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A Novel Use of Ti-POSS as Initiator of L-Lactide Ring-Opening Polymerization

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ABSTRACT: The efficacy of a metal-silsesquioxane, namely, heptaisobutyl (isopropoxyde)titanium-polyhedral oligomeric silsesquioxanes (Ti-POSS), as initiator of the ring-opening polymerization of L-lactide (LLA) has been assessed. Indeed, as demonstrated by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy and gel permeation chromatography (GPC) measurements, a well-controlled polymerization occurs via a coordination-insertion mechanism. Moreover, the above reaction leads to the direct insertion of the silsesquioxane molecule into the polymer backbone, thus producing a hybrid system. Differential scanning calorimetry measurements demonstrated that in comparison with a commercial poly-L-lactide (PLLA), the polymers prepared with Ti-POSS exhibit a higher crystallinity. Indeed, the presence of silsesquioxane molecules, attached to one end of the polymer chains, has been found to appreciably affect the crystal nucleation density. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 4794–4799, 2011

KEYWORDS: M-POSS; PLA; ring-opening polymerization

INTRODUCTION Polylactide (PLA) is a biodegradable aliphatic polyester which is synthesized from lactic acid derived from renewable sources.[1,2] Indeed, PLA has excellent mechanical properties comparable to those of conventional polymers such as polystyrene (PS) and polyethylene (PE) and has been used for medical devices and industrial packaging materials.[3,4] This polymer is mostly synthesized by ring-opening polymerization (ROP) of lactide (LA) using organometallic compounds as initiators or catalysts.[5–8]

Despite the fact that some excellent initiators have been reported for the polymerization of LA, the search for new catalysts that generate well-defined PLAs remains of keen interest. The role of the structure of metal alkoxide complexes in determining PLA molecular weight and molecular weight distribution, as well as the polymerization pathway, is a significant current research issue.

Among the metal salts and coordination compounds studied for the ROP of LA, also titanium-based systems have been considered. Following the pioneering work of Kricheldorf et al.[9] on the use of titanium alkoxides as initiators of the polymerization of lactones, several types of Ti-based complexes have been studied for the ROP of LA to produce PLA.[10–25] Indeed,

some of the above systems enable stereoselective polymerization reactions. These reactions are generally carried out in homogeneous phase; however, for better control of the polymerization process and easier separation of the catalysts from the resulting polymer, it would be desirable for these catalysts to be heterogeneous.[26,27] Only recently, Kim et al.[28] reported on the preparation of silica-supported titanium alkoxide which, when used in the polymerization of PLA, was found to yield polymers with higher molecular weight and melting temperature than those synthesized by homogenous catalysts.

Among the siliceous systems, metal-containing silsesquioxane derivatives represent novel catalysts in the field of both homogeneous and heterogeneous catalysis (such as alkene polymerization, metathesis, or epoxidation).[29–31] These molecules are generally prepared from incomplete condensed structures, that is, open-corner polyhedral oligomeric silsesquioxanes (POSS) molecules that can react with transition metal compounds to form metal-silsesquioxanes (M-POSS). Moreover, M-POSS turned out also to strongly limit thermo-oxidative degradation of polymer nanocomposites.[32–34]

As far as the exploitation of M-POSS in the polymerization of LA is concerned, Di Iulio et al.[35] recently reported on the

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Additional Supporting Information may be found in the online version of this article.

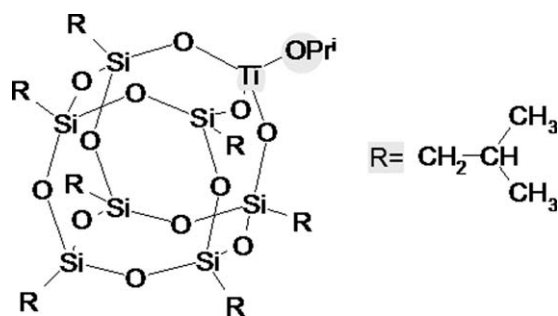**FIGURE 1** Heptaisobutyl (isopropoxyde)titanium-POSS (Ti-POSS)

FIGURE 2 Plot of PLA M_n (circles, size exclusion chromatography relative to polystyrene standards) and index of polydispersity (squares) as a function of conversion (130 °C, [LA]/[Ti] 300).

preparation and characterization of zinc(II) silsesquioxane complexes, showing also a preliminary study on the use of these systems as initiators of the ROP of *rac*-LA. To the best of our knowledge, no report on the exploitation of Ti-based POSS for the polymerization of L-lactide (LLA) has been published so far. Indeed, this work has been focused on the use of the above silsesquioxane (Fig. 1), which is potentially capable of acting as initiator of LA ROP. In particular, as shown in Figure 1, the titanium center in these compounds retains one terminal alkoxide ligand, which is ideal for ROP via the coordination–insertion mechanism established for known metal alkoxide initiators.

RESULTS AND DISCUSSION

The results of bulk ROP of LLA, carried out at 130 °C with various polymerization times (t_p) and [LLA]/[Ti] ratios, are shown in Table 1. Number averaged molar weight and polydispersity index (M_w/M_n, PDI) are plotted in Figure 2 as a function of the conversion (defined as [LLA]$_0$ − [LLA]$_t$/[LLA]$_0$, where [LLA]$_0$ and [LLA]$_t$ are LLA initial and final concentration, respectively), which was calculated by monitoring the polymerization reaction by ^{1}H-NMR and size exclusion chromatography (SEC).

The linear correlation between the polymer molecular weight and monomer conversion, coupled with low PDIs, are indicative of a well-controlled polymerization. Moreover, as the monomer-to-catalyst molar ratio [LLA]/[Ti] decreases from 300 to 75, the relative number-average molecular weight, M_n, decreases while the PDI values of PLA remain almost constant under the conditions of the same conversion (100%). This implies a well-controlled polymerization process (runs 4 and 5).
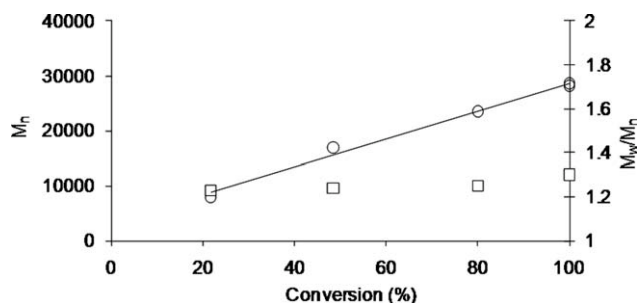
The semilogarithmic plot of conversion versus time is shown in Figure 3. Indeed, a first-order dependence of monomer conversion is consistent with a coordination–insertion mechanism.

In order to validate the polymerization mechanism, ^{1}H NMR measurements were carried out. ^{1}H NMR spectrum of PLA (Fig. 4) synthesized with Ti-POSS reveals only two major set of signals: the well-resolved quartet of CH protons at $\delta \cong 5.1$ ppm and the doublet for CH$_3$ protons at $\delta \cong 1.5$ ppm. Such an absorption pattern is indicative of the isotactic nature of PLA.

Apart from the above strong signals coming from PLA chain, two weak well-resolved signals are observed at 1.0−0.90 and 4.40−4.30 ppm. The latter quartet can be ascribed to methine protons a″ in the end group of the growing PLA macromolecules, which are in the direct vicinity of Ti center.

Signals of the methyl protons b′ and b″ of the end groups coincide with the main chain signal b; quartet of the methane protons a′ and a are also overlapped.

It must be underlined that the signal at about 1.0 ppm is due to POSS moiety, being present also in the spectrum of the neat silsesquioxane. Indeed, this finding reveals that POSS is chemically bound to PLA chains, unreacted silsesquioxane being removed by the purification process. On the basis of the previous described results and taking into account the information gathered by NMR, it is possible to infer that the polymerization proceeds via a coordination–insertion mechanism, as described in the simplified reaction mechanism reported in Scheme 1. This process involves the

TABLE 1 Polymerization of LLA Using Ti-POSS

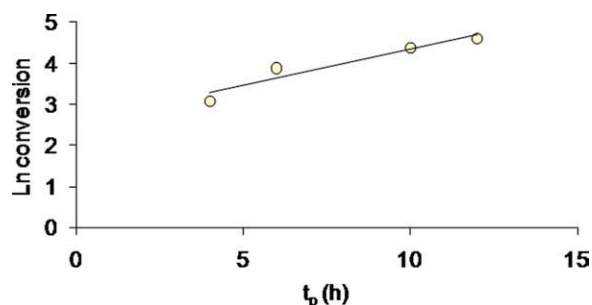| Entries	t_p (h)	[LLA]/[Ti] (mol mol^{-1})	Conv. (%)	M_n	M_w	M_w/M_n	M_v
1	4	300	22	7,900	9,700	1.23	9,000
2	6	300	48	16,900	21,000	1.24	19,000
3	8	300	80	23,500	29,400	1.25	25,000
4	12	300	100	28,600	37,200	1.30	33,000
5	24	300	100	28,200	38,100	1.35	32,000
6	24	75	100	9,500	12,400	1.30	11,700

FIGURE 3 Semilogarithmic plot of LLA conversion with time (130 °C, [LLA]/[Ti] 300).

insertion of LA unit into Ti—O bond of a silsesquioxane molecule and the selective cleavage of the acyl-oxygen bond in LA, which results in the formation of ester end group.

Clearly, the direct insertion of the silsesquioxane molecule to the polymer backbone indicates that M-POSS promotes not only the polymerization of LLA, acting as an initiator, but also allows the obtainment of a hybrid system.

The results of thermal characterization are given in Table 2. As a comparison, in the same table, Differential scanning calorime-

try (DSC) data of a commercial poly-L-lactide (PLLA) (entry 7), characterized by a molecular weight similar to that of the samples prepared by using t_p of 12 and 24 h (entries 5 and 6) are listed. Indeed, PLLA crystallization is strongly affected by molecular weight,[36,37] as can be also deduced from the data reported in Table 2, where the sample with the lowest M_n (entry 1) exhibits the highest crystallinity. The reported crystallinity values provide a mean to indirectly assess the crystallization kinetics, as all the samples were submitted to identical thermal histories. As detailed in the experimental section, the mass fraction of crystals, developed during cooling the sample from the melt, is evaluated from their enthalpy of fusion in a subsequent heating stage. This procedure was required as crystallization on cooling takes place in a broad temperature range, preventing a reliable quantification of the related heat release.

By comparing the commercial sample (entry 7) with those obtained with Ti-POSS (entries 4 and 5), it can be noticed a remarkable increase of the degree of crystallinity, that is, from about 30 to 60%, clearly indicating a faster crystallization kinetics of the latter.

The reason for this different crystallization behavior was investigated in more details by means of a hot stage coupled
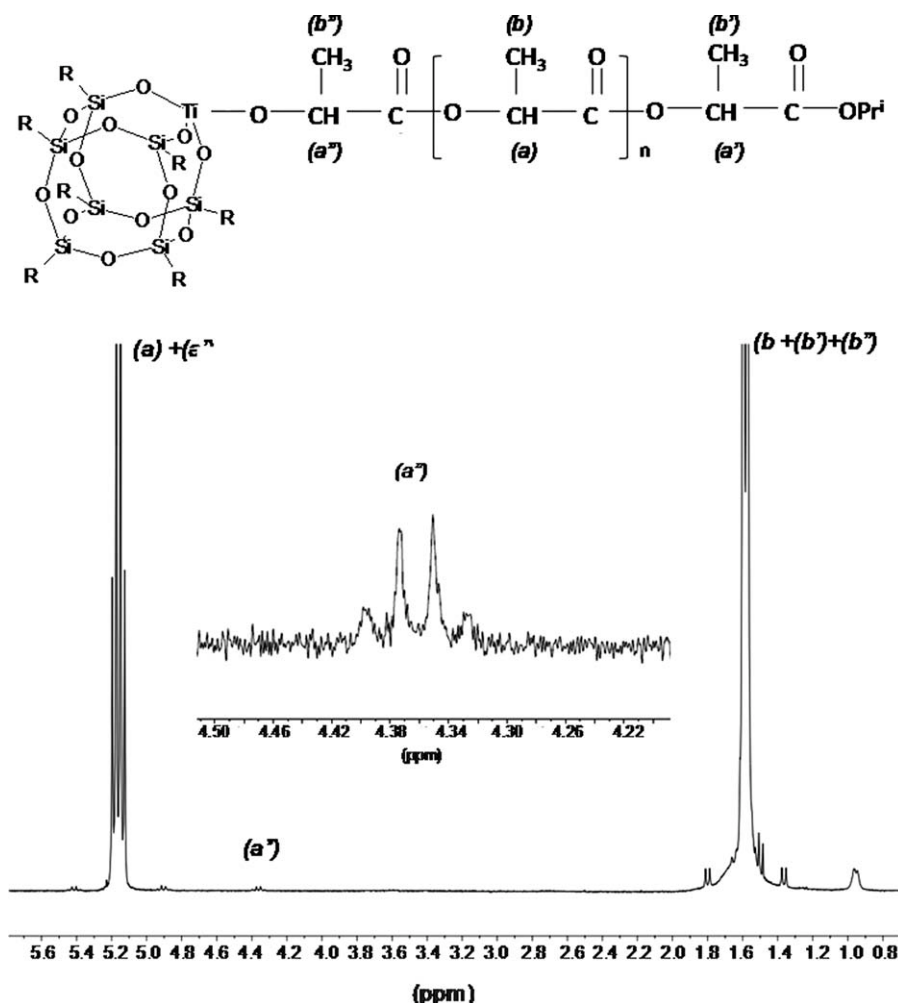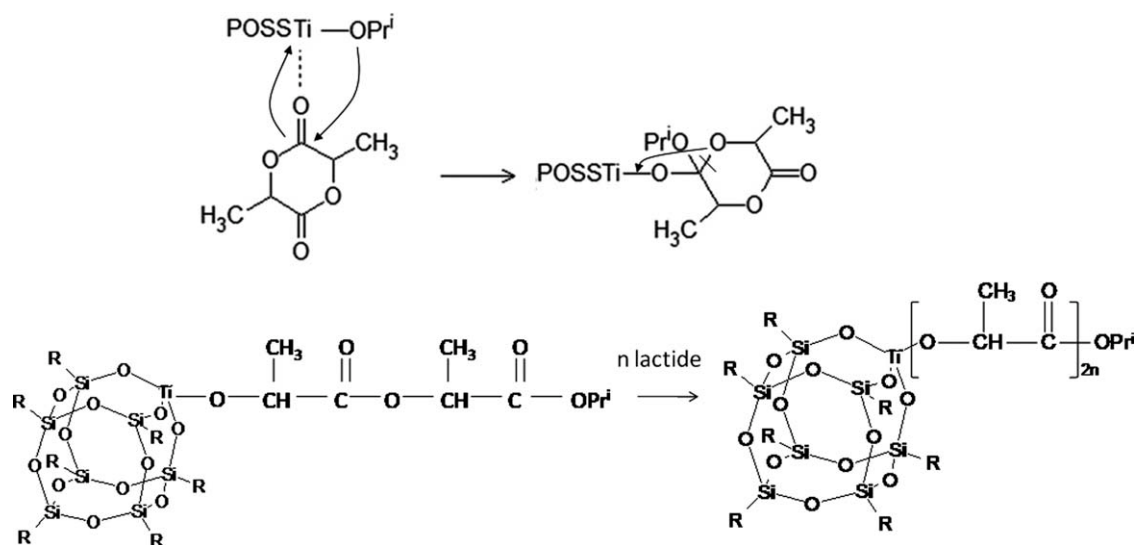

FIGURE 4 ^{1}H NMR spectrum of PLA synthesized at 130 °C for 24 h with a [LLA]/[Ti] of 300 (entry 5 in Table 1).

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SCHEME 1 Proposed mechanism of PLA synthesis with Ti-POSS.

to a polarized optical microscope, which enabled us to separate the contributions of nucleation and growth to the overall crystallization kinetics. Spherulitic growth rates were measured in isothermal conditions at different temperatures between about 135 and 120 °C, revealing no meaningful differences between the synthesized PLA and the commercial sample. Instead, non-negligible differences were detected for what concerns the nucleation density of the two systems. Indeed, Figure 5 compares the morphology exhibited by two samples (PLA synthesized with Ti-POSS at 130 °C for 24 h with a [LLA]/[Ti] of 300 (entry 5 in Table 2) and the commercial PLLA) at 114 °C, during cooling from the melt.

It can be appreciated that the polymer synthesized with Ti-POSS exhibits a higher nucleation density, that is, a greater number of spherulites per unit volume. Moreover, at the same temperature, several of these spherulites show larger dimensions; as the linear growth rate of the spherulites in the two systems is identical, this indicates a higher onset temperature for their nucleation.

The cause of this enhanced nucleation is not immediately clear. It is well known that POSS molecules can act as efficient nucleating agents for a series of polymers,[38,39] including PLLA.[40] However, due to the adopted synthesis and purification procedure, unreacted crystalline Ti-POSS, able to provide nucleation sites, is not expected to be present in a meaningful amount in our samples.

On the other hand, when a POSS derivative is covalently bound to the polymer chain, the resulting effect on crystallization is highly dependent on the specific molecular architecture. For example, the presence of POSS as a pendant group of the backbone chain greatly hinders the crystallization process in PE-POSS copolymers, leading to smaller and defective PE crystallites.[41] The crystallization of polyethylene oxide end-capped with POSS macromonomers, instead, shows a complex behavior influenced by microphase separation of the unlike moieties in the molten state.[42] The present system, in which the crystallizing polymer chains are tethered on one end to a bulky silsesquioxanes molecule, represents a

TABLE 2 DSC Data of PLA Prepared by Using Ti-POSS and of a Commercial PLLA

Entries	M_n	[LLA]/[Ti] (mol mol^{-1})	T_g (°C)	ΔH_c (J g^{-1})	T_m (°C)	ΔH_m (J g^{-1})	Crystallinity[a] (%)
1	7,900	300	36	0	159	68.8	74.3
2	16,900	300	50	0	171	62.5	67.2
3	23,500	300	51	0	172	58.0	62.4
4	28,600	300	50	0	172	56.1	60.3
5	28,200	300	52	8.9	171	62.0	57.1
6	9,500	75	46	4.1	172	61.3	61.5
7	28,300	–	49	25.7	171	54.4	30.8

Glass transition temperature (T_g), enthalpy of cold crystallization (ΔH_c), melting temperature (T_m), and melting enthalpy (ΔH_m) were determined from the second scan.

[a] The degree of crystallinity was determined by subtracting ΔH_c from ΔH_m and by considering a melting enthalpy of 93 J g^{-1} for 100% crystalline PLA.
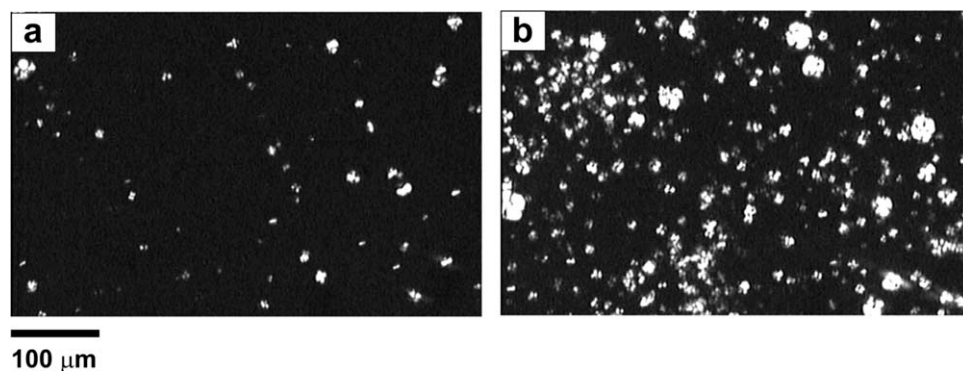
FIGURE 5 Micrographs taken at 114 °C during non-isothermal crystallization of (a) commercial PLLA sample (entry 7 in Table 2) and (b) PLA synthesized with Ti-POSS (entry 5 in Table 2).

novel case still unexplored in the literature. Further investigation is being carried on to highlight the mechanism of the observed nucleating effect.

EXPERIMENTAL

Materials

LLA (Aldrich) was recrystallized with toluene three times before use. Heptaisobutyl (isopropoxide)Ti-POSS (Ti-POSS) was synthesized according to the procedure given in ref. 43.

^{1}H NMR (ppm) (300 MHz, CDCl$_3$) of Ti-POSS: 0.8 ppm (m, CH_2-Si, 14H), 1.08 ppm (m, —CH$_2$CH(CH_3)$_2$ (42H) and —CH—(CH_3)$_2$, 6H), 2.11 (m. —CH$_2$CH(CH$_3$)$_2$, 7H), 4.3 ppm (—O—CH—(CH$_3$)$_3$).

The commercial PLLA (from Aldrich) was characterized by a M_n, calculated by using the following described GPC analysis, of 28,300 and a PDI of 1.3.

L-Lactide Polymerization

Bulk polymerization of LLA was carried out using a flask equipped with a magnetic stirrer. Predetermined amounts of purified LLA and Ti-POSS were charged into the flask under argon atmosphere. The polymerization was carried out at 130 °C for variable time. At predetermined reaction times, the ampoules were rapidly cooled down to room temperature. The obtained polymer was washed with methanol and dried at 50 °C under vacuum for 12 h.

^{1}H NMR

^{1}H NMR spectra were obtained on a Varian 300 NMR, preparing the samples in CDCl$_3$. The ^{1}H NMR spectra were referenced to the residual solvent protons at about 7.26 ppm. Conversion was calculated by ^{1}H NMR from the relative intensity of the methine group of the monomer and the polymer (δCH$_{PLLA}$ = 5.16 ppm; δCH$_{LLA}$ = 5.02 ppm).

DSC

DSC was performed under a continuous nitrogen purge on a Mettler calorimeter, mod. TC10A. Both calibrations of heat flow and temperature were based on a run in which one standard sample (indium) was heated through its melting point. Samples having a mass between 5 and 11 mg were used. The procedure was as follows: first heating scan at

10 °C min^{-1} from 0 °C up to 200 °C, isotherm at this temperature for 2 min, then cooling at 10 °C min^{-1} down to −20 °C and finally, second heating scan from −20 to 200 °C, again at 10 °C min^{-1}. The first scan was meant to erase the prior uncontrolled thermal history of the samples. The degree of crystallinity was determined by subtracting ΔH_c from ΔH_m and by considering the melting enthalpy of 93 J g^{-1} for 100% crystalline PLA.[44]

GPC Analysis

Size exclusion chromatography was carried out in tetrahydrofuran (THF) at 50 °C using a Agilent 1200 series liquid chromatograph equipped with a refractometer index detector, an UV detector (λ = 365 nm) and two STYRAGEL columns (HT2, HT4). Molecular weight and molecular weight distribution of PLAs were calculated in reference to a PS calibration.

In addition, molecular weights were determined using an Ubbelohde viscometer (Type Oa, ASTM D-445). From the intrinsic viscosity of PLA solutions in chloroform at 25 °C, the M_v was determined using the formula: $[\eta] = 5.45 \times 10^{-4} M_v^{0.74}$.

Polarized Optical Microscopy

The development of morphology during melt-crystallization was followed by means of a Leika DMLP polarized optical microscope equipped with a 20× objective lens. The microscope was coupled with a Linkam CSS450 stage to enable a careful control of the thermal history while acquiring optical micrographs with a dedicated digital video-camera. The sample was initially loaded in the cell as a powder, melted, and compressed in a film of ∼20 μm thickness by moving the stage plates gently toward each other. In order to compare polarized optical microscopy with DSC experiments, an analogous temperature protocol was adopted. In particular, the sample was annealed for 2 min at 200 °C and then cooled to room temperature at 10 °C min^{-1}. Optical micrographs were taken during the cooling step, with a frequency of ∼1 °C^{-1}.

CONCLUSIONS

In conclusion, we have shown the efficacy of Ti-based POSS in the ROP of LLA with excellent control on molecular weight and polydispersity. Indeed, the ROP, which proceeds via a

coordination–insertion mechanism, leads to the direct insertion of the silsesquioxane molecule to the polymer backbone, thus producing a hybrid systems.

It is of utmost relevance that, in comparison with commercial PLLA, the polymers prepared with Ti-POSS exhibit a higher crystallinity. Indeed, the presence of silsesquioxane molecules, attached to one end of the polymer chains, has been found to appreciably affect the crystal nucleation density.

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