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Description	

Original Paper

Morphological Stability of the Initially Formed Polymer Particles in Stopped-Flow Propylene Polymerization

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Abstract

The morphological stability of initially formed polymer particles against air was improved in order to study the initial morphology development with Zigler-Natta catalyst olefin polymerization. The stopped-flow polymerization technique was applied to synthesize initial polymer particles in combination with various quenching and stabilizing procedures. When polymerizing particles were quenched with cold heptane maintained at −65°C under N_2 or CO_2, the exposure of the formed particles to air caused the fast formation of cracks on the surface, leading to serious reformation of the particle shape. However, when the particles were quenched with cold heptane under CO_2 and washed with heptane containing an appropriate amount of tetrahydrofuran, the particle morphology was significantly stabilized which hardly changed even after 1 h exposure to air. The established stabilizing procedure is highly useful for various characterizations of the initially formed particles.

Keywords : Morphological stability, Polyolefins, Ziegler-Natta catalyst, Stopped-flow polymerization

1. Introduction

The worldwide polyolefin (PO) production in 2008 was about 110 million tons and is speculated to steadily grow in the long future. Because of this huge capacity, the reaction engineering aspects of the PO production with heterogeneous catalysts such as Ziegler-Natta, Phillips and supported metallocene are of great importance. Especially, the polymer particle morphology strongly affects the plant operation and processing step. A failure of morphological control in a plant leads to a number of serious troubles such as fouling, sheeting, and broadening residence-time distribution. It is recognized that the morphology of polymer particles is mainly determined by that of the original catalyst particles as well as the way how the particles develop[1),2)]. Especially, at the very

early stage of polymerization, the particles are mechanically weakest to be easily broken by the force from the formed polymer and/or the heat attack. Therefore the initial morphological development is the key step for the final polymer particle morphology. The huge impact of the initial stage not only on the final particle morphology but also on the whole polymerization behaviors has invoked a great attention from both the academic and the industrial points of view.

The stopped-flow (SF) technique (**Fig. 1**) explained in details in the experimental part has been widely recognized to be one of the most useful tools for the study of the very initial stage of olefin polymerization[3),4)]. However, the SF technique has been rarely applied to the investigation of the morphological development because the conventional quenching procedure in the SF polymerization completely destroys the particle morphology. Another serious problem in the study of the initial particle morphology is that a large amount of the catalyst and cocatalyst remaining in the initially formed polymer/catalyst particles readily react with moisture in air, leading to the rapid destruction of the particle morphology. The establishment of a way to improve the

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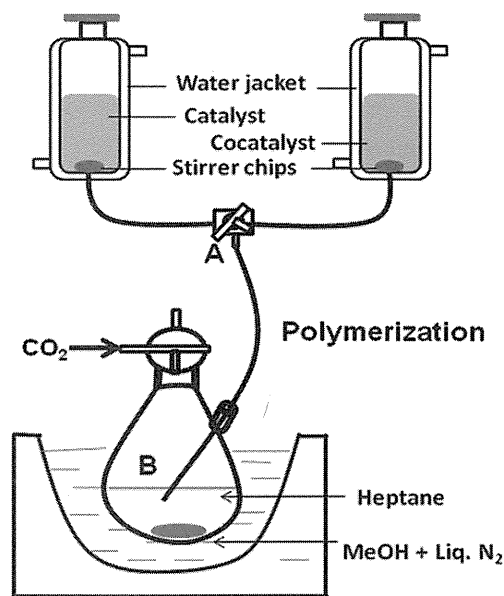
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Fig. 1 Scheme of the stopped-flow polymerization

morphological stability of the initially formed particles under air must be highly valuable for various kinds of ex-situ characterizations of the particles such as microscope observation, spectroscopic analysis, porosity measurement, etc.

In this study, we have successfully established a new quenching and stabilizing procedure for the SF polymerization, which effectively quenched the polymerization reaction and significantly improved the morphological stability of the initially formed polymer/catalyst particles under air.

2. Experimental

Materials

N_2, CO_2, propylene (donated by Japan Polypropylene Co.), ethanol (EtOH) and anhydrous tetrahydrofuran (THF) of research grade were used without further purification. Tri-isobutylaluminium (TiBA, donated by Tosoh FineChem Co.), diisobuthylphthalate (DBP), spherical $Mg(OEt)_2$ and titaniumtetrachloride $(TiCl_4)$ were used as delivered. Heptane of research grade was used as solvent after passing through a column of 4A molecular sieve and bubbling with dry N_2 overnight.

The catalyst used in this study was the spherical $Mg(OEt)_2$-based catalyst, which is one of the most advanced industrial olefin polymerization catalysts, prepared from the spherical $Mg(OEt)_2$ basically according to the procedure in Ref. 5.

SF polymerization and stabilization

The initial polymer/catalyst particles were synthesized by the stopped-flow technique illustrated in **Fig. 1**, in which catalyst slurry and cocatalyst solution saturated with propylene gas at 1 atm were contained in the separate special glass vessels. The downstream flask contained a quenching agent. The polymerization was conducted for 0.5 s, for which only 0.1 g of polypropylene was formed per 1 g of the catalyst. In this study, we set up three new quenching and stabilizing procedures instead of the conventional acidic ethanol :

i) Heptane of 200 ml at $-65°C$ was used to significantly decelerate the polymerization under the N_2 atmosphere. After settling the mixture between the polymerization slurry and quenching heptane, the upper solvent was removed and then the remaining solid particles were washed with 100 ml heptane to remove unreacting components.

ii) A similar quenching and washing procedure to i) was applied under CO_2 rather than under N_2. CO_2 can kill the polymerization by cleaving the metal-alkyl bonds.

iii) A similar procedure to ii) was conducted except the addition of THF in the washing step as a morphological stabilizer, where the THF/Ti molar ratio was optimized to be 200.

After removing the upper solvent, the particles were dried by N_2 flow for 2 h. The detailed information about polymerization and stabilization conditions is summarized in **Table 1**.

Scanning electron microscopy (SEM)

The morphological stability of the initially formed polymer particles under air was examined by Hitachi S-4100 Scanning Electron Microscope. The samples for SEM were prepared in a glove bag under the N_2 atmosphere, then transferred to a deposition device (Hitachi E-1030 Ion Sputter) for the Pt-Pd coating, and finally transferred to the SEM chamber. The two transfer processes were conducted under air for 90 s, which was the shortest exposure time in this study. In addition, the samples were intentionally exposed to air for 1 h before the SEM observation, with an assumption that 1 h might be the maximum exposure time required for possible characterizations.

Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS)

The surface states of the SF particles, especially the state of THF on the particle surface, were examined by DRIFT spectra using a JASCO FT/IR-6100 spectrometer in the N_2 atmosphere.

Table 1. Applied quenching and washing conditions

Run no.	Quenching step 1	Washing step
1	$-65°C$ heptane under N_2	Heptane under N_2 at r.t.
2	$-65°C$ heptane under CO_2	Heptane under CO_2 at r.t.
3	$-65°C$ heptane under CO_2	Heptane under CO_2 containing THF (THF/Ti=200/1)

All spectra were recorded by a MCT detector with a nominal resolution of $4\,cm^{-1}$.
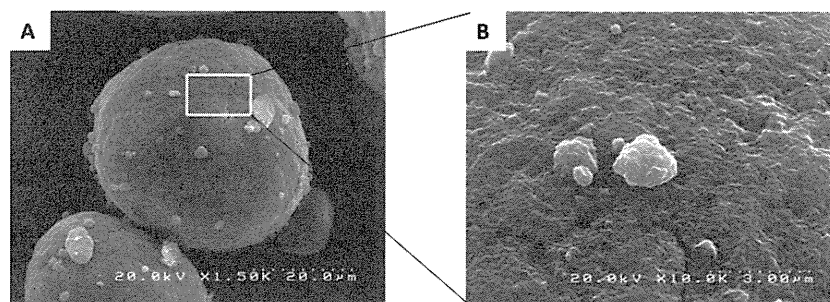
3. Results and discussion

The morphology of the original catalyst is shown in **Fig. 2**. The catalyst particle is dense and spherical with an average diameter of $ca.$ $28.0\,\mu m$. From the higher magnification image (**Fig. 2B**), it is clearly seen that the catalyst particle has a rough and grain-like surface.

The morphology of the initial polymer/catalyst particles, which was prepared with the three different quenching procedures and then exposed to air for 90 s or for 1 h, is shown in **Fig. 3**. For the first quenching procedure, the initially formed polymer/catalyst particles were not stable. Many big cracks appeared on the particle surface after 90 s and the particles turned to a popcorn shape after 1 h under air (**Fig. 3A** and **3A'**, respectively). When CO_2 was applied for the quenching agent, the polymer particles became more stable : after 90 s of the exposure, the cracks still appeared but became much smaller (**Fig. 3B**). However, the particle morphology severely changed after the longer exposure time of 1 h (the cracks became much bigger in **Fig. 3B'**). With the third quenching procedure, when THF was added in the washing step as a stabilizer, the particles were perfectly stabilized for both the short and long exposure time. The particle morphology hardly changed even after 1 h under air (**Fig. 3C** and **3C'**).

As shown in **Fig. 3**, the SF polymer/catalyst particles could experience two stages of damages caused by the exposure to air : the fast crack formation on the particle surface and the slow morphological change to result in a popcorn shape. The mechanism of the particle stabilization by CO_2 and THF is addressed as follows.

It is evident that after the SF polymerization the initially formed particles are mainly composed of the catalyst components, $TiCl_4/MgCl_2/DBP$ and TiBA with a small amount of formed polymer (polymer yield 0.1 g/g-cat.). The components other than DBP and the formed polymer are moisture-sensitive materials. TiBA and $TiCl_4$ intensively react with moisture according to the reactions (1) and (2), respectively. These reactions produce a huge amount of heat and gases, which rapidly cause the cracks on the particle surface (**Fig. 3A** and **3B**). On the other hand, $MgCl_2$ reacts with moisture more mildly to make the $MgCl_2 \cdot (H_2O)_6$ adduct through the reaction (3). This reaction accompanies the reformation of the particle morphology, which might be a driving force of the cracks, and slowly swells the whole particle, leading to the expansion of the cracks and finally to the popcone or molten shape (**Fig. 3A'** and **3B'**).

Fresh heptane can wash out the mobile or only weakly bound TiBA from the SF particles. CO_2 can readily insert into metal-alkyl bonds to form the metal-ester bonds (the reaction (4)). The reaction helps to quench the polymerization more effectively. Moreover, they can partly prevent the fast for-

Fig. 2 Catalyst morphology. B is the magnification of the rectangular area in A

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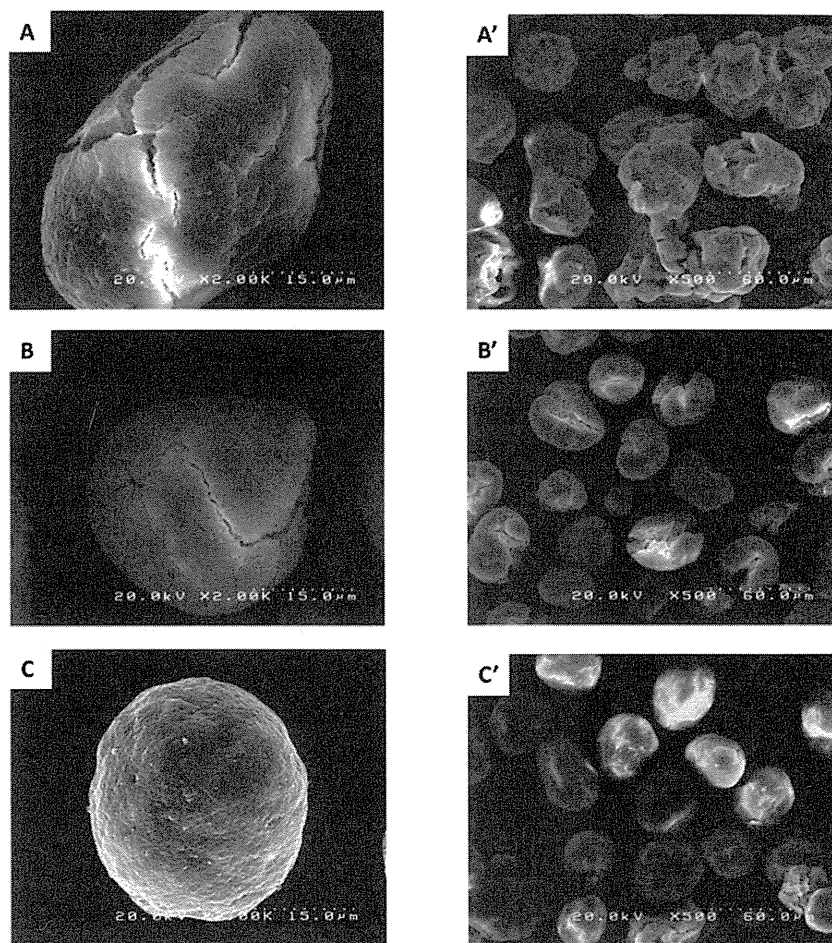

Fig. 3 A (A'), B (B'), and C (C') are SEM images of the polymer/catalyst particles respectively quenched and washed with the procedures i), ii) and iii), and then followed by the exposure to air for 90 s (1 h).

mation of the cracks (compare **Fig. 3A** and **3B**) because the metal-ester bonds are quite inert to moisture. THF can cordinate to both $TiCl_4$ and $MgCl_2$ according to the raections (5) and (6), respectively. The resulting complex, $TiCl_4 \cdot (THF)_2$ must be mobile enough to be removed by the washing step with heptane, while THF is considered to chemisorb on the $MgCl_2$ surface to significantly slow down the formation of the $MgCl_2 \cdot (H_2O)_6$ adduct. Thus, THF is believed to stabilize the initially formed polymer particles by decelerating both the fast and slow reactions. The existance of THF on the particle surface in the SF samples was confirmed by DRIFT in **Fig. 4**, where only the spectra for Run 3 exhibited the peak at 1025 cm^{-1} assigned as the symmetric stretching vibration of the C-O-C group of THF. The ester band of R-CO-OM was not visible in the presence of the dominant amount of DBP with two ester groups per molecule.
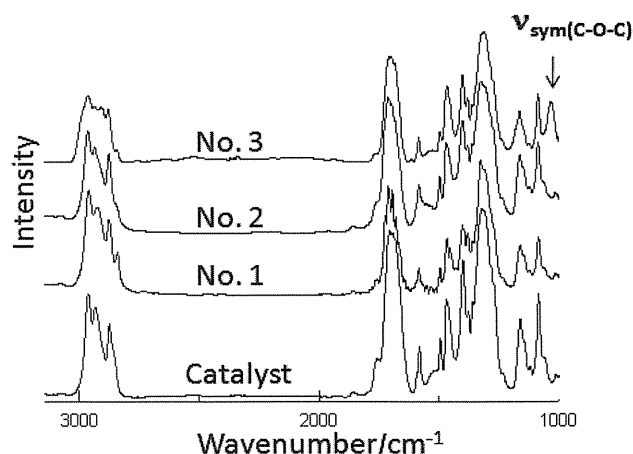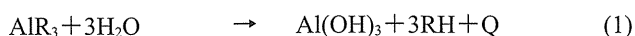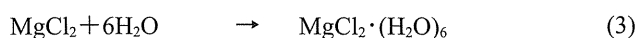

Fig. 4 DRIFT spectra of the fresh catalyst and the SF samples

$$AlR_3 + 3H_2O \quad \rightarrow \quad Al(OH)_3 + 3RH + Q \quad (1)$$

$$TiCl_4 + 2H_2O \quad \rightarrow \quad TiO_2 + 4HCl + Q \quad (2)$$

$$MgCl_2 + 6H_2O \quad \rightarrow \quad MgCl_2 \cdot (H_2O)_6 \quad (3)$$

$$M\text{-}R + CO_2 \quad \rightarrow \quad R\text{-}CO\text{-}OM \quad (M : Al \text{ or } Ti) \quad (4)$$

$$TiCl_4 + 2THF \quad \rightarrow \quad TiCl_4 \cdot (THF)_2 \quad (5)$$

$$MgCl_{2\,Surf.} + x\,THF \quad \rightarrow \quad MgCl_2\ ad.\ (THF)_x \quad (6)$$

4. Conclusion

The morphology of the initially formed polymer/catalyst particles were successfully stabilized against air by a new quenching procedure in the stopped-flow propylene polymerization. Cold heptane and CO_2 effectively freezed and quenched the polymerization, while THF worked as a morphological stabilizer by protecting the particle surface from the moisture. The results of this study are highly meaningful for the future morphological study at the very early stage of polyolefin polymerization, which contributes to the development of new catalyst with highly controlled catalyst and polymer morphologies.

Acknowledgement

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