

# Preparation of High Isotactic Polybutene-1

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**ABSTRACT:** Polymerization of butene-1 (B-1) was carried out with a PP-TiCl<sub>3</sub>/Et<sub>2</sub>AlCl/methyl methacrylate (MMA) catalyst system in *n*-heptane. The influence of temperature, pressure, time and H<sub>2</sub> on molecular weight, isotacticity, and catalytic activity were studied by viscometry, solubility in boiling diethyl ether, and measuring the polymer produced, respectively. The structural properties of the isotactic polybutene-1 (IPB-1) were characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and melt flow index (MFI). The molecular weight of the products can be controlled by H<sub>2</sub>. It was found that the catalyst showed high isotacticity and activity. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2533–2539, 2000

**Key words:** polybutene-1; Ziegler-Natta catalyst; isotacticity; activity; molecular weight

## INTRODUCTION

IPB-1 was first prepared by Natta and coworkers in 1954.<sup>1–3</sup> PB-1 can be widely used in plastic and rubber industries.<sup>4</sup> IPB-1 (with high crystallinity) has excellent resistance under stress. Partially crystalline PB-1 can be used as a rubber, and amorphous PB-1 with low molecular weight can be used as lubricant, adhesive, viscosity index improver, and coating.<sup>5–10</sup> IPB-1 can be blended with PE, PP, EPDM, EVA, Poly(4-methyl-1-pentene), and so on.<sup>11–17</sup>

PP can be used as a support for metal complex catalysts. These catalysts are used in the polymerization of  $\alpha$ -olefins.<sup>18–20</sup>

The PP-TiCl<sub>3</sub>/Et<sub>2</sub>AlCl/MMA catalyst has been supplied for the production of high isotactic IPB-1 for the first time. Also, in this article, we present the results of the investigations on the polymerization catalyzed by an active PP-supported Ti catalyst (PP-TiCl<sub>3</sub>). The catalyst PP-TiCl<sub>3</sub>/

Et<sub>2</sub>AlCl/MMA exhibits a high stereospecificity and activity. The characterization of the resulting products are also reported; such results can be of interest for preparing high isotactic PB-1 by this catalyst.

## EXPERIMENTAL

### Materials

The solvents, Et<sub>2</sub>AlCl, 2,6-di-*tert*-butyl-*p*-cresol and MMA (synthesis grade) were purchased from Merk Co. (Germany). PP-TiCl<sub>3</sub>(LYNX 900) and B-1 were purchased from the Engelhard Co. (USA) and Tabriz Petrochemical Co. (Iran), respectively.

### Catalyst

Et<sub>2</sub>AlCl and MMA (as an external donor) were stirred with a magnetic stirrer in 500-mL Erlenmeyer flask for 30 min under nitrogen atmosphere, and then TiCl<sub>3</sub>, supported on PP, was added by a 10-mL glass syringe. The solution was diluted by *n*-heptane (60 mmol TiCl<sub>3</sub>/L). The mo-

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**Table I Effect of Temperature on Catalytic Activity<sup>a</sup>**

Temp., °C	45	50	55	60	70
Activity (kgPB-1/g Ti)	3.5	3.9	4	4	4.1

<sup>a</sup> Polymerization conditions: Pm = 7 kg/cm<sup>2</sup>, Time = 2 h, PH<sub>2</sub> = 0.

lar ratio of Ti : Al : MMA was selected 1 : 5 : 0.1, respectively. This is the same as the catalyst that was used for the preparation of isotactic polypropylene.<sup>20</sup>

### Polymerization

Polymerization was carried out in a 2-L reactor (stainless steel) equipped with a mechanical seal stirrer (mixing speed is around 500 rpm, T form). After running out of all moisture and oxygen by nitrogen, 1 L of *n*-heptane was added. After 10 min, 4 mL Et<sub>2</sub>AlCl (20% wt in *n*-heptane) and a 5 mL catalyst (60 mmol TiCl<sub>3</sub>/lit) were added by a 10-mL glass syringe, and then the reactor was warmed up to the required temperature (Table I). B-1 was supplied continuously at the required pressure (Table II). The polymerization was quenched after 2 h. In the polymerizations in which hydrogen was used, hydrogen was injected at the required pressure (Table III) before B-1 was supplied. The polymerization was quenched by addition of 80 mL of methanol, and washed with 500 mL of deionized water, and then the polymer was filtered and dried *in vacuo* at 35–40°C for 6 h to constant weight.

### Polymer Fractionation

Atactic fraction was extracted with boiling diethyl ether. The boiling ether-insoluble fraction is IPB-1, and the boilig ether-soluble fraction is atactic.<sup>21,22</sup> The recovered fractions were dried *in vacuo* at 35–40°C to constant weight. The wt % of

**Table II Effect of Pressure on Catalytic Activity<sup>a</sup>**

Pm (kg/cm <sup>2</sup> ) <sup>b</sup>	3.4	4.8	5.5	7	7.8
Activity (kgPB-1/g Ti)	2.9	3.2	3.7	4	4.1

<sup>a</sup> Polymerization conditions: Temp. = 60°C, Time = 2 h, PH<sub>2</sub> = 0.

<sup>b</sup> Monomer pressure.

**Table III Effect of H<sub>2</sub> on B-1 Polymerization<sup>a</sup>**

PH <sub>2</sub> (kg/cm <sup>2</sup> )	<i>M<sub>w</sub></i> (×10 <sup>-5</sup> )	Activity (kgPB-1/gTi)	Isotacticity (%)	MFI (190°C/2.16 kg)
0	24.7	4	88.2	0.07
0.05	7.09	6.2	92.4	0.4 <sup>b</sup>
0.125	5.41	8.7	93.2	1.0 <sup>c</sup>
0.25	3.92	18.1	93.9	1.6
0.5	1.94	16.6	85.3	19
1	1.65	15	79	—
2	1.28	13.3	73	—
3	0.79	8.4	68.6	—
4	0.54	6	62.6	—

<sup>a</sup> Polymerization conditions: Temp. = 60°C, Pm = 7 kg/cm<sup>2</sup>, Time = 2 h.

<sup>b</sup> Pipe grade.<sup>25</sup>

<sup>c</sup> Film grade.<sup>25</sup>

ether-insoluble polymer in a whole sample is referred to as the isotactic index (Table III).

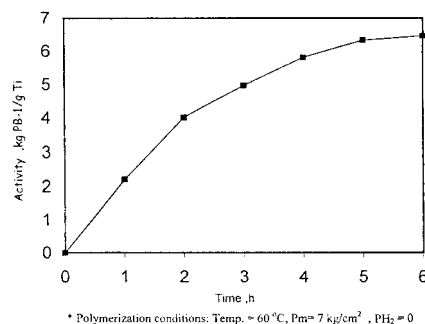
### Characterization

The interinsic viscosity of PB-1 was determined in decalin solution with 0.2% of 2,6-di-*tert*-butyl-*p*-cresol as an antioxidant at 110°C with an Ubbelohde viscometer (Schott Gerate, range 0.3–6).<sup>23</sup>

The selected concentrations of PB-1 in decalin were 0.1, 0.2, 0.3, and 0.4 (g/dL), so flow times for all samples exceeded 150 s in all cases. The molecular weight of PB-1 (Table III) was calculated according to the following equation<sup>23</sup>

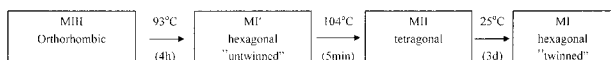
$$[\eta] = 9.49 \times 10^{-5} \bar{M}_w^{0.73}$$

The crystallinity of the polymer was determined by DSC<sup>24</sup> (a Mettler TA 3000 system) at a heating rate 5 K/min under N<sub>2</sub>. The heat of fusion



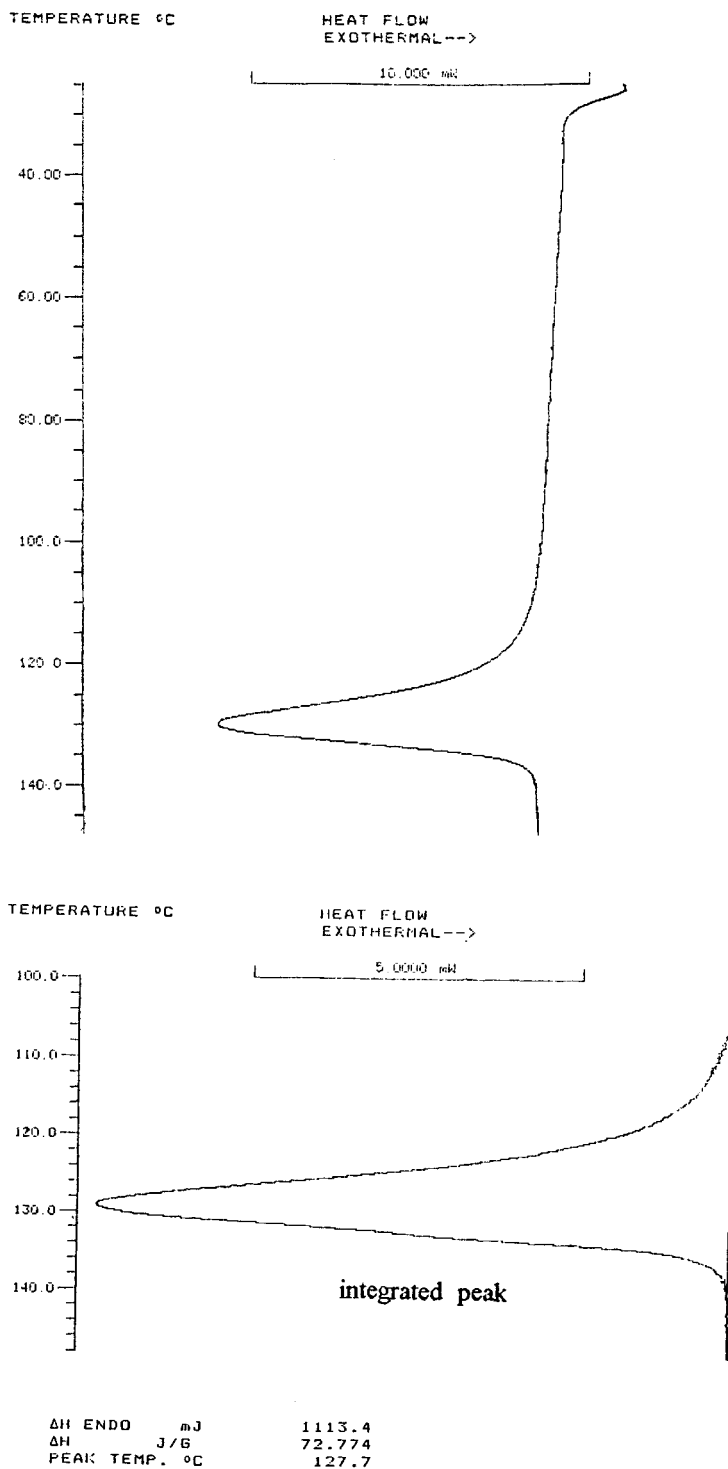
<sup>a</sup> Polymerization conditions: Temp. = 60°C, Pm = 7 kg/cm<sup>2</sup>, PH<sub>2</sub> = 0

**Figure 1** Effect of time on the catalyst yield.



**Figure 2** Flow chart showing formation of different modifications of isotactic polybutene-1.

of 100% crystalline MI, MII, and MIII (Fig. 2) are 125.5, 71.1, and 117.2 J/g, respectively. The morphology of the surface of the polymer was depicted by SEM (a Cambridge Instrument stereoscan



**Figure 3** DSC of form I.

360). The crystalline modifications and decomposition were determined by FTIR (a unicam "mattson 1000") and TGA (a TGA V5.1 A Dupont 2000) at a heating rate of 20°C/min under N<sub>2</sub>, respectively. MFI (g/10 min) was measured using a Zwick 4100 in accordance with ASTM D 1238 (at 190°C/2.16 kg). Activity has been determined in terms on the produced PB-1 (kg) per the used Ti (g) in the polymerization.

## RESULT AND DISCUSSION

Catalytic activity of B-1 is sensitive to polymerization temperature, pressure, and H<sub>2</sub> (Tables I, II, and III). As Tables I and II show, the catalyst shows a maximum activity (the most production) at ≥55°C and at pressures more than 6 kg/cm<sup>2</sup> (4 kg PB-1/g Ti).

Hydrogen is used for controlling molecular weight as a chain transfer agent. Unlike propene polymerizations,<sup>26,27</sup> the isotacticity and catalytic activity of the PB-1 were slightly increased until a pressure of 0.25 kg/cm<sup>2</sup> (93.9% and 18.1 kg PB-1/gTi, respectively) and then decreased by the addition of H<sub>2</sub> (Table III).

The H<sub>2</sub> activation for heterogeneous catalytic  $\alpha$ -olefin polymerizations has been explained by various investigators in terms of a higher concentration of the monomer as a result of chain transfer, which detaches macromolecules from the active centers,<sup>28</sup> reduction of the amount of the dead polymer chains containing terminal double bonds capable of competing with the monomer in the formation of a  $\pi$ -complex with the active centers,<sup>29</sup> and oxidative addition of H<sub>2</sub> to T · i<sup>2+</sup> ions and activation of previously deactivated of Ti<sup>3+</sup> ion by hydrogenolysis.<sup>30</sup>

As it is shown in Fig. 1, the catalyst yield increases as the time of polymerization increases. The selected time of the polymerizations were 1, 2, 3, 4, 5, and 6 h in the same conditions.

### Polymer Characterization

#### MFI

The rheological properties of the polymers was studied by the melt flow index (MFI). As is observed from Table III, MFI increases by addition of H<sub>2</sub> because the molecular weight decreases. The MFI (190°C/2.16 kg) of 0.4 and 1.0 correspond to the pipe and film grades, respectively.<sup>25</sup>

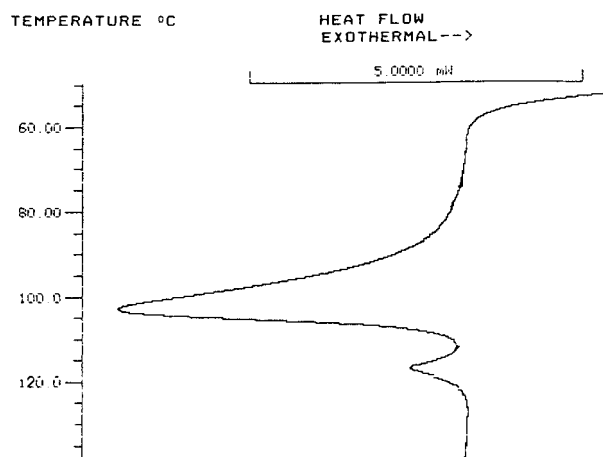


Figure 4 DSC of the polymerization product.

#### Isotacticity

The isotacticity of the overall polymers is high. In the case of using H<sub>2</sub>, isotacticity was slightly increased and then decreased (Table III). The isotacticity obtained from pipe and film grades are 92.4 and 93.2%, respectively.

#### FTIR

Four crystalline modifications of IPB-1 are known, as depicted in Figure 2.<sup>31–33</sup> The different forms can be determined by FTIR spectroscopy. The characteristics bands are at 925 and 810 cm<sup>-1</sup> (Form I), 925, and 792 cm<sup>-1</sup> (Form I'), 900 cm<sup>-1</sup> (Form II), 900 and 810 cm<sup>-1</sup> (Form III).<sup>33</sup>

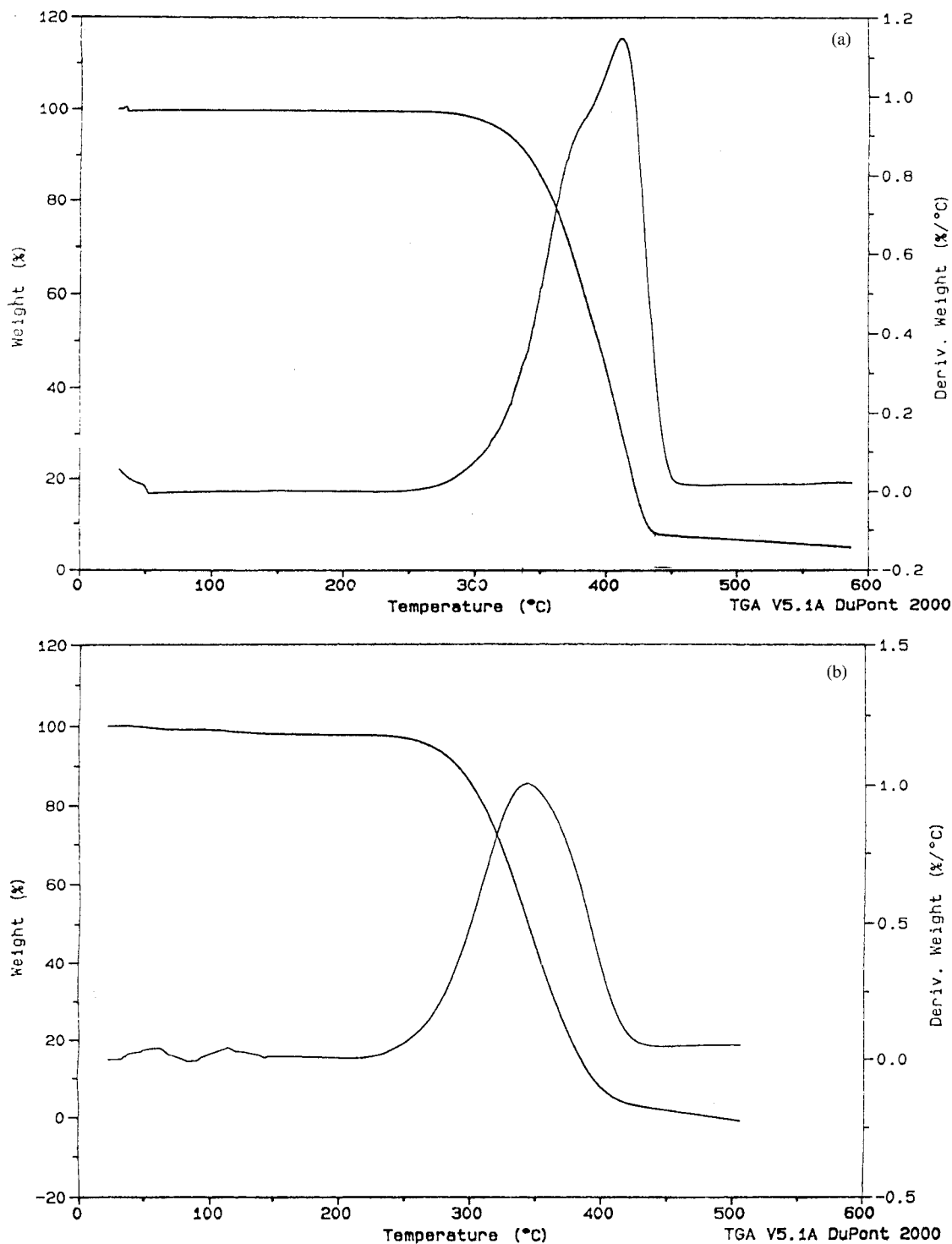
#### DSC

The crystallinity has been determined by DSC.<sup>24</sup> The crystallinity of form I is 58% (Fig. 3). DSC shows a melting point at 127.7°C.

DSC of the polymerization product (the overall product) has been shown in Figure 4. This figure shows two peaks—the peaks at 103.6°C and 117.6°C are attributed to the melting of form I' and form II,<sup>34</sup> respectively.

#### TGA

TGA shows that form I is more heat resistance than the overall product. Form I is decomposed at 300–440°C [Fig. 5(a)], whereas overall product is decomposed at 250–420°C [Fig. 5(b)]. The weight reduction of form I is more than the overall product.

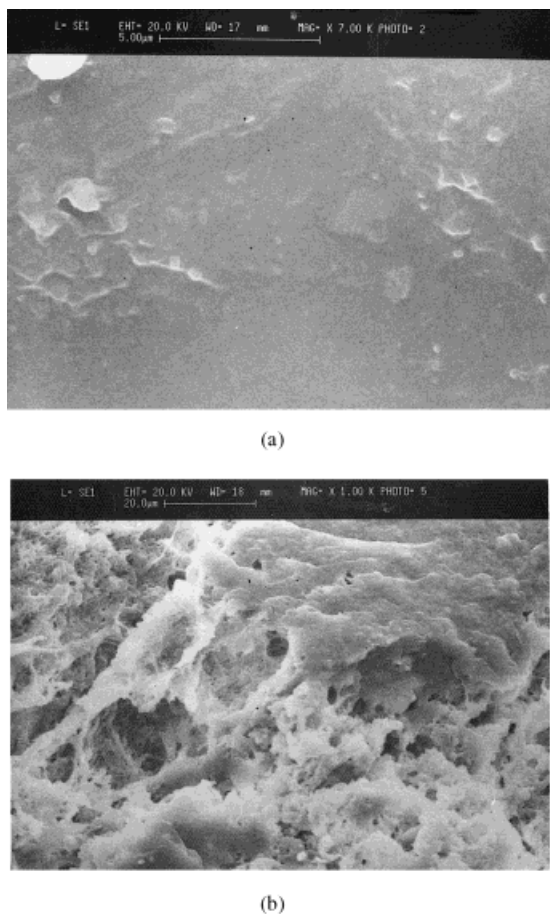


**Figure 5** (a) TGA of form I, (b) TGA of the polymerization product.

### Surface Characteristics

The SEM was used to study the morphology of the polymers (Fig. 6). As figures show, the surface of

the form I is smooth [Fig. 6(a)], whereas on the surface of the overall product, cavities and pores are observed [Fig. 6(b)]. These cavities and pores are attributed to running out the solvent and



**Figure 6** SEMs: (a) polymerization product; (b) form I.

water from the polymerization product during drying. After melting the polymer for preparing form I (Fig. 2), the cavities and pores are filled with melted polymer. In this way, the surface of form I is observed as smooth.

## CONCLUSION

IPB-1 was prepared by PP-TiCl<sub>3</sub>/Et<sub>2</sub>AlCl/MMA. The catalyst has shown high isotacticity and activity. The optimum activity of the catalyst is at 55–60°C, and the pressure of 6–7 kg/cm<sup>2</sup>. The molecular weight of polymers has decreased with increase in the pressure of H<sub>2</sub>, but isotacticity and activity have first increased until the pressure of 0.25 kg/cm<sup>2</sup> and then decreased. Pipe and film grades of IPB-1 (two important and commercial grades of IPB-1) have been produced at the pressure of 0.05 kg/cm<sup>2</sup> and 0.125 kg/cm<sup>2</sup> H<sub>2</sub>, respectively. The DSC of form I has shown a peak at 127.7°C, whereas the

DSC of the overall product has shown two peaks at 103.6 and 117.6°C that were attributed to form I' and form II, respectively. TGA has shown that form I is more heat resistance than the overall product (forms I' and II).

The surface of form I was smooth; in contrast, the surface of the overall product showed “bumps” and “crates” (Fig. 6).

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