

Nucleating Agent for Poly(L-lactic acid)—An Optimization of Chemical Structure of Hydrazide Compound for Advanced Nucleation Ability

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ABSTRACT: A series of compounds having hydrazide groups was prepared and evaluated as nucleating agent for poly(L-lactic acid) by differential scanning calorimetry. Hydrazide compounds derived from benzoic acid, 2-hydroxybenzoic acid, 3-*tert*-butylbenzoic acid, and 2-aminobenzoic acid, where two of hydrazide compounds connected by four methylene chain were evaluated in series. Benzoylhydrazide type was found to be more effective on the enhancement of crystallization of poly(L-lactic acid). Effects of connecting length of methylene chain numbers between two of benzoylhydrazide on the nucleation ability were also evaluated. Benzoylhydrazide-type compound having 10 methylenes, that is, decamethylenedicarboxylic dibenzoylhydrazide demonstrated excellent nucleation ability, and the resulted crystalliza-

tion temperature and enthalpy of PLA with the compound of 1 wt % loading were 131°C and 46 J g⁻¹. The achieved crystallization temperature and enthalpy were over 10°C and over 10 J g⁻¹ higher than PLA with conventional nucleating agents, such as talc and ethylenebis(12-hydroxystearylamide). Thus, the improvement in processability, productivity, and heat resistance of PLA is suggested to be achieved by using decamethylenedicarboxylic dibenzoylhydrazide as a nucleating agent. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 198–203, 2007

Key words: nucleating agent; nucleation; poly(L-lactic acid); crystallization temperature; crystallization enthalpy; hydrazide

INTRODUCTION

Crystallizability and the degree of crystallinity of crystalline polymers are one of the most important characteristics from the standpoint of practical applications such as plastics, because the characteristics strongly affect the processability and productivity of mold processing and performance of molded articles.¹ Several nucleating agents, which enhance the crystallization rate, are widely used for crystalline polymers, in particular, for polypropylene.^{2,3} For example, sodium methylene bis(2,4-di-*tert*-butylphenyl)phosphate (trade name NA-11, ADEKA, Japan) is a well known nucleating agent for polypropylene, and the compound makes it possible to enhance significantly the nuclei generation during polypropylene crystallization process, resulting in enhancing over 30% of modulus and drastically decreasing molding cycle time. Although the increase in isotacticity via improving catalyst isospecificity is known to improve stiffness, an addition of nucleating agents is more easy way and cost effective.⁴ Thus, nucleat-

ing agents are very useful for practical use of crystalline polymers.

Poly(L-lactic acid) (PLA) is a well known biodegradable polymer, and is produced from renewable resources such as corn, potato, and so on.⁵ Currently, there is an increasing interest in utilizing PLA in applications that are not limited to just disposable and biodegradable. PLA is now expected as carbon neutral material from the viewpoint of reduction of carbon dioxide emission and saving of resources.⁶ To promote the utilization of PLA, several attempts have been made for developing PLA compounds and its molded article instead of bulk polymers, and related modifiers for PLA. Although PLA has an advantage on environmental protection and/or renewable resources, there is a critical issue concerning the crystallization rate and heat resistance of molded articles.⁷ Despite the PLA is crystalline polymer, no crystallization essentially proceeds and observed under higher cooling rate such as a practical molding condition. In usual, glassy molded articles of PLA are just obtained in fabrication via practical processing with higher cooling rate. As a result, the heat resistance such as heat distortion or heat deflection temperature (HDT) of the articles is very low and is around 50–60°C, which concerns

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glass transition temperature, T_g of PLA.⁷ Thus, PLA as neat resin is limited to application to disposable goods, which needs no heat resistance. Conclusively, the lower HDT prevents the expansion and diversification of PLA applications.

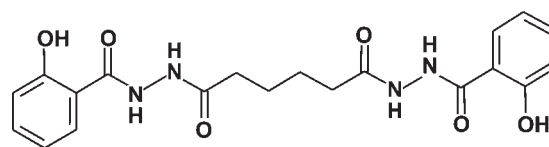
Screenings of conventional compounds and developments of nucleating agents for PLA were conducted by several groups to improve the processability, productivity in processing, and heat resistance. Suzuki et al. claimed in their patent that certain aliphatic amide compounds, for example ethylenebis(12-hydroxystearylamide) (EBHSA) accelerate the crystallization of PLA.⁸ Although the compound accelerated crystallization rate of PLA, the achieved molding cycle time was not enough, that is approximately seven times longer than that of bulk polymers such as polypropylene.⁹ Other groups claimed in their patents that 1,4-cyclohexanedicarboxylic dianilide and indigo enhanced the crystallization of PLA.^{10,11} Although, these compounds as nucleating agents are found to be effective, and to increase crystallization temperature, crystallization rate, and the degree of crystallinity, the performance is also not enough for practical use from the viewpoint of substitution of bulk polymer such as polypropylene. In addition, there are some limitations in utilizing the above-mentioned compounds, e.g. indigo-colored articles. To promote the utilizing PLA from the viewpoint of environmental issue, an advanced nucleating agent having more powerful nucleation ability without any drawbacks is expected. In the course of our studies, tetramethylenedicarboxylic disalicyloylhydrazide (N-1, Scheme 1), which resembled in chemical structure known as metal deactivator for polyolefins, was found to be effective as a nucleating agent for PLA.^{12,13} PLA with N-1 of 1 wt % was demonstrated to enhance the crystallization resulted in increasing crystallization temperature (T_c). The T_c of PLA with N-1 exhibited higher than that with EBHSA. Thus, the hydrazide group is considered to be a potential basic structure to design an advanced nucleating agent.

In this study, a series of organic compounds having hydrazide groups was evaluated as a nucleating agent for PLA by using differential scanning calorimeter (DSC), and it was aimed to optimize the chemical structure of hydrazide compound and to obtain comparable T_c to bulk polymers such as polypropylene.

EXPERIMENTAL

Materials

The characteristics of PLA-used were the weight-averaged molecular weight of 160 K, the melting temperature of 175°C, and the optical purity of L-lactic acid in the polymer was 99.4% ee. As reference nucleating agents for the hydrazide compounds, talc (fine particle size grade, Micro Ace P-6, Japan Talc,



Scheme 1 Tetramethylenedicarboxylic disalicyloylhydrazide (N-1).

Japan) and EBHSA (MA-WAX-O, KF Trading, Japan, without any purification) were used. Typical synthesis procedure of hydrazide compound (decamethylenedicarboxylic dibenzoylhydrazide) was as follows: benzoic hydrazide (Tokyo Kasei Kogyo, Japan) of 0.041 mol, *N,N*-dimethylacetamide (Tokyo Kasei Kogyo, Japan) of 50 mL was mixed, and the mixture was purged under nitrogen atmosphere with 20 mL min⁻¹. Dodecanedioyl dichloride (Sigma Aldrich) of 0.019 mol was added onto the mixture, followed by adding pyridine (Kokusan Chemical, Japan) of 0.057 mol, and the mixture was stirred at room temperature for 1 h, heated up to 70°C, and held at 70°C for 1 h with stirring. Reaction mixture was poured onto water of 300 mL and stirred, followed by filtrating. Obtained crude product was washed three times by water of each 400 mL at room temperature, and then washed by methanol (Wako Pure Chemical Industries, Japan) of 300 mL at 50°C to eliminate raw materials and by-products. The product yield was 7.04 g and 80.9 wt % based on benzoic hydrazide. The product assignment and purity were estimated by using ¹³C-NMR (FT-NMR Lambda 400, JEOL, Japan) and liquid chromatograph (JASCO PU-980 HPLC with UV ($\lambda = 254$ nm) detector JASCO UV-970, JASCO, Japan: Senshu Pak PEGASIL ODS Column having 4.6 mm ϕ \times 250 mm, tetrahydrofuran/water = 75/25 v/v as eluent, column temperature of 40°C, flow rate of 0.7 mL min⁻¹), and the purity was over 99 wt %. ¹H-NMR chart of decamethylenedicarboxylic dibenzoylhydrazide was shown in Figure 1. A series of nucleating agents having hydrazide group was synthesized according to above-mentioned procedure.

Evaluation of nucleation ability

Nucleating agent were dry-blended with PLA pellets, and the mixture (1 wt % of nucleating agent was loaded) was dried at a temperature of 90°C for 5 h *in vacuo*. The dried mixture was extruded by using twin-screwed extruder (Labo Plastomill Micro, Toyo Seiki Seisaku-sho, Japan) at a temperature of 210°C. Crystallization temperature (T_c) as a peak top temperature and crystallization enthalpy (ΔH_c) was determined by using differential scanning calorimetry (Diamond DSC, PerkinElmer, USA) with following procedure and temperature program: PLA of 5 mg was cut from dried pellet, and then rolled up by aluminum pan.

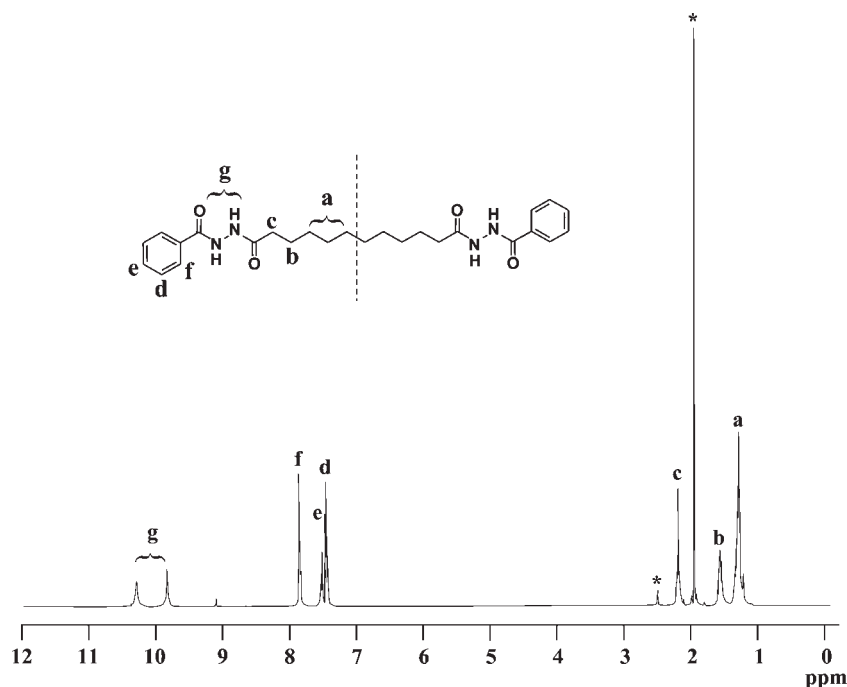


Figure 1 $^1\text{H-NMR}$ chart of decamethylenedicarboxylic dibenzoylhydrazide (N-15, Table IV). Asterisks denote the peaks ascribed to dimethylsulfoxide as solvent.

The sample was heated from room temperature to 210°C with a heating rate of $50^\circ\text{C min}^{-1}$, held for 5 min at 210°C , and then cooled with a cooling rate of $-20^\circ\text{C min}^{-1}$ from 210 to 30°C . Crystallization behavior was observed by using optical microscope, OM (BX51, Olympus, Japan) having heating and cooling (THMS 600, Linkam Scientific Instruments, UK) with temperature controller and digital camera (KY-F75, Victor Company of Japan, Japan) assisted by a computer. Polarizing microscopic observation (POM) was conducted by the OM with cross-Nicol prism under similar temperature program for DSC measurement.

RESULTS AND DISCUSSION

Talc and EBHSA are known as typical market available nucleating agents, and enhance the crystallization of PLA as mentioned in the Introduction. Table I shows the T_c and ΔH_c of PLA with talc, EBHSA, and N-1 of 1 wt % loading. Here, the DCS data was obtained with a cooling rate of $-20^\circ\text{C min}^{-1}$. Under this cooling rate, no clear exothermic peak due to crystallization was observed on the PLA without any nucleating agents. On the other hand, the peaks due to crystallization were observed for the PLA with talc, EBHSA, and N-1, and T_c and ΔH_c were estimated to be 102°C and 26 J g^{-1} , 110°C and 35 J g^{-1} , and 114°C and 17 J g^{-1} , respectively. Thus, the compounds listed in Table I were confirmed to enhance drastically the crystallization of PLA. N-1 provided the highest T_c among them, and EBHSA gave high-

est ΔH_c among them. Since higher T_c is considered to lead to higher molding cycle time, N-1 is believed to provide better productivity in molding among them. On the other hand, the ΔH_c is in connection with the degree of crystallinity (χ_c). Thus, the improvement in mechanical properties using EBSHA is expected to be better than that of others. The melting enthalpy of 100% crystalline of PLA ($\Delta H_{m,0}$) was reported to be 93 J g^{-1} .¹⁴ The χ_c was proposed to be estimated by using $\chi_c (\%) = 100 \cdot (\Delta H_m + \Delta H_c) / 93$. Since the ΔH_m of PLA polymerized by using zinc-bis(2,2-dimethyl-3,5-heptanedionato-O,O') was reported to be 100 J g^{-1} , the χ_c of the PLA was calculated to be over 100%. Ikada and coworkers pointed out this problem on the estimation of crystallinity.¹⁵ Considering the uncertain situation on crystallinity, no χ_c was estimated from DSC enthalpy in combination with the equation in this study. However, the observed

TABLE I
DSC Crystallization Temperature and Crystallization Enthalpy of Poly(L-lactic acid) with Nucleating Agents^a

	T_c^b ($^\circ\text{C}$)	ΔH_c^b (J g^{-1})
Talc	102	26
EBHSA ^c	110	35
N-1 ^d	114	17

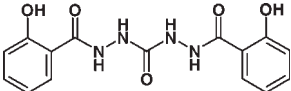
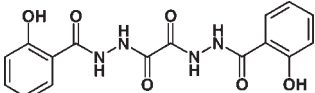
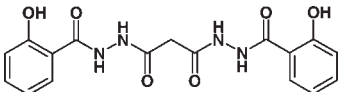
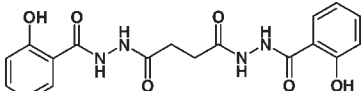
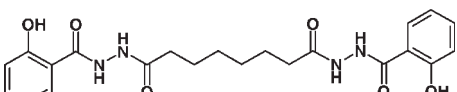
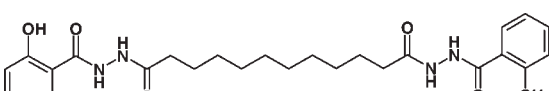
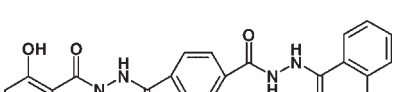
^a Loading level of nucleating agent, 1 wt %.

^b Measured by DSC.

^c Ethylene bis(12-hydroxystearylamide).

^d See Scheme 1.

TABLE II
Effects of Carbon Length of Dicarboxylic Disalicyloylhydrazide Compound on Nucleation Ability for PLA^a

Chemical structure	Abbreviation	T_c^b (°C)	ΔH_c^b (J g ⁻¹)
	N-2	95	<1
	N-3	96	6
	N-4	92	<1
	N-5	92	<1
	N-6	106	28
	N-7	100	9
	N-8	93	<1

^a Loading level of nucleating agent, 1 wt %.

^b Measured by DSC.

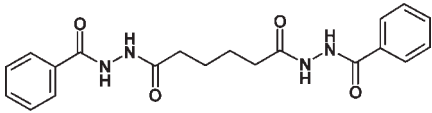
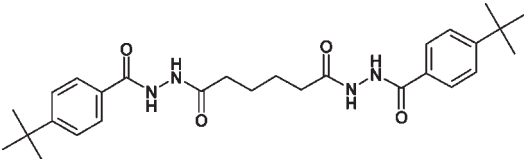
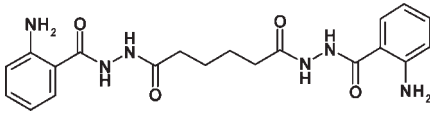
ΔH_c of PLA with nucleating agents listed in Table I was apparently and considerably lower than $\Delta H_{m,0}$. This indicates that the χ_c of PLA nucleated by talc, EBHSA, and N-1 was very low.

Table II summarizes the evaluation results of dicarboxylic disalicyloylhydrazide derivatives having different methylene chain numbers. The obtained T_c and ΔH_c of N-1 (Table I) and N-2 to N-8 (Table II) were ranging from 92 to 114°C and lower than from 1 to 28. Highest T_c in this series was of N-1, and highest ΔH_c was of N-6. No apparent tendency associated with a variation of methylene numbers was observed (N-1 to N-7). In addition, it was found that rigidity of the chain, which connected the salicyloylhydrazide groups had no significant influence on the nucleation ability (comparison of N-8 tied by aromatic group with others having methylene chain). Although, N-1 having four methylene length and N-6 having six methylene chain numbers exhibited superior nucleation ability, among them from the viewpoint of better balance between T_c and ΔH_c , the

ability does not improve significantly by the changing of the "connection" group.

Table III shows the effects of substituent of benzene rings of hydrazide compound on nucleation ability for PLA. Here, hydrazide compounds derived from benzoic acid (nonsubstituent: N-9), 2-hydroxybenzoic acid (OH group: N-1), 3-*tert*-butylbenzoic acid (*tert*-butyl group: N-10), and 2-aminobenzoic acid (amino group: N-11), where two of hydrazide compounds connected by four methylene chain were evaluated in series. Among them, N-11 exhibited lower T_c and lower ΔH_c . N-10 gave comparable T_c to N-1, but its ΔH_c was minimal. N-9 exhibited higher T_c than N-1 and doubled ΔH_c of N-1. Thus, N-9 having no substituent on the benzene ring was demonstrated to perform as most effective nucleating agent among the compounds listed in Tables I, II, and III. This suggests that carboxylic dibenzoylhydrazide is more effective as basic structure for enhancing PLA nucleation. Taking into consideration the above-mentioned results, a series of compounds having dif-

TABLE III
Effects of Substituent of Benzene Ring of Hydrazone Compound on Nucleation Ability for PLA^a

Chemical structure	Abbreviation	T_c^b (°C)	ΔH_c^b (J g ⁻¹)
	N-9	116	36
	N-10	113	<1
	N-11	96	<1

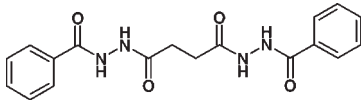
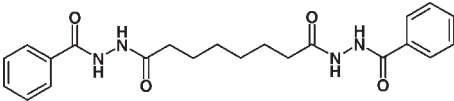
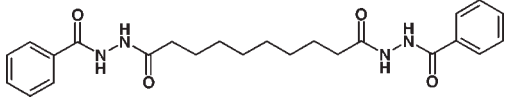
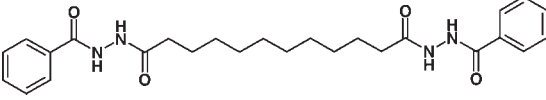
^a Loading level of nucleating agent, 1 wt %.

^b Measured by DSC.

ferent methylene numbers based on the dicarboxylic dibenzoylhydrazone was prepared and their nucleation ability was evaluated by DSC measurement. Table IV summarizes the T_c and ΔH_c of PLA nucleated by dicarboxylic dibenzoylhydrazone having methylene chain numbers of 2, 6, 8, and 10. The compound having methylene chain numbers of 4 was listed in Table I as N-1. It was found that the T_c and ΔH_c increased with the methylene numbers: the nucleation ability of dicarboxylic dibenzoylhydrazone-based compounds improved with increasing of methylene

number, and N-13, N-14, and N-15 exhibited superior nucleation ability when compared with N-1. In particular, excellent enhancement in nucleation was observed for PLA with N-15 having 10 methylene chain numbers resulting in achieving T_c of 131°C and ΔH_c of 46 J g⁻¹. Figure 2 shows the microphotographs observed by polarized optical microscopy (POM) at 140, 120, and 100°C during crystallization with a cooling rate of -20°C min⁻¹. Morphology at 120°C was the same as that at 100°C. Thus, the crystallization of PLA with N-15 was confirmed by POM

TABLE IV
Effects of Carbon Length of Dicarboxylic Dibenzoylhydrazone Compound on Nucleation Ability for PLA^a

Chemical structure	Abbreviation	T_c^b (°C)	ΔH_c^b (J g ⁻¹)
	N-12	99	12
	N-13	122	36
	N-14	127	40
	N-15	131	46

^a Loading level of nucleating agent, 1 wt %.

^b Measured by DSC.

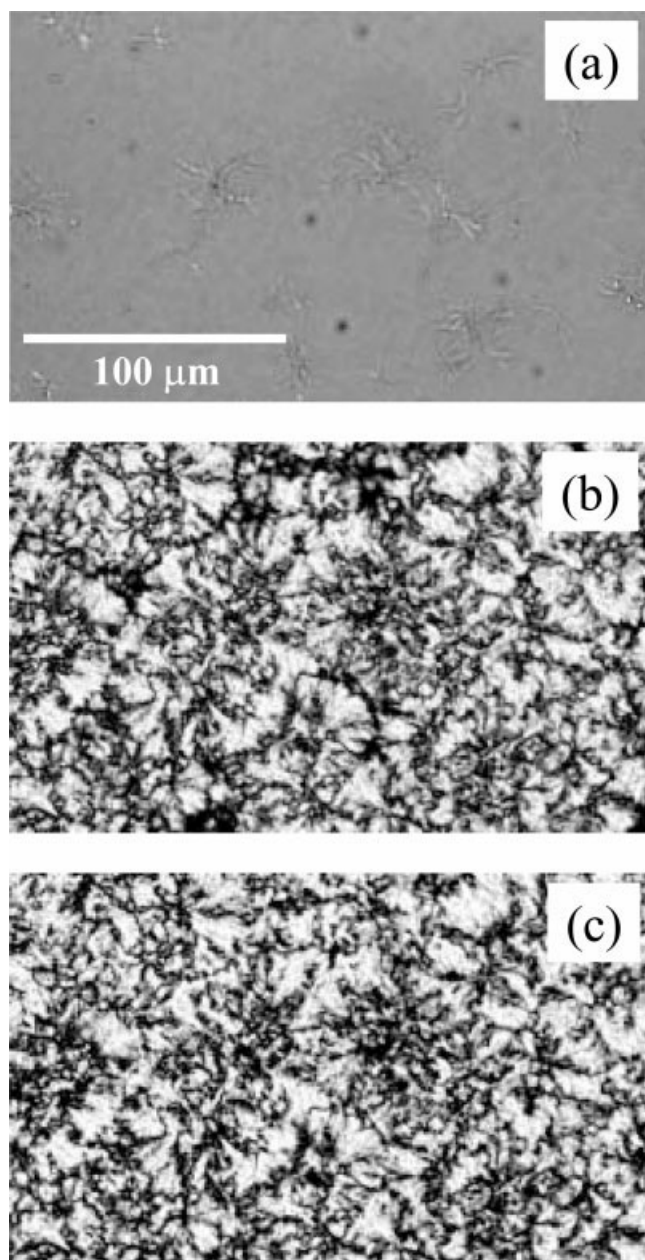


Figure 2 Polarized optical microscopic observation during crystallization of PLA nucleated by decamethylenedicarboxylic dibenzoylhydrazide (N-15, see Table IV). Magnification was denoted as a bar scale in photograph. Cooling rate was $-20^{\circ}\text{C min}^{-1}$; (a) at 140°C , (b) at 120°C , (c) and at 100°C .

almost proceeded at 120°C . The POM result on PLA with N-15 is consistent with DSC.

Since the HDT of over 120°C is in general required for polypropylene grades as automotive parts from the standpoint of heat resistance, polypropylene is nucleated by advanced nucleating agents. The resulted T_c of nucleated polypropylene is $\sim 130^{\circ}\text{C}$ in usual. As mentioned earlier, T_c relates the HDT in usual. Taking this into consideration, the HDT or heat resistance of PLA with N-15 of 1 wt % is con-

sidered to be comparable to automotive grades of polypropylene. This result is of considerable importance for practical application of PLA.

CONCLUSIONS

To develop an advanced nucleating agent for PLA, an optimization of chemical structure of compound having hydrazide group was performed via evaluation of a series of compounds having variety of methylene chain numbers and substituents. Benzoylhydrazide type was found to be most effective on the enhancement of PLA crystallization. An increase in the methylene chain numbers improved the nucleation ability of benzoylhydrazide-type compound, and decamethylenedicarboxylic dibenzoylhydrazide was found to provide highest crystallization temperature and enthalpy among compounds evaluated in this study. The achieved crystallization temperature and enthalpy of PLA with the compound were 131°C and 46 J g^{-1} , which was comparable to nucleated polypropylene. Thus, decamethylenedicarboxylic dibenzoylhydrazide was considered to be a potential compound as nucleating agent for practical use. It is expected that this result contributes the promotion of PLA utilization as molded articles, resulting in contributing the environmental issue via reduction of carbon dioxide emission.

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