in rheology IX, Tomas Bata University in Zlín, Jul 2023, (Poster).
- [5] **Janchai, K.**; Yamaguchi, M. Rheological properties and crystallization behaviors of Polypropylene blends with low-density polyethylene. ANTEC® 2024, St. Louis, MO, USA, March 2024 (Oral). **TRAVEL AWARD.**

- [6] **Janchai, K.;** Yamaguchi, M. Enhancement of shear-induced crystallization of polypropylene by addition of low-density polyethylene. 2nd International Summit on Biopolymers and Polymer Science, Portal Potulgal, June 2024 (Oral).
- [7] **Janchai, K.;** Yamaguchi, M. Effect of the addition of low-density polyethylene on the rheological properties and crystallization behaviors under shear flow for polypropylene. Polymer Engineering and Science International 2024, Tokyo, Japan, July 2024, (Poster). **BEST POSTER AWARD**
- [8] **Janchai, K.;** Kitabatake, Shion; Yamaguchi M, Shear-induced crystallization of polypropylene by the addition of low-molecular-weight polymers. The International Conference on Advanced Materials and Technology (ICAMT 2024) Hanoi, Vietnam, Oct 2024, (Poster).

Domestic Conferences

- [1] **Janchai, K.;** Kida, T.; Inoue, T.; Iwasaki, S.; Yamaguchi, M. Crystallization behavior under flow field for isotactic polypropylene containing a fibrous nucleating agent. 日本化学会北陸地区講演会, November 2021, (Poster).
- [2] **Janchai, K.;** Kida, T.; Inoue, T.; Iwasaki, S.; Yamaguchi, M. Crystallization under shear flow for isotactic polypropylene containing sorbitol-derivative. 第 71 回高分子学会年次大会, 1P4B028, May 2022, (Poster).

- [3] **Janchai, K.;** Inoue, T.; Iwasaki, S.; Kida, T.; Yamaguchi, M. Role of nucleating agent on chain orientation of polypropylene crystallized under shear flow 第 71 回高分子討論会, 1Pc035, September 2022, (Poster).
- [4] **Janchai, K.;** Kida, T.; Yamaguchi, M. Appropriate processing condition to enhance crystallization rate for poly(3-hydroxybutyrate-co-3-hydroxyhexanoate). 第 72 回高分子学会年次大会, 1P4B028, May 2023, (Poster).
- [5] **Janchai, K.;** Yamaguchi, M. Effect of low-density polyethylene addition on rheological properties and crystallization behavior for polypropylene. 第 72 回高分子討論会, 1Pa043, September 2023, (Poster).

Awards

- [1] Best Poster Award, International Chemistry Conference, Online, June 2022
- [2] Travel Award, ANTEC International Conference, March 2024, St. Louis, MO, USA.
- [3] プラスチック成形加工学会第 34 回論文賞
- [4] Best Poster Award, Polymer Engineering, and Science International July 2024, Tokyo, Japan